INELASTIC LIGHT SCATTERING STUDY OF CORRELATED ELECTRON SYSTEMS

By

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And approved by

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My thesis study focuses on exploring correlated electron systems by means of inelastic light scattering. Specifically, I investigate quadrupolar fluctuations and crystal-field (CF) excitations in 4f-electron systems, and the nature of unconventional insulating phases in 5d-electron systems. The light-scattering experimental technique offers both high energy resolution and the ability to disentangle the long-wavelength excitation spectra into individual symmetry channels. Such advantages are particularly useful to study the questions focused by my thesis.

Heavy-fermion metal CeB$_6$ exhibits an antiferroquadrupolar ordering of $T_2g$ (xy type) symmetry below 3.2 K. We perform a comprehensive spectroscopic study of this material, discussing its electronic, magnetic, and phononic excitations [1]. In particular, we find the spectral linewidth of the CF excitations is broadened by Kondo effect, and the tendency towards finite-wavevector quadrupolar ordering induces ferromagnetic correlations which manifest as long-wavelength magnetic fluctuations.

Another heavy-fermion metal, YbRu$_2$Ge$_2$, enters a ferroquadrupolar phase of $B_{1g}$ ($x^2-y^2$ type) below 10 K. We study the quadrupolar fluctuations, CF excitations, and lattice
dynamics of this compound [2]. We show that the electronic static Raman susceptibilities in quadrupolar symmetry channels follow nearly Curie-law behavior; the relatively strong coupling to the lattice in the B1g channel enhances the vanishingly small electronic Weiss temperature to the temperature of quadrupole phase transition at 10 K.

Ferroelectric insulator TbInO3 has been proposed to be a spin-liquid candidate. To understand its ground-state property, we study its low-energy CF excitations [3]. We show that the ground state of the Tb3+ ions is a non-Kramers doublet. We also demonstrate that the obtained CF level scheme is consistent with specific heat data. In addition, we observe hybrid excitations involving coupled CF and phonon modes, suggesting strong spin-lattice interaction. The complex spin Hamiltonian of TbInO3 renders this material a suitable platform to investigate the effects of non-Kramers doublet ground state on a triangular magnetic lattice.

Paramagnetic insulator Ba5CuIr3O12 hosts face-sharing Ir octahedra forming quasi-one-dimensional chains. We explore the electronic structure of this system [4]. We show that the insulating mechanism of this iridate cannot be described by the commonly-adopted $J_{\text{eff}}=1/2$ local moment picture. Instead, the shorter Ir-Ir distance in face-sharing geometry leads to strong covalency between neighboring Ir4+ ions; this strong covalency results in the formation of molecular orbits as the low-energy electronic degree of freedom. To further illustrate the nature of the insulating state of Ba5CuIr3O12, we also study the thermodynamic properties of this compound [5]. While the temperature dependence of the magnetic susceptibility and specific heat suggests weak antiferromagnetic correlations, the magnetization does not saturate up 59 T. This phenomenon can be understood in the framework of random singlet state, and we obtain the exchange coupling distribution from the magnetization data.

Zero-gap semiconductor Ta2NiSe5 is one promising candidate of excitonic insulator, a coherent electronic phase resulting from the formation of a macroscopic population of excitons. We study its critical excitonic fluctuations and emergent coherence [6]. The
quadrupolar excitonic mode exhibits significant softening close to the phase transition, and its coupling to noncritical lattice modes enhances the transition temperature. On cooling, we observe gradual emergence of coherent superpositions of band states at the gap edge. Moreover, we explore the effect of sulfur doping [7, 8]. We find that the critical excitonic fluctuations diminish with the sulfur doping, and eventually shift to high energies, characteristic of a quantum phase transition. However, a symmetry-breaking transition at finite temperatures is detected at all doping level, exposing a cooperating lattice instability that takes over for large doping level. The study therefore reveals a failed excitonic quantum phase transition, masked by a preemptive structural order.
Acknowledgments

Collaboration is a crucial part of research, and what reviewed in this dissertation is not a single person’s work. I would like to express my sincere gratitude to the people who helped in my thesis study.

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Chapter 1

Introduction

Inelastic light scattering not only probes intrinsic properties of crystals, but also reveals how light and matter interact. In inelastic scattering process, a small portion of the outcoming light has frequency different from that of the incoming light. This process can be understood in both macroscopic level and microscopic level. The meeting point of experimental and theoretical study is the scattering cross section. This quantity is not only experimentally measurable, but also links the response function which can be derived theoretically.

Derivations in this chapter follows Ref. [9–12]. Basics of solid state physics can be found in classic texts [13] and are not repeated here. General principles that are essential for understanding inelastic light scattering are discussed in Sec. 1.1. Various elementary excitations in solids and how they are probed by inelastic light scattering are described in Sec. 1.2. The scope of this thesis is described in Sec. 1.3.

1.1 Theoretical aspects of inelastic light scattering

Scattering of light is a common phenomenon in daily life: the high blue sky, glorious red sunset, and bright morning rays through leaves of a tree. These examples are light scattered from gaseous media; light is scattered by liquids and solids as well. The majority of scattered light has the same frequency as the incoming light; such scattering process is referred to as elastic scattering. Elastic scattering of light by particles whose size is much smaller than the light wavelength is named after Lord Rayleigh, who conducted systematic theoretical research on this subject. A small portion of the scattered light, however, has a frequency
different from that of the incoming light. This inelastic scattering process can be classified by the magnitude of the frequency shift: if the frequency shifts by less than $1 \text{cm}^{-1}$, it belongs to Brillouin scattering; if the frequency shifts by more than $1 \text{cm}^{-1}$, it belongs to Raman scattering. The inelastically scattered light contains two components: Stokes part whose frequency is less than the frequency of the incoming light, and anti-Stokes part whose frequency is higher than the frequency of the incoming light. This thesis study focuses on investigating the properties of crystals by measuring the Stokes part of Raman scattering.

Raman scattering is caused by excitations of the crystal, whose complex amplitude is denoted by $X(r, t)$. Examples of $X(r, t)$ are vibrational displacement of atoms from their equilibrium position, or deviation of magnetization from perfect alignment in a ferromagnet. The effect of the excitations is represented macroscopically by an contribution to the susceptibility. The $i$-th Cartesian component of the polarization at position $r$ and time $t$, induced by $j$-th Cartesian component of the incident field is

$$
P^i(r, t) = \epsilon_0 [\chi^{ij}(\omega_i) E^j_i(r, t) + \chi^{ij}(\omega_i, \pm \omega) X(r, t) E^j_i(r, t)],
$$

where $\epsilon_0$ is the dielectric constant of vacuum, $E_i$ is the incident macroscopic electric field with frequency $\omega_i$, $\chi(\omega_i)$ is the first-order susceptibility at frequency $\omega_i$, $\chi(\omega_i, \omega)$ is the second-order susceptibility describing the modulation, $\omega$ is the frequency of the excitation, the repeated superscripts are summed over $x$, $y$ and $z$. In the absence of any excitation, only the first term exists in (1.1). With excitations, a whole series of terms in increasing powers of $X$ appears in the square brackets of (1.1) if perturbation theory is carried to higher orders.

The first-order polarization from the first term of (1.1) oscillates at the same frequency as the incident field and contributes only to elastic scattering. The second-order polarization from the second term of (1.1) oscillates at frequencies different from $\omega_i$ because $X$ is a time-dependent function. This part of the polarization radiates the inelastic contribution to the scattered light. The second-order polarization can be separated into $P_s$ which produces the
Stokes component and \( P_{as} \) which generates the anti-Stokes component:

\[
P^i_s(K_s, \omega_s) = \epsilon_0 \chi^{ij}(\omega_i, -\omega) X^*(q, \omega) E^j_i \tag{1.2}
\]

\[
P^i_{as}(K_{as}, \omega_{as}) = \epsilon_0 \chi^{ij}(\omega_i, \omega) X(q, \omega) E^j_i \tag{1.3}
\]

where

\[
\omega_s = \omega_i - \omega \tag{1.4}
\]

\[
\omega_{as} = \omega_i + \omega \tag{1.5}
\]

\[
K_s = k_i - q \tag{1.6}
\]

\[
K_{as} = k_i + q . \tag{1.7}
\]

The electric field generated by the Stokes polarization has frequency \( \omega_s \), and the spatial dependence of its amplitude is determined from Maxwell’s equations. Once the scattered field is known, the period-averaged scattered intensity, proportional to the square of the electric field amplitude, can be calculated. Putting everything together, the spectral differential cross section for Stokes scattering is given by

\[
\frac{\partial^2 \sigma}{\partial \Omega \partial \omega_s} = \frac{\omega_i \omega_s^2 \alpha V \eta_s |\epsilon_0 \epsilon_i^j \chi^{ij}(\omega_i, -\omega)|^2}{(4\pi \epsilon_0)^2 c^4 \eta_i} \langle X(q, \omega) X^*(q, \omega) \rangle , \tag{1.8}
\]

where \( \alpha \) is the scattering volume, \( V \) is the total volume of the sample (which is always cancelled by a factor \( 1/V \) appearing in the power spectrum), \( \eta_i \) and \( \eta_s \) are the refractive indices of the medium for the incident and scattered light, \( \epsilon_i^j \) is the i component in Cartesian coordinate of a unit vector parallel to the electric field of the scattered light, \( \epsilon_s^j \) is similarly the j component of a unit vector parallel to the electric field of the incident light, \( c \) is the speed of light in vacuum.

According to fluctuation-dissipation theorem, for Stokes scattering the power spectrum \( \langle X(q, \omega) X^*(q, \omega) \rangle \) satisfies the relationship

\[
\langle X(q, \omega) X^*(q, \omega) \rangle = \frac{\hbar}{\pi} [n(\omega, T) + 1] \text{Im} \chi(q, \omega) , \tag{1.9}
\]
where \( h \) is the reduced Planck constant, \( n \) is the Bose-Einstein factor, and \( \chi \) is the Raman response function. This response function is an intrinsic property of the crystal, which can be both experimentally measured and theoretically calculated. It is therefore the bridge between Raman experiment and theory.

Understanding Raman scattering in the microscopic level starts from the quantum-mechanical Hamiltonian of the coupled light field and scattering medium. This Hamiltonian consists of three parts: the light-field Hamiltonian \( H_{\text{Light}} \) including both incident and scattering fields, the Hamiltonian \( H_{\text{Medium}} \) of the scattering medium, and the coupling \( H_{\text{Coupling}} \) of the electrons in the medium to the light. \( H_{\text{Medium}} \) is further divided into \( H_0 \), a sum of the Hamiltonians of the various kinds of elementary excitations in the medium, and \( H_1 \), the interactions between these excitations.

Each scattering event in the microscopic theory corresponds to a transition between an initial state \( |i\rangle \) and a final state \( |f\rangle \) of the scattering medium, these being eigenstates of \( H_0 \),

\[
H_0|i\rangle = \hbar \omega_i|i\rangle \\
H_0|f\rangle = \hbar \omega_f|f\rangle .
\]  

The radiation field simultaneously undergoes a transition from an initial state with \( n_I \) incident photons and \( n_S \) scattered photons to a final state with \( n_I - 1 \) and \( n_S + 1 \) photons, where

\[
H_{\text{Light}}|n_I, n_S\rangle = (n_I \hbar \omega_I + n_S \hbar \omega_S)|n_I, n_S\rangle \\
H_{\text{Light}}|n_I - 1, n_S + 1\rangle = [(n_I - 1) \hbar \omega_I + (n_S + 1) \hbar \omega_S]|n_I, n_S\rangle .
\]  

Stokes component corresponds to the process in which each scattered photon losses energy \( \hbar (\omega_I - \omega_{\text{Stokes}}) \) creating excitation in the crystal. Similarly, anti-Stokes component represents the process in which each scattered photon gains energy \( \hbar (\omega_{\text{AntiStokes}} - \omega_I) \) from the crystal. The occurrence of scattered photons at particular frequencies \( \omega_{\text{Stokes}} \) and \( \omega_{\text{AntiStokes}} \) depends on the ability of the crystal to absorb or emit energy in quanta of magnitude \( \hbar \omega \). The intensity peaks in an Raman spectrum therefore correspond to the
various excited states of the crystal. So it is possible to determine the excitation energies by measurement of frequency shifts of the scattered light from $\omega_I$, and obtains information regarding the excited-state lifetimes by measurement of the frequency widths of the intensity peaks.

Scattering cross section is proportional to the rate of transitions between the initial and final states. This transition rate is obtained from time-dependent perturbation theory, and includes contributions of first and higher orders in the matrix elements of the interaction parts of the Hamiltonian, namely $H_{\text{int}}$ and $H_1$.

Consider the interaction of light with a collection of electrons, where the $j$th electron has momentum operator $p_j$ and position vector $r_j$. The light field is included in the electronic Hamiltonian by making the replacement

$$p_j \rightarrow p_j + e A(r_j)$$

and the resulting coupling term reads

$$H_{\text{int}} = \frac{e^2}{2mc^2} \sum_j A^2(r_j) + \frac{e}{2mc} \sum_j [p_j \cdot A(r_j) + A(r_j) \cdot p_j],$$

where the first and second terms are often referred to as the $A^2$ and $A \cdot p$ parts, respectively.

The matrix element of the $A^2$ part between the initial and final states is

$$\langle f, n_f - 1, 1 | H_{AA} | i, n_i, 0 \rangle \sim \epsilon_I \cdot \epsilon_S \langle f | \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} | i \rangle .$$

The wavelength of light is on the order of 100 nm while the lattice constant is on the order of 0.1 nm. Thus $\mathbf{q} \cdot \mathbf{r}_j$ is very small, and in turn the $A^2$ part is important only for scattering by electronic transitions with the same initial and final band states.

The matrix element of the $A \cdot p$ part is

$$\langle f, n_f - 1, 1 | H_{AA} | i, n_i, 0 \rangle \sim \sum_l \sum_{j,j'} \left[ \frac{\langle f | e^{-i \mathbf{k}_I \cdot \mathbf{r}_j} \epsilon_I \cdot \epsilon_S \cdot p_j | l \rangle \langle l | e^{i \mathbf{k}_I \cdot \mathbf{r}_{j'}} \epsilon_I \cdot p_j | i \rangle}{\omega_i + \omega_I - \omega_l} + \frac{\langle f | e^{i \mathbf{k}_I \cdot \mathbf{r}_j} \epsilon_I \cdot p_j | l \rangle \langle l | e^{i \mathbf{k}_I \cdot \mathbf{r}_{j'}} \epsilon_S \cdot p_{j'} | i \rangle}{\omega_i - \omega_I - \omega_S} \right].$$
Figure 1.1: Diagrammatic representations of the three types of interaction that contribute to inelastic light scattering. The interaction in (a) corresponds to $H_{AA}$; the interaction in (b) and (c) corresponds to $H_{PA}$.

The $A \cdot p$ part is linear in the photon creation and destruction operators, and its contribution to the scattering is in second-order. The matrix element contains momentum operators of electrons and in turn allows interband transitions.

An alternative to the transition rate method of calculating cross sections is to derive the power spectrum. The quantum-mechanical form of the power spectrum is related to a retarded Green function by fluctuation-dissipation theorem. Various ways of calculating cross sections are essentially different forms of the same basic theory, and results derived by different methods are closed related.

We conclude this section by emphasizing the importance of symmetry considerations in Raman scattering. The time translational symmetry of the Hamiltonian and space translational symmetry of the crystal lead to the conservation of energy (1.4), (1.5) and momentum (1.6), (1.7), respectively. In non-magnetic systems, the time-reversal symmetry of the scattering processes results in a general relationship between Stokes and anti-Stokes cross sections. Crystal lattice is also invariant under rotational and reflectional operations. These symmetries are characterized by the point group of the lattice. The point group symmetry determines the symmetry properties of the second-order susceptibility, which in turn determines the symmetry properties of the spectral differential cross section and Raman response.

The spatial properties of the excitations are described by irreducible representations of the point group of the crystal. Let $\Gamma_X$ be the irreducible representation of the excitation
under study. In the microscopic theory with an initial state $|i\rangle$ of symmetry $\Gamma_i$ and a final state $|f\rangle$ of symmetry $\Gamma_f$, the excitation symmetry is that of the operator $|f\rangle\langle i|$, which projects the initial state to the final state. Therefore

\[ \Gamma_X = \Gamma_f \times \Gamma_i^* . \]  

(1.18)

The transformation properties of the incident and scattered light are described by the three-dimensional polar-vector representation $\Gamma_{PV}$ of the point group considered, because the electric field and polarization are both polar vectors.

The relation 1.2 between Stokes polarization, excitation amplitude and incident field must be invariant under all the symmetry operations of the point group. This invariance has two significant consequences for light scattering. The first consequence is the existence of selection rules. The invariance is satisfied only when the two sides of 1.2 have the same transformation properties. According to group theory, only $\Gamma_X$ that occur in the decomposition of $\Gamma_{PV}^* \times \Gamma_{PV}$ are allowed excitation symmetries. The second consequence is the restrictions on the components of the second-order susceptibility for allowed excitation symmetries. For each allowed $\Gamma_X$, some of the components are required to vanish while others are required to have related values.

The decomposition $\Gamma_{PV}^* \times \Gamma_{PV}$ contains only even-parity representations for the point groups containing inversion operation. On the contrary, the selection rules for electric-dipole absorption restrict the participating excitations to those of odd parity. Thus a rule of mutual exclusion applies for crystals invariant under inversion, in that light scattering and electric-dipole absorption have no allowed excitation symmetries in common.

1.2 Elementary excitations in solids

1.2.1 Electronic excitations

Electrons in crystals occupy Bloch states, and elementary excitations of conduction electrons in turn can be divided into intraband and interband transitions. Consider for example one
Figure 1.2: Cartoons showing (a) intraband electronic excitation and (b) interband electronic excitation.

completely filled valence band and one partially filled conduction band. In the intraband case, the incident photon transfers part of its energy to the system creating a particle-hole pair [Fig. 1.2(a)]. In the interband case, the photon excites an electron from the valence band to an intermediate state, which decays via a particle from the conduction band into the hole left behind in the valence band [Fig. 1.2(b)]. Intraband scattering is nonresonant while interband scattering may be resonant if the intermediate state coincides with a real electronic state.

The Raman response for nonresonant scattering in weakly correlated systems simplifies to a correlation function of an effective charge density

\[ \tilde{\rho}(q) = \sum_{k,\sigma} \gamma(k, q) c_{k+q,\sigma}^\dagger c_{k,\sigma} . \]  

(1.19)

The scattering amplitude, also called Raman vertex, is determined from the Raman matrix elements and light polarization vectors as

\[ \gamma(k, q) = \sum_{\alpha,\beta} \gamma_{\alpha,\beta}(k, q) \epsilon_{\alpha}^i \epsilon_{\beta}^s , \]  

(1.20)

where

\[ \gamma_{\alpha,\beta}(k, q) = \delta_{\alpha,\beta} + \frac{1}{m} \sum_{k_v} \frac{\langle k + q | p_{\alpha}^i | k_v \rangle \langle k_v | p_{\beta}^s | k \rangle}{E_k - E_{k_v} + \hbar \omega_i} \]

\[ + \frac{\langle k + q | p_{\alpha}^i | k_v \rangle \langle k_v | p_{\beta}^s | k \rangle}{E_{k+q} - E_{k_v} - \hbar \omega_s} \]  

(1.21)

with \( p \) being the momentum density matrix element. In the limit \( \hbar \omega_{i,s} \ll |E_{k_v} - E_k| \), the
Raman matrix elements are given by the inverse effective mass

$$\gamma_{\alpha,\beta}(k) = \frac{1}{\hbar^2} \frac{\partial^2 E_k}{\partial k_\alpha \partial k_\beta}.$$  \hspace{1cm} (1.22)

For strongly correlated systems, it is inconvenient to start from the $A^2$ and $\mathbf{A} \cdot \mathbf{p}$ parts. Instead, $H_{int}$ is derived from the effective Hamiltonian. Consider the two-dimensional Hubbard model

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} + U \sum_i n_{i,\uparrow} n_{i,\downarrow},$$  \hspace{1cm} (1.23)

where $\langle i,j \rangle$ denotes a sum over nearest neighbors. The interaction of light with the electrons is obtained by adding a phase to the creation and annihilation operators,

$$c_{i,\sigma} \rightarrow c_{i,\sigma} \exp^{-i(e/\hbar)c \int_{-\infty}^{r_i} \mathbf{A} \cdot dl}.$$  \hspace{1cm} (1.24)

Expanding in powers of $A$ gives

$$H_{int} = \frac{e}{\hbar c} \hat{\mathbf{j}} \cdot \mathbf{A} + \frac{e^2}{2\hbar^2 c^2} \sum_{\alpha,\beta} A_\alpha \hat{\gamma}_{\alpha,\beta} A_\beta,$$  \hspace{1cm} (1.25)

where

$$\hat{j}_\alpha(q) = \sum_k \frac{\partial \epsilon(k)}{\partial k_\alpha} c_{\alpha}^\dagger(k + q/2)c_\alpha(k - q/2)$$  \hspace{1cm} (1.26)

is the $\alpha$-component of the current operator $\hat{\mathbf{j}}$ and

$$\hat{\gamma}_{\alpha,\beta}(q) = \sum_k \frac{\partial^2 \epsilon(k)}{\partial k_\alpha \partial k_\beta} c_{\beta}^\dagger(k + q/2)c_\beta(k - q/2)$$  \hspace{1cm} (1.27)

is the stress tensor operator. The corresponding Raman matrix elements have similar expressions as (1.20) and (1.21):

$$M_{F,I}(q) = \sum_{\alpha,\beta} M_{\alpha,\beta}(k, q)e_\alpha^\dagger e_\beta,$$  \hspace{1cm} (1.28)

\[
M_{\alpha,\beta}(q) = \langle F|\hat{\gamma}_{\alpha,\beta}(q)|I \rangle + \sum_v \left\{ \frac{\langle F|\hat{j}_\beta(q)v|I \rangle \langle v|\hat{j}_\alpha(q)v|I \rangle}{E_v - E_I - \hbar \omega_i} \right. \\
+ \left. \frac{\langle F|\hat{j}_\alpha(q)v|I \rangle \langle v|\hat{j}_\beta(q)v|I \rangle}{E_v - E_I + \hbar \omega_s} \right\}. \hspace{1cm} (1.29)
\]
Crystal-field (CF) transitions of localized electrons on rare-earth ions are also explored in this thesis study. Because the 4\textit{f} orbit is compact, even when the 4\textit{f} ions fully occupy sites of a crystal lattice, the interaction between neighboring ions is so weak that these ions can be treated as free ions. The free-ion 4\textit{f} energy levels have degeneracies and symmetries governed by the three-dimensional rotation group appropriate to an ion in free space. The CF at the ion site splits the free-ion energy levels in a manner determined by the compatibility between irreducible representations of the rotation group and the site group. The wavefunctions for an energy level of a single ion in a crystal field are characterized by an irreducible representation of the site group. Specifically, states of ions with even numbers of electrons are characterized by single-group irreducible representations, while states with odd numbers of electrons are characterized by double-group irreducible representations. The all double-group representations are at least two-dimensional, corresponding physically to the Kramers degeneracy of odd-electron ions. The excitation symmetry is found by Eq. (1.18).

### 1.2.2 Magnetic excitations

In magnetically ordered phases, elementary excitations are magnons. By analog with electronic excitations, light scattering from magnons would happen through magnetic dipole interaction between the spin fluctuations and the magnetic vector of light. However, this interaction is very weak and electric dipole interaction provides a much more efficient mechanism. The magnons cause a spatially periodic modulation of the permittivity of the medium, and light is scattered by the permittivity fluctuations. Therefore, one-magnon light scattering, in both ferromagnets and antiferromagnets, can only be observed in systems with a finite spin-orbit coupling (SOC). Two-magnon scattering in ferromagnets is the second-order effect of one-magnon scattering, and in turn is extremely weak. Two-magnon scattering in antiferromagnets, however, can occur via an exchange mechanism [Fig. 1.3].

Above magnetic transition temperature, thermal fluctuations are strong enough to destroy magnetic ordering, and one-magnon light scattering disappears. Nevertheless, even
above the Néel temperature, two-magnon scattering in antiferromagnets persists because local correlations exist and hence the exchange pathway is still valid. Such scattering is also called paramagnon scattering to emphasize that it happens above the phase transition temperature.

In some special systems, no magnetic ordering occurs even at zero temperature, though the exchange interaction is relatively large. Quantum fluctuations induced by low dimensionality and geometrical frustrations both lead to absence of magnetic ordering. Nevertheless, magnetic excitations can be induced by inelastic light scattering in these systems. For one-dimensional antiferromagnetic Heisenberg chains, multi-spinon scattering is possible. Without SOC, the lowest order scattering is four-spinon excitations while with SOC, the lowest order scattering is two-spinon excitations. These excitations lead to a broad continuum in Raman spectra. For two-dimensional quantum spin liquids, besides broad magnetic continuum, collective modes in the magnetic symmetry channel has also been predicted theoretically.

1.2.3 Phononic excitations

In the field of chemistry and biology, inelastic light scattering is mostly used for the study of vibrational spectra of molecules. In solids, the elementary excitations corresponding to the collective vibrations of crystal lattice are phonons. Lattice vibrations create time-dependent
electric polarization, which in turn modulates the dynamical electric susceptibility and lead to scattering of light. Light scattering essentially probes zero-wavelength phonons, and the corresponding vibrational symmetries can be classified by irreducible representations of the crystal point group. The symmetries of the zero-wavevector vibrations are obtained by constructing the $3n$-dimensional representation of the crystal point group based on three orthogonal unit vectors located on each atom in the primitive cell, where $n$ is the number of atoms in the primitive cell. Then this representation need to be reduced into a sum of irreducible representations of the point group. The number and dimensions of the resulting irreducible representations give the number of different vibrational frequencies and the degeneracies of the corresponding modes of vibration.

Three of the degrees of freedom of the primitive cell at zero wavevector correspond to rigid displacements of the cell along the three coordinate axes. These three lattice vibrations are the acoustic modes. Their zero-wavevector symmetries are always the irreducible representations associated with a polar vector in the appropriate point group. The remaining vibrational modes at zero wavevector with nonzero frequencies are the optic modes. The symmetry of vibrational ground state is always the identity representation of the point group; knowing the symmetries of the excited states, the excitation symmetry is again found by Eq. (1.18).

1.3 Scope of the thesis

1.3.1 Overview

A major theme of condensed matter physics is the behavior of electrons in crystals. A periodic potential leads to Bloch states in which electrons occupy, and electronic properties are described in the framework of band theory [13]. A large number of systems, with weak correlation among electrons, have been well understood; electronic properties of these systems can be calculated at a quantitative level by virtue of density functional theory [14].
One challenge remaining is to expend our understanding to systems with intermediate or strong electron correlation. Different degrees of freedom, including charge, spin, orbit, and/or lattice are simultaneously active and coupled in these strongly correlated materials, which results in a wide range of intriguing phenomena [15]. Because of the complexity caused by strong correlation, density functional theory cannot well describe these systems, and there are many fundamental questions remain to be answered. Two aspects of correlated electron systems are addressed in this thesis: one is the quadrupolar fluctuations and crystal-field excitations of 4f-electron systems; the other is the nature of unconventional insulating phases in 5d-electron systems.

Exchange of virtual collective fluctuations could induce interaction between itinerant electrons. For instance, superconducting pairing is induced by the exchange of phonons in the case of conventional s-wave superconductors. Other collective modes, spin fluctuations as an example, could result in high-temperature and heavy-fermion superconductors. Following this line of thought, it is desired to investigate quadrupolar fluctuations, and the relationship between local quadrupole moments and itinerant conducting electrons. Due to the interplay of spin and orbital degrees of freedom, 4f electrons often carry quadrupole moment, providing a suitable platform for my study. Besides probing the fluctuations of quadrupoles directly, it is also crucial to study the CF excitations of 4f electrons to truly understand the nature and interaction between the quadrupole moment. This requirement is because CF potential, as the smallest energy scale compared to Coulomb repulsion and spin-orbit coupling (SOC), determine the ground state of 4f-electron systems. We choose two 4f-electron metals, CeB$_6$ and YbRu$_2$Ge$_2$, to study systems with quadrupolar ordering at finite wavevector and zero wavevector, respectively. The two compounds not only have high lattice symmetry (cubic for CeB$_6$ and tetrahedral YbRu$_2$Ge$_2$), but the 4f ions (Ce$^{3+}$ and Yb$^{3+}$) have a simple electronic configuration (one electron for Ce$^{3+}$ and one hole for Yb$^{3+}$). Thus, without undesired complexity, these two materials could illustrate in a clear way the physics of quadrupoles.
The importance of understanding the CF level scheme is not limited to the study of quadruple moments. It also helps to identify other uncommon correlated phases. One example is provided by spin liquids. These unconventional magnetic states have no long-range order, but have strong spin correlation and long-range entanglement. One way to identify these systems is to search for contribution which should be attributed to the magnetic excitations related to the proposed spin-liquid ground state in heat capacity. To properly evaluate the heat-capacity data, the CF contribution must be correctly subtracted. To illustrate this process, and extend our ability of analyzing CF excitations to systems with more complex electronic configuration, we study the CF level scheme of TbInO$_3$. Tb$^{3+}$ ion has eight $4f$ electrons, leading to much more complicated CF level scheme than those of Ce$^{3+}$ and Yb$^{3+}$.

Because of the extensiveness of $5d$ orbits, $5d$ electrons tend to be itinerant and $5d$-electrons systems are usually conductors. However, there are certain mechanisms which could render these systems insulating. Studying these uncommon insulating phases will broaden the our scope of understanding about electron correlation. I am particularly interested in two of them: SOC-induced insulator and excitonic insulator.

The best example to illustrate SOC-induced insulator is iridates. For Ir$^{4+}$ ions with $5d^5$ electron configuration in oxygen octahedra, the dominating CF potential splits the $5d$ orbits, forming a lower-energy $T_{2g}$ band. The strong SOC further splits the $T_{2g}$ band, resulting in a narrow half-filled $j_{\text{eff}} = 1/2$ state. Coulomb repulsion then leads to an insulating phase. The relatively large energy scale of SOC is essential for such unconventional insulating state to exist. This mechanism works for corner- or edge-shared Ir octahedra, for which the covalency between Ir ions is smaller compared to the SOC. On the contrary, for face-shared Ir octahedra the covalency can become larger than the SOC and render the $j_{\text{eff}} = 1/2$ picture invalid. A natural question comes: is $j_{\text{eff}} = 1/2$ physics the mechanism behind insulating iridates composed of face-shared Ir octahedra? Paramagnetic insulator Ba$_5$CuIr$_3$O$_{12}$, hosting face-sharing Ir octahedra forming quasi-one-dimensional chains, offers an opportunity
Excitonic insulator is an interesting insulating phase because it corresponds to a macroscopic quantum coherent state formed by electron-hole pairs, or call them excitons. Coherent states are formed by boson quasiparticles, and lead to quantum-mechanical behaviors at macroscopic scale, with superconductivity as an example. For a semimetal, if the exciton binding energy exceeds the band overlap, spontaneous band hybridization will be favored, and a macroscopic number of excitons will form. Studying materials with this unconventional insulating ground state will deepen our understanding of macroscopic quantum phenomena in condensed matter systems. Ta$_2$NiSe$_5$ is one promising candidate of excitonic insulator.

1.3.2 Multipolar Interactions

The study of CeB$_6$ and YbRu$_2$Ge$_2$ is associated charge quadrupoles, and that of TbInO$_3$ and Ba$_5$CuIr$_3$O$_{12}$ is related to magnetic dipoles. In this subsection a general discussion of multipolar interactions is provided.

Low-temperature electronic properties result from open shells of the constituent atoms. The electrons belonging to these shells may either be localized or show an itinerant behavior. Whereas the spatially extended s- and p-states almost always assume a band character, d- and f-electrons display various degrees of localization, ranging from totally localized to highly itinerant situations. Unlike f-electrons, d-electrons usually have weaker spin-orbit coupling and are more sensitive to the crystal field potential. This often leads to a large or even complete quenching of the orbital degrees of freedom of d electrons [16]. On the contrary, the interplay of spin and unquenched orbital degrees of freedom of f shells facilitates the formation of multipoles. f-electron systems are therefore a good choice for systematic investigation of multipolar interactions.

In solids, the f-electrons of a single ion produce charge and current distributions. The charge distribution can be parametrized by a series of electric multipoles; similarly, the
current distribution is related to a series of magnetic multipoles [17]. Under time reversal, the electric multipoles are even whereas the magnetic multipoles are odd. If the wave function of the f-electrons has definite parity (i.e. with negligible configuration mixing), odd-order electric multipoles and even-order magnetic multipoles must vanish.

The active multipoles (i.e. the multipoles which have non-zero magnitude for a f-electron ion in a crystal) are determined by the single-ion Hamiltonian. This Hamiltonian contains three main contributions: the electronic Coulomb repulsion $H_C$, the spin-orbit coupling $H_{SO}$ and the crystal-field (CF) potential $H_{CF}$. Generally, $H_C$ is the dominant interaction, and $H_{SO}$ is introduced through the LS coupling scheme. However, if the spin-orbit interaction is much larger than the Coulomb interaction, the effect of $H_{SO}$ should be considered before introducing $H_C$ as a perturbation. This corresponds to the jj coupling scheme. The CF potential experienced by the ions depends on the compound into which they are embedded, and particularly on the local symmetry of the crystallographic site they occupy. When $H_{CF}$ is much weaker than $H_C$ and $H_{SO}$, $H_{CF}$ can be restricted to the lowest J-manifold subspace.

The multipoles can interact in a diversity of ways. The classical interactions arise from the effect of the electric and magnetic fields produced by a certain ion on surrounding ions [18]. Such couplings are usually very weak and can be neglected. The direct-exchange comes from the exchange part of the Coulomb interaction, coupling the multipoles of two ions whose wave functions overlap [19]. In most cases, indirect coupling mechanisms are more important than direct exchange, whose strength rapidly decreases with increasing ion-ion distance. The super-exchange arises from the effective coupling via ligands shared by two ions [20]. The conduction-electron mediated interactions are important in metallic compounds: the multipoles at a given ion produce a polarization of the charge and spin distribution of conduction electrons, which is felt by a second ion and results in effective ion-ion interactions [21]. There are two main mechanisms providing this kind of coupling: Coulomb interactions (both direct and exchange) and effective two-body interactions arising from virtual valence fluctuations. There is also phonon-mediated interactions where
the interactions are transmitted by lattice vibrations [22]. Notice that magnetic multipoles don’t couple with the phonons due to time-reversal invariance. Which interacting mechanism being dominant not only depends on the specific properties of the compound under consideration, but also gets influenced by external parameters such as temperature, applied pressure and magnetic field.

Multipoles and their interactions have great fundamental interest because there are many important physical phenomena involving multipoles [23]: multipolar ordering, quadrupolar Kondo effect and quadrupole-fluctuation-mediated superconductivity (SC), to name a few. Ordering of high-rank multipoles is difficult to be directly probed by many experimental techniques. URu$_2$Si$_2$ is a striking case for which no conclusion on the nature of the ‘hidden order’ was reached since the observation of its low-temperature ordering phenomena in 1984 [24–26]. Only in recent years, Raman-scattering study demonstrates that the hidden order of URu$_2$Si$_2$ is a commensurate chirality density wave with hexadecapole order parameter [27, 28]. Quadrupolar Kondo effect refers to the possibility that if the crystal-field ground state of the localized f-electrons is a non-Kramers doublet, the fluctuating quadrupolar moment of this ground state could interact with the conduction electrons to produce strongly correlated properties, which is analogous to the ordinary Kondo effect [29]. Transport [30] and ultrasonic [31] measurement suggests that this effect is important for PrInAg$_2$. Finally, Sb nuclear quadrupole resonance study [32] provides evidence for quadrupole-fluctuation mediated superconductivity in PrOs$_4$Sb$_{12}$, the only known Pr-based heavy fermion superconductor in 2002 [33]. In the SC state, the spin-lattice relaxation rate shows neither a coherent peak just below $T_c$ nor a $T^3$ power-law behavior. It is suggested that PrOs$_4$Sb$_{12}$ be an isotropic heavy-fermion superconductor, which may argue for Cooper pairing via quadrupolar fluctuations.

The experimental methods used to study multipolar interactions can be divided into
indirect techniques and direct techniques, depending whether it couples to multipoles directly. Measurements of macroscopic properties, such as specific heat and magnetic susceptibility, may display anomalies indicating a phase transition without a ferromagnetic dipolar component, giving hints to a multipolar ordering [34–37]. Electric quadrupolar degrees of freedom may couple to lattice distortions of the same symmetry; measurements of elastic constants in this situation provide insights about the symmetry properties of a multipolar ordering [34, 38, 39]. However, for an unambiguous identification of the order parameter, microscopic probes that couple directly to the multipole degrees of freedom are required. Resonant X-ray scattering (RXS) fulfills this requirement [40–43]. RXS occurs when a polarized photon is virtually absorbed by exciting a core electron to empty states, and subsequently reemitted when the excited electron and the core hole recombine [44]. This method benefits from the large signal under resonant condition, but a quantitative treatment of the results is often difficult because RXS involves excited electronic states [45]. On the contrary, nonresonant x-ray diffraction can bring information on the magnitude and the orientation of the aspherical charge distribution that is easier to understand [46]. The experimental difficulty for probing periodical aspherical electronic densities is related to the extremely weak intensity of the associated Bragg reflections; high-brilliance synchrotron radiation is usually needed [47]. X-ray diffraction is particularly powerful for characterizing electric quadrupole ordering, which can also be studied by neutron diffraction in applied fields where induced magnetic dipole moments reveal the periodicity and symmetry of the underlying quadrupolar order [48–51]. Nuclear magnetic resonance experiments are also very valuable in the sense that it is able to characterize not only field-induced magnetic moments from the field orientation dependence of the hyperfine splitting at the corresponding nuclei, but also the electric quadrupole order from the oscillatory spin-echo decay resulting from the electric field gradient [52].

Our experimental method, Raman scattering, is not one of the common tools used in the field of multipole systems. Compared with the methods mentioned above, Raman scattering
has both advantages and difficulties. First, Raman scattering couples directly to the charge degree of freedom, and serves as a direct technique for studying multipolar interaction in f-electron systems. Notice that quadrupolar excitations involves \( \Delta L_z = \pm 2 \); among conventional experimental probes only inelastic photon scattering can induce such excitations. Second, this technique probes dynamical information, and is sensitive to quadrupolar fluctuations. Third, the symmetry of the excitations can be identified by polarization-dependent Raman measurement. This is because the inelastic light-scattering process is sensitive to the point group symmetry of the lattice. Moreover, with suitably chosen experimental setup, Raman scattering can achieve extremely high spectral resolution [53], which inelastic X-ray cannot easily match [54]. Raman scattering therefore has the ability to specify the symmetry of low-energy or quasielastic excitations. Furthermore, the temperature or magnetic field dependence of physical properties (energy, lifetime and intensity, etc.) of these excitations can be obtained by analyzing the Raman spectra. The usefulness of Raman scattering for studying multipole systems has been demonstrated [27, 28]. However, Raman scattering investigation of multipolar interactions also has two main limitations. One limitation is the temperature range. Because of the laser heating, it is difficult to reach extremely low temperature. Thus, the multipolar ordering temperature of some systems may be too low to perform Raman study. Another limitation is the momentum transfer range. The momentum carried by visible photon is negligible compared to the Brillouin zone size. Raman process therefore cannot directly couples to multipolar order parameters with a finite wavevector.

1.3.3 Spin Liquids

The study of TbInO\(_3\) and Ba\(_5\)CuIr\(_3\)O\(_{12}\) is motivated by the possibility of spin-liquid phase. In this subsection a general discussion of spin liquids is provided.

Spin liquids (SL) generally refer to highly correlated or entangled spin systems without magnetic ordering. These systems are interesting due to their exotic nature and possible
applications in quantum computation [55–57].

Quasi-one-dimensional (1D) magnetic systems usually order at sufficiently low temperature due to finite interchain coupling. Nevertheless, above the magnetic ordering temperature, the elementary excitations are fractional spin-1/2 and charge neutral fermions called spinons [58, 59]. Spinon dispersion has been measured by inelastic neutron scattering (INS) experiments [60–62], which confirms the relevant theories.

Two-dimensional (2D) SL materials are typically based on geometrical frustration and/or anisotropic magnetic interactions. Non-bipartite 2D structures, including kagome and triangular lattices, are theoretically suggested to host SL ground state [63, 64], and supporting experimental evidences have appeared [65, 66]. Bipartite honeycomb lattice, though absent of geometrical frustration, nevertheless could render SL state when bond-dependent anisotropic couplings are present [67]. Magnetic systems with honeycomb lattice which do not order down to lowest temperature have yet to be found.

For three-dimensional (3D) compounds, Pr-, Tb- and Yb-based rare earth pyrochlores [68–70] are promising to realize emergent quantum electrodynamics with magnetic and electric monopoles, as well as gauge photons, serving as elementary excitations. Suffice it to say that SL states can arise from a variety of distinct scenarios in condensed matter physics, and they have been attracting great interest in this field.

Among 2D realizations of SL, triangular lattice is of particular interest. Though non-bipartite, the degree of frustration for triangular lattice is not as strong as kagome lattice. Simple nearest-neighbor antiferromagnetic (AFM) Heisenberg model with S=1/2 renders long-range magnetic order for triangular lattice, but not so for kagome lattice. To realize robust SL behavior in triangular lattice, additional frustration, especially anisotropic couplings is therefore desired [71, 72]. Studying the interplay of geometrical frustration and anisotropic interaction in triangular-lattice systems could enrich our understanding of the physics of SL systems.
Chapter 2

Experimental

The inelastic light scattering technique involves measurement of scattered light at frequencies shifted from the incident light. The differential cross section is very small because the scattering process is of second order in the electron-photon interaction. In addition, typical cross sections for electronic or magnetic scattering are smaller by several orders of magnitude than those of vibrations. Pursuing the desired sensitivity, the experimental technique evolves mainly in three aspects: (1), the light source: from filtered sunlight [73] to mercury lamps to laser; (2), the spectrum analyzer: from quartz-prism monochromators to holographically fabricated grating spectrometers; (3), the detector: from photographic plates to photo-multipliers to charge-coupled devices. Among these improvements, the introduction of laser truly revolutionized the inelastic light scattering community. Meanwhile, the application of computers has provided great ease in conducting experiments, collecting data and analyzing the results.

The experimental system used in this thesis study represents the state-of-the-art technique of inelastic light scattering. This system, supporting control of excitation energy, light polarization and temperature, has extraordinary performance regarding sensitivity and stray-light rejection. An overview of the whole system is presented in Sec. 2.1. Various aspects of the apparatus are described in Sec. 2.2. Finally, the data processing procedures are discussed in Sec. 2.3.
Figure 2.1: Schematic of the experimental system used in this thesis study for inelastic light scattering measurements. Adapted with permission from Ref. [74].

2.1 Overview

The experimental system is composed of the optical and cryogenic subsystems [Fig. 2.1]. The optical subsystem consists of a Krypton laser as the light source, various components along the optical path, and a triple-stage spectrometer. The optical components first improve the quality and adjust the polarization and intensity of the incoming light; second focus the beam to a tiny spot on the sample surface; third select outcoming light with a particular polarization. The cryogenic subsystem enables temperature control from 2 to 300 K. The data are collected digitally and transferred into a computer for analysis.

2.2 Apparatus

2.2.1 Optical subsystem

Light source

A continuous-wave rare-gas (Krypton) laser (Coherent Innova 302C) is used as the light source.

There are many reasons for this choice. A delta function would be the ideal frequency distribution for the light source in inelastic light scattering experiments. A laser is by far the
best approximation to this ideal. Besides, the Krypton laser beam is of small size (1.5 mm diameter) and is well collimated (0.5 mrad full angle divergence), and in turn can be readily directed over large distance and eventually focused to a small area (50 × 100 µm²). The excellent collimation comes from the long laser cavity. Moreover, the output laser beam is of linear polarization by virtue of a built-in Brewster window. This Krypton laser also provides a wide choice of lines (14 different lines from infrared to ultra-violent region), and excellent power stability (± 0.5% in 8-hour period).

The principal component of a rare-gas laser is a plasma tube which provides optical gain at the laser frequency [Fig. 2.2]. A power supply for exciting the discharge, and a water cooling system for temperature control are required. In the discharge process, rare-gas ions are gradually trapped in the walls of the tube, and a gas reservoir will replenish the plasma tube when the tube pressure is below a certain threshold. The resonator provides feedback to the amplifying plasma tube, producing oscillation. The resonator mirrors are external to the plasma tube to avoid damage by the discharge. The two ends of the plasma tube are aligned at Brewster angle. At Brewster angle the electric-field component in the plane of incidence is transmitted with no reflection and the perpendicular component is partly reflected. This results in an effectively low-Q system for the perpendicular component, so that the laser output is completely plane polarized in the plane of incidence. The Brewster prism is used for wavelength selection.
Table 2.1: The color, wavelength, and energy of the laser lines used in this thesis study.

<table>
<thead>
<tr>
<th>Color</th>
<th>Wavelength (nm)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infra-red</td>
<td>752</td>
<td>1.65</td>
</tr>
<tr>
<td>Red</td>
<td>676</td>
<td>1.83</td>
</tr>
<tr>
<td>Red</td>
<td>647</td>
<td>1.92</td>
</tr>
<tr>
<td>Yellow</td>
<td>568</td>
<td>2.18</td>
</tr>
<tr>
<td>Green</td>
<td>530</td>
<td>2.34</td>
</tr>
<tr>
<td>Green</td>
<td>520</td>
<td>2.38</td>
</tr>
<tr>
<td>Blue</td>
<td>482</td>
<td>2.57</td>
</tr>
<tr>
<td>Blue</td>
<td>476</td>
<td>2.60</td>
</tr>
</tbody>
</table>

For Coherent Innova 302C used in this thesis study, the tube current is set to 30 A when the laser is switched on or off, and typical operating current is between 32 and 38 A. The cooling water has a flow rate of 9.6 L/min. The two resonator mirrors need to be changed, and the Brewster prism need to be fine tuned to select a particular laser line and optimize its output power. A built-in aperture is used to obtain TEM\(_{00}\) mode. Some commonly-used laser lines are listed in Table 2.1.

The main disadvantage with this laser is that other emission lines of the Krypton plasma discharge, which have energy very near that of the laser line in use, when elastically scattered from a sample of poor optical quality, may produce spurious features in measured Raman spectra as intense as expected inelastic scattering features. The prism monochromator and pinhole in the optical path serve to remove these unwanted plasma discharge lines.

**Optical path**

The optical path from the laser to the sample surface to the entrance slit of the spectrometer, mainly serves four proposes: (1), removing extra plasma discharge lines; (2), control the intensity and polarization of the incident light; (3), facilitating real-time measurement of laser intensity; (4), focus the beam onto the sample surface; (5), collect most of the scattering light with a particular polarization. All the lens used are aberration corrected.
The removal of unwanted plasma discharge lines are achieved by the prism monochromator and pinhole. The beam coming from the Krypton laser first enters the prism monochromator, where four flint prisms with an equilateral triangle cross section disperse the beam. After passing through the monochromator, the laser line of interest is deflected precisely 90°, while the extra lines have a small angular deviation from 90° because of the dispersion. The beam then travels 1.5 m until it arrives at the pinhole which only allows the laser line to pass. An objective and a concave lens are placed across the pinhole, expanding the beam diameter from 1.5 mm to 10 mm. The pinhole diameter $D$ matches the diffraction limit of the objective

$$D = \frac{4f\lambda}{\pi d},$$

where $f = 11.0$ mm is the objective focal length, $\lambda$ is the laser wavelength and $d = 1.50$ mm is the incoming beam diameter. For convenience, the pinhole diameter is fixed to 4.7 $\mu$m, which roughly corresponds to $\lambda \simeq 500$ nm.

In order to control the intensity of the incident light, three reflective, high-power, neutral-density (ND) filters are used. The optical density $d$ of a ND filter is defined by the relationship

$$\frac{I_t}{I_0} = 10^{-d},$$

where $I_t$ is the transmitted light intensity, $I_0$ is the incident light intensity. Therefore OD 0.1 corresponds to 80% intensity transmission, and OD 0.5 corresponds to 30% intensity transmission.

Four different polarizations of the incident light are need: horizontal-linear, vertical-linear, left-circular and right-circular polarizations. On the one hand, the two linear polarizations are achieved by the use of a half-lambda wave-plate and a cube polarizor. When the angle between the polarization of incident light and the slow axis of the wave-plate is $\theta$, the light polarization will be rotated by $2\theta$ relative to the original polarization. Because of the internal Brewster window, the beam coming out of the laser is vertically polarized. Thus when vertical-linear polarization is needed, $\theta$ is zero and the polarizor is rotated to pass
light with vertical-linear polarization; when horizontal-linear polarization is required, \( \theta \) is 45° and the polarizor is rotated to pass light with horizontal-linear polarization. The polarizor is necessary because the retardation of the half-lambda wave-plate is precisely half wave only when the light wavelength is 500 nm. Without the polarizor, pure polarization cannot be generally prepared. On the other hand, the two circular polarizations are realized by the use of a Berek compensator which can introduce an arbitrary retardation to the beam. It has an orientation setting and a retardation setting. To transform linearly-polarized light into circularly-polarized light, the orientation is set be 45° and the retardation is set be quarter wave. At quarter wave retardation, the actual value indicated on the retardation knob varies according to the light wavelength.

After the beam expander, a thin quartz plate in the optical path directs 5% intensity into a light power meter. Besides showing the light intensity on a liquid crystal display (LCD) screen, the power meter sends the readings to a computer for data processing.

The focusing lens focuses the 10 mm diameter beam to a spherical 50 \( \mu \)m diameter spot on the sample surface. When a larger defect- and strain-free area can be found on the sample surface, the focusing lens is tilted about 20° to produce an elongated elliptical spot to reduce the power density and, in turn, laser heating. The incident angle is 17°, and the specular reflection is blocked.

The scattered light is collected by a 38 mm diameter lens, corresponding to a collection cone of 30°. A cube polarizor alone can select scattered light with horizontal-linear or vertical-linear polarization. A 50 mm diameter quarter-lambda wave-plate made of mica is put in front of the cube polarizor when circularly polarized light need to be collected. Although the retardation of mica is relatively wavelength-independent for visible light, 1-3% polarization leakage is observed.
**Spectrometer**

A custom designed triple-stage spectrometer is used in this thesis study. Every stage is Czerny-Turner type [75]; the first two stages operates in subtractive mode and the third stage disperses the light. The gratings are holographically-made reflective planar gratings, blazed at 500 nm. They are moved by sine bar configuration, with the step motors controlled by a computer. The mirrors have off-axis parabolic shape and are fixed in position. This particular shape eliminates chromatic aberration. A flat mirror is installed right behind the entrance slit. It delivers the incoming light to a high-sensitivity color camera so that the images of both the sample and the entrance slit can be observed during alignment. This mirror is automatically removed from the optical path during data collection.

The image of the sample surface is focused at the entrance slit. Thus, adjusting the dimensions of the entrance slit controls the area from which signal is collected. However, the horizontal dimensions of the entrance slit, exit slit and light detector pixel must match. If the slit dimension is larger than the pixel size, the spectral resolution is reduced; while if the slit dimension is smaller than the pixel size, the sensitivity is reduced because less light is collected.

Contemporary research-grade reflective gratings are ruled either mechanically or holographically. The latter ruling method introduces less defects and is thus preferred. The grating A blazed grating is optimized to achieve maximum grating efficiency in a given diffraction order. The grating lines of a blazed grating possess a sawtooth-shaped cross section [Fig. 2.3], which concentrate the diffracted power to a desired diffraction order. In our case, the grating efficiency is maximized in the first order, and the optimization can only exactly be achieved for 500 nm.

The key to understand the working principle of a blazed reflective grating is the grating function in the first order

\[ \sin \alpha + \sin \beta = \frac{\lambda}{d}, \quad (2.3) \]
Figure 2.3: Schematic of the light path for a reflective grating.

where $\alpha$ is the incident angle, $\beta$ is the diffracted angle, $\lambda$ is the light wavelength and $d$ is the distance between two nearest grating grooves [Fig. 2.3]. This equation can also be written as

$$\sin \frac{\alpha + \beta}{2} \cos \frac{\alpha - \beta}{2} = \frac{\lambda}{2d}.$$  \hspace{1cm} (2.4)

Because the position of the mirrors is fixed, $\alpha - \beta$ is a constant, and $\lambda$ in turn linearly depends on $\sin(\frac{\alpha+\beta}{2}) = \sin(\phi)$. Sine bar configuration allows precise control of $\sin(\phi)$ using a step motor [Fig. 2.4]. Therefore, different parts of the spectrum can be projected onto the light detector by changing the extension of the screw in the sine bar configuration.

Dispersion and resolution are two important factors of a grating. The angular dispersion $d\beta/d\lambda$ at the first order is given by

$$\frac{d\beta}{d\lambda} = \frac{1}{d\cos\beta}.$$  \hspace{1cm} (2.5)

Figure 2.4: Schematic of the sine bar configuration used to control the grating orientation.
The linear dispersion $dx/d\lambda$ is obtained by noticing $dx = f \tan (d\lambda) \simeq f \, d\lambda$:

$$\frac{dx}{d\lambda} = \frac{f}{dcos\beta},$$

\hspace{1cm} (2.6)

where $f$ is the focal length of the spectrometer. The resolving power $\lambda/d\lambda$ at the first order is simply the groove density. Although high groove density improves resolution, the simultaneously measurable spectral range is reduced because the light detector has a finite size. Therefore three sets of gratings with 150, 600 and 1800 mm$^{-1}$ groove density are prepared to meet different needs.

Although the specular reflection is blocked, because the sample surface is usually not atomically flat, elastically scattered light still enters the collection cone. Such elastic component is stronger than the inelastic component by orders of magnitude. If strong elastic component entered the light detector, the corresponding pixels would suffer permanent damage. To remove the elastic component, the first two stages are used in the subtractive mode as a spectral band-pass filter. Mirror $M_2$ focus the dispersed light on the intermediate slit $S_2$. The horizontal dimension of $S_2$ determines the frequency range of the passing light. Mirrors $M_3$ and $M_4$ relay the light to the other intermediate slit $S_3$, which serves the same purpose as $S_2$. Because grating $G_2$ recombines the dispersed light, only the third stage contributes to the dispersion of the output light. The spectral resolution of the 1800 mm$^{-1}$ grating at 532 nm is 0.9 cm$^{-1}$.

**Light detector**

A back-illuminated, liquid-nitrogen-cooled, electron multiplying charge coupled device (EM-CCD) camera (Andor) is used as the light detector.

First of all, a camera is needed to simultaneously record the whole spectrum from the spectrometer. Contemporary research-grade digital cameras can be divided into two class: EMCCD or scientific complementary metal–oxide–semiconductor (sCMOS). Only EMCCDs can deliver the extreme sensitivity required for the most light-starved conditions.
Ordinary CCDs are forward-illuminated, and part of incoming photons are scattered off by the electronic components on the front surface, reducing the sensitivity. Back-illumination prevents such loss, and >95% quantum efficiency between 500 and 600 nm has been achieved. Cooling with liquid-nitrogen significantly reduces the noise caused by thermal fluctuations, and electron multiplying almost eliminates the readout noise, rendering the signal only shot noise limited.

Because the spectrometer only disperses the light in the horizontal direction, all the pixels along the same column are binned into a stripe. Stripes can be further binned to increase the signal-to-noise ratio at the cost of reducing spectral resolution.

The relationship between pixel number and light wavelength is determined by measuring the sharp spectral lines of gas discharge lamps at given grating positions. The wavelength of these emission lines is known, and the pixel numbers where they appear are measured. Fitting the wavelength-pixel pairs with the spectrometer equations gives the desired relationship.

2.2.2 Cryogenic subsystem

A continuous-flow helium-cooled cryostat (Oxford Instruments) is used. Liquid helium is transferred from a 60 L dewar (Airgas) to a small liquid reservoir. The supply rate is controlled by a flow meter. This reservoir is connected to the cryostat through a needle valve which regulates the cooling power. Temperature between 300 and 3 K can be routinely reached and stabilized by adjusting the supply rate and cooling power. The shielding layer reducing thermal radiation is cooled by the back-flow of helium gas, and the vacuum layer reducing thermal conduction need to be pumped to $10^{-6}$ Torr. A heating coil is installed in the cryostat, which can be used for stabilizing the temperature, or collecting data on warming. A thermometer measures the environmental temperature near the sample. The temperature on the sample surface, however, is higher than the environmental temperature due to laser heating. A proportional–integral–derivative (PID) controller is available for
automatic temperature control.

2.3 Data Processing

It takes multiple steps to convert the detected signal into Raman response: 1, subtracting the background function; 2, multiplying by the response function; 3, removing spectral spikes; 4, performing optical corrections; 5, multiplying by the thermal factor; 6, analyzing the errors.

2.3.1 Calibrations

Proper data processing requires accurate calibration curves. Specifically, light detector background function and instrumental response function are needed.

Background Function

Faint light leaking into the experiment room and black-body radiation of various components contribute to a background to the detected signal. This background can be safely neglected in most experiments. However, in special cases, especially for measuring fine features of electronic excitations in metals, the signal is extremely weak and comparable to the background. For such experiments, the background need to be measured and subtracted from the detected signal.

Response Function

The throughput of the spectrometer and light detector depend on the polarization and frequency of the collected light. Response function specifies the ratio of the intensity of detected light to the intensity of incoming light for a particular setting. A calibration lamp having known spectral intensity is used, and the response function is obtained by dividing the measured spectral intensity by the known spectral intensity. The background-subtracted
signal is first normalized by the collection time and laser power, and then divided by the response function.

### 2.3.2 Spectral Spike Removal

Secondary cosmic rays, containing high-energy charged particles and photons, induce significant counts at the CCD pixel hit, and in turn produce spikes in collected spectra [76]. In order to remove them, the whole collection time is divided to several consecutive frames. A simple algorithm is to compare the values recorded during every frame to their average, and discard values which are more than 3 standard deviations larger than the average. At least 3 frames are needed for this algorithm. More advanced methods for spike removal exist [77].

### 2.3.3 Optical Corrections

The signal is proportional to the differential cross section \( \frac{d\sigma'}{d\Omega'} \), where \( \Omega' \) is the solid angle defined by the collection lens, and \( \sigma' \) is the measured cross section. \( \frac{d\sigma'}{d\Omega'} \) is first converted to \( \frac{\partial^2\sigma}{\partial\Omega'\partial\lambda_S} \) by virtue of the spectrometer equations. The latter is in turn converted to \( \frac{\partial^2\sigma}{\partial\Omega'\partial\omega_S} \), which is called spectral differential cross section in theoretical studies, or scattering intensity in experimental literature. Due to refraction at the sample surface, the solid angle \( \Omega \) inside the crystal is different from the solid angle \( \Omega' \) of the collection lens. The ratio of them satisfy

\[
\frac{\Omega'}{\Omega} = \frac{1 - \cos\theta'}{1 - \cos\theta}.
\]

(2.7)

For small \( \theta' \),

\[
d\Omega' = n(\lambda)^2 d\Omega.
\]

(2.8)

Reflection at the sample surface further introduces a correction factor, and the real scattering intensity is the measured scattering intensity times \( \frac{1}{(1-R(\lambda_L))(1-R(\lambda_S))} \), where \( R(\lambda) \) is the reflection coefficient at wavelength \( \lambda \), \( \lambda_L \) is the wavelength of the laser and \( \lambda_S \) is the wavelength of the scattered light. Moreover, because of finite penetration depth, another
correction factor which depends on the laser spot size $A$ and absorption coefficient $\alpha$, need to be taken into account. Combining the three optical corrections, the real scattering intensity is

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \sim n(\lambda)^2 \frac{\alpha(\lambda_L) + \alpha(\lambda_S)}{A(1 - R(\lambda_L))(1 - R(\lambda_S))} \frac{\partial^2 \sigma'}{\partial \Omega' \partial \omega}.$$  \hspace{1cm} (2.9)

The scattering intensity contains both Raman signal and photoluminescence signal. Only the Raman part is related to Raman response by fluctuation-dissipation theorem. To distinguish Raman signal from photoluminescence signal, excitation-dependent measurements are needed.

### 2.3.4 Error Analysis

To assess the error of measured values, the first step is to determine the probability mass function. The probability of detecting $N$ photons at each pixel within a certain period of time follows Poisson distribution

$$P_\mu(N) = e^{-\mu} \frac{\mu^N}{N!},$$  \hspace{1cm} (2.10)

where $\mu$ is the average number of photons detected in the time period. The standard deviation of Poisson distribution is $\sqrt{\mu}$ [78], and the signal-to-noise ratio is in turn also $\sqrt{\mu}$. To double the signal-to-noise ratio, the light power or collection time need to be multiplied by four times. For most experiments, $\mu$ is larger than ten. In this case, the Poisson distribution $P_\mu(N)$ can be well approximated by a Gaussian distribution

$$G_{\mu,\sigma}(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}},$$  \hspace{1cm} (2.11)

with $X = \mu$ and $\sigma = \sqrt{\mu}$.

Consider $k$ repeated measurements. For the $i$-th measurement, the result is denoted as $x_i$. The best estimation $\bar{X}$ for $X$, and the best estimation $\bar{\sigma}$ for $\sigma$ are

$$\bar{X} = \frac{1}{k} \sum_{i=1}^{k} x_i.$$  \hspace{1cm} (2.12)
\[ \tilde{\sigma} = \sqrt{\frac{1}{k-1} \sum_{i=1}^{k} (x_i - \tilde{X})^2} , \quad (2.13) \]

and the corresponding standard deviation, \( \sigma_{\tilde{X}} \) and \( \sigma_{\tilde{\sigma}} \), for these estimations are

\[ \sigma_{\tilde{X}} = \frac{\tilde{\sigma}}{\sqrt{k}} \quad (2.14) \]
\[ \sigma_{\tilde{\sigma}} = \frac{\tilde{\sigma}}{\sqrt{2(k-1)}} \quad . \quad (2.15) \]

The scattering intensity or Raman response plotted in Raman spectra are derived from \( \tilde{X} \), and their error bars come from \( \sigma_{\tilde{X}} \).
Chapter 3

Quadrupolar fluctuations and crystal-field excitations in 4f-electron systems

In this chapter, the work on 4f-electron systems CeB₆, YbRu₂Ge₂ and TbInO₃ is presented. There are two main themes: fluctuations of quadrupole moments, and local crystal-field (CF) excitations.

A comprehensive spectroscopic study of CeB₆ is presented in Sec. 3.1. The CF physics of this material is explored in detail by both experiments and calculation. We further show that the tendency towards finite-wavevector quadrupolar ordering induces ferromagnetic correlations which manifest as long-wavelength magnetic fluctuations. Investigation of the CF excitations and quadrupolar fluctuations of YbRu₂Ge₂ is in Sec. 3.2. The zero-wavevector quadrupolar fluctuations are directly probed, and we show evidence for the coupling of CF transitions and phonon modes of the same symmetry. The work on the low-energy CF level scheme of TbInO₃ is shown in Sec. 3.3. Evidence for the coupling of CF modes and phonon modes also exist in this compound. In particular, we demonstrate the important role played by CF level scheme in evaluating the heat-capacity data for contribution related to spin-liquid phase.
3.1 Quadrupolar fluctuations and crystal-field excitations in CeB$_6$

Strongly correlated $d$- and $f$-electron systems support a rich variety of low-temperature phases, including magnetism and superconductivity [15, 79–81]. Among these phases, long-range order of multipoles, namely high-rank electric or magnetic moments, has great interest [16, 23, 82, 83]. For example, second-rank quadrupolar moments could lead to novel phenomena including the quadrupolar Kondo effect [29] and quadrupole-fluctuation-mediated superconductivity [32]. In $d$-electron systems, the orbital angular momentum is usually quenched by large crystal-field (CF) splitting, hindering multipolar moments. $f$-electron systems, on the other hand, are suitable choices to study multipolar interactions and ordering phenomena by virtue of the interplay of the spin and orbital degrees of freedom. Indeed, the actinide dioxides, in which 5$f$-electrons play an important role, serve as a paradigm for understanding the physics of multipolar interactions [23]. Quadrupolar orderings have also been discovered in a number of 4$f$-electron compounds [82, 84–88].

CeB$_6$, with its simple chemical composition, lattice structure, and electronic configuration, is considered a prototypical example of heavy-fermion metal with quadrupolar ordering. This material has a cubic structure (space group Pm$ar{3}$m, No. 221; point group O$_h$) composed of cerium ions and boron octahedrons [Fig. 3.1(a)]. Every Ce$^{3+}$ ion has only one electron in its 4$f$ orbital and O$_h$ site symmetry. CeB$_6$ undergoes a second-order phase transition into a non-magnetic phase at $T_Q = 3.2$ K, before developing an antiferromagnetic (AFM) order below $T_N = 2.3$ K [89, 90]. The AFM phase has a double-Q commensurate magnetic structure with $Q_1=(0.25, 0.25, 0)$ and $Q_2=(0.25, 0.25, 0.5)$ [91, 92]. As for the non-magnetic phase, neutron scattering shows no structural transition at $T_Q$ [92]. Resonant X-ray diffraction determines that this non-magnetic phase involves an orbital ordering with wavevector (0.5, 0.5, 0.5) [93], and the $C_{44}$ elastic constant, related to $\epsilon_{xy}$-type strains, shows an anomaly at $T_Q$ [38]. Based on these results, it is generally believed that the non-magnetic phase is a two-sublattice arrangement of Ce$^{3+}$ $O_{xy}$-type electric quadrupole moments, with a wavevector (0.5, 0.5, 0.5) [82]. This proposed antiferroquadrupolar (AFQ)
model is consistent with experimental data in the presence of magnetic field \([94–98]\), but to our knowledge, up to now there is no direct evidence demonstrating the \(O_{xy}\)-type AFQ order in zero field. A sketch of field-temperature phase diagram for CeB\(_6\) is shown in Fig. 3.1(b). All experimental results reported in this study correspond to the zero-field paramagnetic (PM) phase, namely, the data is acquired at \(T > T_Q\).

In the recent years multiple experimental studies have revealed the importance of unexpected ferromagnetic (FM) correlations in the low-temperature ordering phenomena of CeB\(_6\). In the AFQ phase with finite magnetic field, electron spin resonance (ESR) with narrow linewidth was uncovered, pointing to existence of FM correlations \([99]\). Theoretical study suggested that such FM correlations result from AFQ ordering \([98]\). A zone-center excitation at the (110) point, following the energy of ESR, was found by inelastic neutron scattering (INS) \([100]\). In the AFQ phase at zero magnetic field, this finite-energy mode collapses into a quasi-elastic peak \([101]\). Moreover, intense FM fluctuations were uncovered in the AFM phase, suggesting propensity to FM instability \([101]\).

Both the AFQ and AFM phases are closely related to the CF ground state \([82]\). In CeB\(_6\), 6-fold degenerate \(^2F_{5/2}\) is the ground multiplet, and 8-fold \(^2F_{7/2}\) is the lowest-energy excited multiplet \([Fig. 3.2]\). These two multiplets were identified in photoemission spectroscopy studies \([102, 103]\) by the self-energy effects \(^1\). From group theory analysis \([107]\), the cubic

\(^1\)Photoemission spectroscopy probes energy states below the Fermi level, thus, ARPES cannot directly access the \(^2F_{7/2}\) multiplet. However, virtual excitations to the narrow \(^2F_{7/2}\) multiplet contribute to the self energy of the spectral function, making the \(^2F_{7/2}\) multiplet identifiable in the photoemission spectra.
Figure 3.2: Schematic energy diagram illustrating the splitting of 4f orbital by spin-orbital coupling and cubic crystal field.

CF potential splits the $^2F_{5/2}$ multiplet into quartet $\Gamma_8$ and doublet $\Gamma_7$ states, and the $^2F_{7/2}$ multiplet into doublet $\Gamma_6^*$, doublet $\Gamma_7^*$, and quartet $\Gamma_8^*$ states. For the $^2F_{5/2}$ multiplet, the $\Gamma_8$ state is the ground state [108–111] and the $\Gamma_7$ state has an energy of 372 cm$^{-1}$ at room temperature [109, 112]. For the $^2F_{7/2}$ multiplet, the energy of the CF levels has not been determined experimentally.

In order to better understand the low-temperature ordering phenomena in CeB$_6$, a more detailed study of the interplay of CF excitations, lattice dynamics and the FM correlations is required. Raman spectroscopy is a suitable technique providing symmetry-resolved excitation spectra of electronic, magnetic, and phononic degrees of freedom. As a photon-in-photon-out inelastic scattering process, polarization-resolved Raman scattering has the unique advantage of high energy-resolution and the ability to disentangle the excitation spectra into individual symmetry channels. The symmetry of a particular excitation can be identified by controlling the polarization of the incident and scattered light [9]. This

Details of this mechanism can be found in Refs. [104–106]

$^2$Asterisks are used to distinguish the CF states of the $^2F_{7/2}$ multiplet (\(\Gamma_6^*, \Gamma_7^*\) and \(\Gamma_8^*\)) from those of the $^2F_{5/2}$ multiplet (\(\Gamma_7\) and \(\Gamma_8\)).
an experimental method has been successfully used to study CF excitations [113, 114]; it is a well-fitted choice of investigating the intra- and inter-multiplet CF excitations of CeB₆. Moreover, Raman scattering makes it possible to study the excitations in the magnetic dipolar (T₁g of O_h group) and electric quadrupolar (E_g and T₂g of O_h group) channels separately. Thus, the relationship between the quadrupolar correlations and FM correlations can be clarified. Notice that quadrupolar excitations involve a change of the component of angular momentum along the quantization axis by two quantum units. Among conventional experimental probes, only photons can induce quadrupolar excitations.

In this Section, we present a comprehensive study of CeB₆ using optical secondary-emission spectroscopy. We identify an intense photo-luminescence feature corresponding to 5d − 4f recombination process. We analyze the temperature-dependence of both intra- and inter-multiplet CF excitations, and illustrate the interaction between light and CF states by a model Hamiltonian calculation. We draw information about the electron-phonon interaction by studying lattice dynamics. We observe dynamical magnetic fluctuations related to the ordered broken-symmetry states. Especially, we demonstrate two virtues of Raman scattering which have not been generally appreciated: first, the temperature dependence of the parameters of CF excitations reveals the interaction between f-electrons and itinerant electrons; and second, the low-energy Raman response probes dynamical fluctuations related to exotic multipolar ordering.

3.1.1 Experimental

Single crystals of CeB₆ were grown in Al flux by slow cooling from 1450 °C. The crystals were removed from the Al flux by leaching in NaOH solution [115, 116]. The sample measured in this study was cleaved in ambient condition to expose its (001) crystallographic plane; the cleaved surface was then examined under a Nomarski microscope to find a strain-free area.

Raman-scattering measurements were performed in a quasi-back scattering geometry
Table 3.1: The relationship between the scattering geometries and the symmetry channels. Every scattering geometry is represented by $E_iE_s$, where $E_i$ and $E_s$ are the polarizations of incident and scattered light; $X$, $Y$, $X'$ and $Y'$ are the [100], [010], [110] and [1T0] crystallographic directions; R and L are right and left circular polarizations. $A_{1g}$, $E_g$, $T_{1g}$ and $T_{2g}$ are the irreducible representations of the $O_h$ group.

<table>
<thead>
<tr>
<th>Scattering Geometry</th>
<th>Symmetry Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>$A_{1g}+4E_g$</td>
</tr>
<tr>
<td>XY</td>
<td>$T_{1g}+T_{2g}$</td>
</tr>
<tr>
<td>X'X'</td>
<td>$A_{1g}+E_g+T_{2g}$</td>
</tr>
<tr>
<td>X'Y'</td>
<td>$3E_g+T_{1g}$</td>
</tr>
<tr>
<td>RR</td>
<td>$A_{1g}+E_g+T_{1g}$</td>
</tr>
<tr>
<td>RL</td>
<td>$3E_g+T_{2g}$</td>
</tr>
</tbody>
</table>

from sample placed in a continuous helium-gas-flow cryostat. A set of lines from a Kr$^+$ ion laser, 476, 531, 647, 676 and 752 nm, were used for excitation. Incident light with less than 10 mW power was focused into a 50×100 $\mu$m$^2$ spot. The temperature points reported in this paper were corrected for laser heating, which was estimated to be 0.5 K/mW $^3$.

Six polarization configurations were employed to probe excitations in different symmetry channels. The relationship between the scattering geometries and the symmetry channels [9] is given in Table. 3.1. The algebra used to decompose measured spectra into four symmetry channels is shown in Table. 3.2.

We used a custom triple-grating spectrometer with a liquid-nitrogen-cooled charge-coupled device (CCD) detector for analysis and collection of the scattered light. Low-resolution gratings with 150 lines per mm were used to measure the broad PL feature, while high-resolution gratings with 1800 lines per mm were used for measurements of the sharp Raman features. The data were corrected for the spectral response of the system.

For first-order scattering processes, the measured secondary-emission intensity $I(\omega, T)$ is related to the Raman response $\chi''(\omega, T)$ by $I(\omega, T) = [1+n(\omega, T)]\chi''(\omega, T)+L(\omega, T)$, where $n$ is the Bose factor, $\omega$ is excitation energy, $T$ with temperature, and $L(\omega, T)$ represents photoluminescence. For the second-order acoustic-phonon scattering process to be discussed in

---

$^3$We mainly followed the procedure discussed in Ref. [117] to estimate the laser heating. The optical absorption coefficient data were extracted from the optical data [118–120], while the thermal conductivity data were taken from Ref. [121].
Table 3.2: The algebra used to decompose the data into four symmetry channels for CeB$_6$.

<table>
<thead>
<tr>
<th>Symmetry Channel</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$(1/3)(XX + X'X' + RR - X'Y' - RL)$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$(1/6)(X'Y' + RL - XY)$</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>$(1/2)(XY + RR - X'X')$</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$(1/2)(XY + RL - X'Y')$</td>
</tr>
</tbody>
</table>

SubSec. 3.1.5, assuming the two constitute excitations have the same energy, $I(\omega, T)$ and $\chi''(\omega, T)$ are related by $I(\omega, T) = [1 + n(\omega/2, T)]^2\chi''(\omega, T) + L(\omega, T)$.

3.1.2 Overview

In Fig. 3.3 we present a typical secondary-emission spectrum over a large energy range, covering Raman features of distinct origins. Among the Raman features, quasi-elastic excitations have the lowest-energy. Second-order acoustic phonon excitations are at around 200 cm$^{-1}$, while first-order optical phonon excitations are near 1000 cm$^{-1}$. The energy of the intra-multiplet CF excitation is around 400 cm$^{-1}$, while that of the inter-multiplet CF excitations is more than 2000 cm$^{-1}$. The PL continuum arises from a broad PL peak at around 2.0 eV. In the following subsections we will discuss every spectral feature separately in details.

3.1.3 Photo-Luminescence

In Fig. 3.4(a) we show the excitation dependence of the PL feature at room temperature. The PL peak has 2.0 eV excitation threshold, and excitations below 2.0 eV threshold show predominantly Raman features. The PL feature is centered at 1.95 eV, just below the threshold energy, and has about 0.4 eV full width at half maximum (FWHM). Upon cooling the peak shifts slightly to higher energy [Fig. 3.4(b)].

The optical conductivity shows a shoulder at around 2.0 eV [118–120], suggesting an optical gap. Band-structure calculations further indicate a 2.0 eV gap between the Ce dispersive 5$d$-band bottom and flat 4$f$-band [122–124]. We therefore attribute the PL peak to
Figure 3.3: An overview of the low-temperature secondary-emission intensity measured in XY geometry at 20K with 476 nm excitation in log-log scale. The top scale is the absolute energy of the secondary-emission photons in electron-Volts. The bottom scale is the energy loss, the laser-photon energy minus the scattered-photon energy, also called the Raman shift, in spectroscopic units cm\(^{-1}\). The Raman features are superposed on a strong photo-luminescence continuum. Different Raman features are schematically represented by different colors: cyan, quasi-elastic (QE) Raman excitations; blue, the continuum of electronic Raman excitations; orange, second-order acoustic-phonon (AP) excitations and first-order optical-phonon (OP) excitations; red, crystal-field (CF) excitations; and green: the continuum of the photo-luminescence (PL).
Figure 3.4: Excitation and temperature dependence of the secondary-emission intensity measured in XY geometry for CeB$_6$. (a) Excitation dependence of the secondary-emission intensity $I(\omega,300\,\text{K})$ measured in XY geometry at 300 K. For clarity, each spectrum is vertically shifted by a factor proportional to the excitation energy. The broad peak which does not change in the absolute emission energy with excitation energy is a photo-luminescence feature, while the sharp modes which follow the excitation energy are the Raman features. (b) Temperature dependence of the photo-luminescence feature measured in XY geometry with 476 nm excitation.
the recombination of the electron-hole excitations between the 5d- and 4f-bands. Transitions between d- and f-states are dipole allowed, and the energy separation of the 5d-band bottom and the 4f-band is consistent with the energy of this PL peak. The enhancement of PL intensity for excitations above the 2 eV threshold results from the increase of the density of states (DOS) for the 4f to 5d interband transition.

3.1.4 Crystal-Field Excitations

Identification

In total, there are four CF excitations from the \( \Gamma_8 \) ground state to the higher states within the \( ^2F_{5/2} \) and \( ^2F_{7/2} \) multiplets: one intra-multiplet excitation and three inter-multiplet excitations [Fig. 3.2]. In Fig. 3.5 we present the spectrum of the four CF excitations measured at 15 K. Four peaks at 380 cm\(^{-1}\), 2060 cm\(^{-1}\), 2200 cm\(^{-1}\) and 2720 cm\(^{-1}\) are observed. The 380 cm\(^{-1}\) excitation is the intra-multiplet \( \Gamma_8 \rightarrow \Gamma_7 \) transition. Among the three inter-multiplet excitations, only the \( \Gamma_8 \rightarrow \Gamma_8^* \) transition can have a finite \( A_{1g} \) component [107]. In the inset of Fig. 3.5 we show that among the inter-multiplet excitations only the one at 2200 cm\(^{-1}\) contains an \( A_{1g} \) component. The 2200 cm\(^{-1}\) excitation is therefore assigned to the \( \Gamma_8 \rightarrow \Gamma_8^* \) transition. The CF excitation at 2720 cm\(^{-1}\), in turn, can only be a transition between the \( \Gamma_8 \) ground state and the \( \Gamma_8^* \), \( \Gamma_7^* \) or \( \Gamma_6^* \) states. Raman scattering cannot distinguish between \( \Gamma_8 \rightarrow \Gamma_6^* \) and \( \Gamma_8 \rightarrow \Gamma_7^* \) transitions because they both contain the same irreducible representations [107]: \( \Gamma_8 \otimes \Gamma_6^* = \Gamma_8 \otimes \Gamma_7^* = \Gamma_{eg} \oplus \Gamma_{T_{1g}} \oplus \Gamma_{T_{2g}} \). However, we will show in 3.1.4 that the electron-cloud distribution of the \( \Gamma_6^* \) state has the smallest overlap with the boron octahedrons, the \( \Gamma_8^* \) state has intermediate overlap, and the \( \Gamma_7^* \) state has the largest overlap. Because of the Coulomb repulsion between cerium and boron electrons, the \( \Gamma_7^* \) state has the highest energy while the \( \Gamma_6^* \) state has the lowest energy. Indeed, within the \( ^2F_{5/2} \) multiplet because the \( \Gamma_7 \) state has more overlap with the boron octahedrons it has a higher energy than the \( \Gamma_8 \) state. Therefore, the 2720 cm\(^{-1}\) excitation is assigned to the \( \Gamma_8 \rightarrow \Gamma_7^* \) transition, and the 2060 cm\(^{-1}\) excitation is assigned to the \( \Gamma_8 \rightarrow \Gamma_6^* \) transition.
Figure 3.5: Raman response $\chi''(\omega,15\text{ K})$ of the CF excitations measured in XY scattering geometry ($T_{1g}+T_{2g}$) with 476 nm excitation at 15 K. Three axis breakers are used on the horizontal axis in order to show the four excitations together. The spectral resolution is 3.5 cm$^{-1}$. Inset: $\chi''(\omega,15\text{ K})$ measured in XX scattering geometry ($A_{1g}+4E_g$) at 15 K. The spectral resolution of the inset is about 30 cm$^{-1}$. 
Figure 3.6: Temperature dependence of the energy (a-c) and FWHM (d-f) of the $\Gamma_8 \rightarrow \Gamma_7$, $\Gamma_8 \rightarrow \Gamma_8^*$ and $\Gamma_8 \rightarrow \Gamma_7^*$ CF excitations shown in Fig. 3.5. The line-joined square labels in (a-c) represent the excitation energies calculated by our model Hamiltonian calculation. The error bars represent one standard deviation of the Lorentzian fit.

**Temperature Dependence**

In Fig. 3.6 we present the temperature dependence of the energy and FWHM of three CF excitations. The spectral parameters of the CF excitations were obtained by fitting the measured spectral peaks with a Lorentzian lineshape.

On cooling from 304 K to 15 K the lattice contraction strengthens the electrostatic potential at the Ce sites resulting in increase of the $\Gamma_8 \rightarrow \Gamma_7$, $\Gamma_8 \rightarrow \Gamma_8^*$, and $\Gamma_8 \rightarrow \Gamma_7^*$ transition energy by 7 cm$^{-1}$, 5 cm$^{-1}$, and 18 cm$^{-1}$ respectively. A discussion of the change of the energy of the CF states with increasing CF potential will be given in 3.1.4.

At room temperature, the CF spectral lines of CeB$_6$ are broader than those measured from Ce$^{3+}$ ions embedded in insulators, e.g. Ce-doped Y$_2$O$_3$ [125] or Ce-doped LuPO$_4$ [126].

\footnote{The energy of the $\Gamma_8 \rightarrow \Gamma_7$ transition shows monotonic temperature dependence. The earlier reports, Ref. [109, 112], showed no temperature dependence of the transition energy on cooling from 300 K to 20 K, followed by a rapidly hardening on cooling below 20 K.}
The broadening could be caused by two factors: first, lattice of Ce$^{3+}$ ions leads to small dispersion of the narrow 4$f$-bands; and second, hopping of conduction electrons among the boron sites induces fluctuations of the electrostatic potential at the Ce sites, which broadens FWHM.

On cooling, the FWHM of the $\Gamma_8 \rightarrow \Gamma_7$ and $\Gamma_8 \rightarrow \Gamma_7^*$ CF transitions decrease from 300 K to 80 K, but anomalously increases below 80 K [Fig. 3.6 (d) and (f)]. The decrease of FWHM is expected because lattice vibrations, causing fluctuations of the electrostatic potential at Ce sites, diminish with cooling. In order to understand the anomalous increase of FWHM below 80 K, it is important to notice that the electrical resistivity of CeB$_6$ has its local minimum at 80 K. The resistivity upturn below 80 K results from the Kondo effect [89] due to increase in the rate of conduction electron scattering from the local moments at the Ce sites on cooling [127, 128]. The Kondo effect shortens the lifetime of the $\Gamma_7$ and $\Gamma_7^*$ CF states, so the FWHM of the $\Gamma_8 \rightarrow \Gamma_7$ and $\Gamma_8 \rightarrow \Gamma_7^*$ CF transitions increases below 80 K. Nevertheless, the FWHM of the $\Gamma_8 \rightarrow \Gamma_8^*$ CF transition does not show an upturn below 80 K [Fig. 3.6 (e)]. This is because the $\Gamma_8^*$ state has smaller overlap with the boron octahedrons than the $\Gamma_7$ and $\Gamma_7^*$ states, therefore, it is less influenced by the increased conduction electron scattering rate.

Our data do not display directly the splitting of the $\Gamma_8$ CF ground state. However, the minimum FWHM of the $\Gamma_8 \rightarrow \Gamma_7$ is around 33 cm$^{-1}$ [Fig. 3.6 (d)] if the splitting of the CF ground state is small, it would not be resolved. The previous studies suggested a splitting of 20 cm$^{-1}$ [109, 129], which does not contradict our data.

**Model Hamiltonian Calculation**

To shed light on the nature of the CF transitions, we perform a model Hamiltonian calculation. We use the following single-ion Hamiltonian

$$H = E_0 + H_{SOC} + H_{CF} .$$  (3.1)
The first term $E_0$ represents the energy of unperturbed $4f$ shell. The value $E_0$ is chosen to put the $\Gamma_8$ ground state at zero energy. The second term

$$H_{SOC} = \xi \hat{L} \cdot \hat{\sigma} \quad (3.2)$$

describes the effect of SOC. Here $\xi$ is the SOC coefficient, $\hat{L}$ is the orbital angular momentum operator and $\hat{\sigma}$ are Pauli matrices. The third term

$$H_{CF} = B_4(\hat{O}_4^0 + 5\hat{O}_4^4) + B_6(\hat{O}_6^0 - 21\hat{O}_6^4) \quad (3.3)$$

is the general expression for a CF potential of cubic site symmetry [130], where $\hat{O}_4^0$, $\hat{O}_4^4$, $\hat{O}_6^0$ and $\hat{O}_6^4$ are Stevens operators [131], and $B_4$ and $B_6$ are the CF coefficients ⑤:

$$B_4 = A_4 <r^4> \beta , \quad (3.4)$$

$$B_6 = A_6 <r^6> \gamma , \quad (3.5)$$

$A_4$ and $A_6$ are the geometrical coordination factors determined by the charge configuration around the Ce sites. Regardless of the specific configuration, $A_4 \sim a^{-5}$ and $A_6 \sim a^{-7}$, where $a$ is the lattice constant; $<r^4>$ and $<r^6>$ are the mean fourth and sixth powers of the radii of the Ce$^{3+}$ $4f$-orbital, and $\beta$ and $\gamma$ are the Stevens multiplicative factors [131].

The effects of SOC and CF potential on the energy and angular electron-cloud distribution of the CF levels are illustrated in Fig. 3.7. In the absence of the SOC, the CF eigenfunctions could be classified by the irreducible representations (IRs) of $O_h$ double group. The relevant IRs are the one-dimensional $A_{2u}$, three-dimensional $T_{2u}$, and three-dimensional $T_{1u}$ for the orbital part of the wavefunction, and two-dimensional $\Gamma_6$ for the spin part. The 14-fold degenerate $4f$ orbital would be split into 2-fold $A_{2u} \otimes \Gamma_6$, 6-fold $T_{2u} \otimes \Gamma_6$, and 6-fold $T_{1u} \otimes \Gamma_6$ orbitals. Finite SOC splits further these orbitals and results in mixing of wavefunctions derived from different orbitals. The symmetry of the split states is given by the decomposition of the direct products into direct sums of IRs of $O_h$ double group [107]: $A_{2u} \otimes \Gamma_6 = \Gamma_7$, $T_{2u} \otimes \Gamma_6 = \Gamma_8 \oplus \Gamma_7$, and $T_{1u} \otimes \Gamma_6 = \Gamma_6 \oplus \Gamma_8$.

⑤When comparing the CF coefficients across different literature, additional constants are needed [132, 133].
Figure 3.7: Eigenenergies and eigenstates derived from the model Hamiltonian calculation. (a) Evolution of the 4f-orbital energy with CF potential and SOC strength. [from left to center] Increasing CF potential in the absence of SOC (a1), and then increasing SOC strength in the existence of full CF potential (a2); [from left to center] increasing SOC in the absence of CF potential (a3), and then increasing CF potential in the existence of full SOC (a4). In this panel, the full SOC strength is $\xi=610\text{ cm}^{-1}$, and the full CF potential strengths are $B_4=-0.758\text{ cm}^{-1}$ and $B_6=-0.0165\text{ cm}^{-1}$. (b) The wavefunctions and the angular electron-cloud distribution of the eigenstates. [left] The wavefunctions of the eigenstates when only CF potential is present. Red denotes positive value while blue denotes negative value; [middle] the angular electron-cloud distribution of the eigenstates when both SOC and CF potential are present; [right] the angular electron-cloud distribution of the eigenstates when only SOC is present.
On the other hand, if cubic CF were absent, the 4f orbital would be split into 8-fold $^{2}F_{7/2}$ ($J = L + S$) and 6-fold $^{2}F_{5/2}$ ($J = L - S$) multiplets. Finite CF potential splits the two multiplets and induces mixing of wavefunctions derived from different multiplets. The symmetry of the split states is given by the compatibility table showing the mapping of IRs of the full rotational group into IRs of $O_{h}$ double group [107]: $^{2}F_{7/2} = \Gamma_{8} \oplus \Gamma_{7} \oplus \Gamma_{6}$, and $^{2}F_{5/2} = \Gamma_{8} \oplus \Gamma_{7}$. With both SOC and CF present, the CF eigenfunctions should be classified by the IRs of the double group, namely two-dimensional $\Gamma_{6}$, two-dimensional $\Gamma_{7}$, and four-dimensional $\Gamma_{8}$.

We diagonalize the Hamiltonian (3.1) in the basis of $|L,m_{L},S,m_{S}>$, where $L,m_{L},S,m_{S}$ are quantum numbers corresponding to $\hat{L},\hat{L},\hat{S},\hat{S}$ operators, respectively. After diagonalization, the CF transition energies can be expressed in terms of $\xi$, $B_{4}$ and $B_{6}$. We obtain these three parameters by fitting the energies of three CF transitions to the data at 15 K (the weakest $\Gamma_{8} \rightarrow \Gamma_{6}^{*}$ transition is not accounted in this procedure). The obtained set of parameters comprises $\xi=610$ cm$^{-1}$, $B_{4}=-0.758$ cm$^{-1}$ and $B_{6}=-0.0165$ cm$^{-1}$. The same values automatically render the energy of weakest transition at 2070 cm$^{-1}$, which is close to the observed value at 2060 cm$^{-1}$. The value of $\xi$ (610 cm$^{-1}$) is also consistent with the estimated value for the Ce$^{3+}$ ion embedded in LuPO$_{4}$ (614 cm$^{-1}$) [126]. Such consistency demonstrates the reliability of the model (3.1).

We can further use this single-ion model to describe the temperature dependence of the CF excitation energy. Here we assume that $\xi$ is temperature-independent, and that the temperature dependence of the $B_{4}$ and $B_{6}$ coefficients comes from the temperature dependence of the lattice constant $a(T)$. We therefore rewrite $B_{4}$ and $B_{6}$ as $B_{4}(T)=C_{4}a(T)^{-5}$ and $B_{6}(T)=C_{6}a(T)^{-7}$, where $C_{4}$ and $C_{6}$ are temperature-independent factors. The temperature dependence of the lattice constant $a(T)$ is obtained from the Refs. [92, 134]. Then, we determine the values of $\xi$, $C_{4}$ and $C_{6}$ by matching the calculated values with the measured data at 300 K. Finally, we use the determined $\xi$, $C_{4}$ and $C_{6}$ to calculate CF excitation energies below 300 K. The results are shown in Fig. 3.6 (a-c). The discrepancy between the
measured data and the calculated values below 200 K results from unaccounted terms in the model Hamiltonian [Eq. (3.1)]; for an example, interactions between localized \( f \)-electrons and the itinerant conduction electrons.

By virtue of the obtained eigenfunctions, the Raman intensity of the four CF transitions can be calculated. For non-resonant scattering, the Raman response \( \chi''(\omega) \) has the following expression [11]:

\[
\chi''(\omega) \sim \frac{1}{Z} \sum_{i,f} |\langle f|\hat{R}_{\mu\nu}|i\rangle|^2 e^{-E_i/kT} \delta(E_f - E_i - \hbar\omega),
\]

where \( Z \) is the partition function, \(|i\rangle, |f\rangle\) are the initial and final state with energy \( E_i \) and \( E_f \), \( \omega \) is the Raman shift, and \( \hat{R}_{\mu\nu} \) is the effective Raman operator. In our case, \(|i\rangle\) is the CF ground state and \(|f\rangle\) is one of the excited CF states. For nonresonant Raman scattering, \( \hat{R}_{\mu\nu} \) is a quadrupolar operator depending on the crystallographic symmetry and scattering geometry \( \mu\nu \) [126, 135, 136]. For XY scattering geometry in a cubic crystal, \( \hat{R}_{XY} \) transforms in the same way as quadrupole \( xy \) under the symmetry operations of \( O_h \) point group:

\[
\hat{R}_{XY} = \frac{1}{2}(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x) = \frac{1}{4\hbar}(\hat{L}_+^2 - \hat{L}_-^2),
\]

where \( \hat{L}_+ \) and \( \hat{L}_- \) are the ladder operators of the orbital angular momentum. We note that because light only couples to the electron’s orbital degree of freedom, the effective Raman operator should be written in terms of the orbital angular momentum operators, rather than the total angular momentum operators. Expression (3.7) should accordingly be evaluated in the basis of \(|L,m_l\rangle|S,m_s\rangle\).

In Fig. 3.8 we compare the calculated and measured CF transition intensity. Because the 476 nm excitation is resonant with interband transitions (see SubSec. 3.1.3) but the expression (3.7) is only valid for non-resonant scattering, we expect discrepancy between the calculated and measured results. Nevertheless, the relative intensity of the three intermultiplet transitions is reproduced.
3.1.5 Phononic Excitations

An overview of the phonon modes is presented in Fig. 3.9(a). From group-theory analysis, CeB$_6$ has three Raman-active optical phonon modes: A$_{1g}$, E$_g$ and T$_{2g}$. Their respective energies are 1271, 1143 and 681.7 cm$^{-1}$ at 300 K, consistent with previous results [137, 138]. Their lineshapes at 300 K and 4 K are presented in Fig. 3.9(b); no anomaly is observed on cooling. The E$_g$ and T$_{2g}$ optical phonon modes exhibits asymmetric lineshape. The underlying electronic continuum likely results from electronic interband transitions: according to the calculated and measured band structure [122–124], many direct interband transitions are allowed and in turn can contribute to the nearly flat continuum below 1500 cm$^{-1}$ (≈0.2 eV).

The peak at 194 cm$^{-1}$ is not fully polarized. It originates from second-order scattering of acoustic branches at the Brillouin-zone boundary [138], where the flat dispersion gives rise to a large density of states. From this peak, we infer that the maximum of the acoustic phonon frequency is around 100 cm$^{-1}$, which is consistent with the INS data [139]. Another feature at 373 cm$^{-1}$ shows larger T$_{2g}$ contribution and smaller E$_g$ contribution. It is the $\Gamma_8 \rightarrow \Gamma_7$ CF excitation discussed in SubSec. 3.1.4. The peak at 1400 cm$^{-1}$ has strong A$_{1g}$ contribution and very weak E$_g$ contribution. It results from second-order scattering of the T$_{2g}$ phonon mode [138]. The symmetry-decomposed spectra further reveal an A$_{1g}$
Figure 3.9: The Raman-active phonon modes of CeB$_6$. (a) Symmetry-decomposed Raman response $\chi''(\omega,300\,\text{K})$, measured with 532 nm excitation at 300 K. Inset in (a): Symmetry-decomposed Raman spectrum of the second-order acoustic phonon scattering peak, measured with 752 nm excitation at 300 K. Thermal factor $[1 + n(\omega/2,T)]^2$ is used to derive this particular inset; the other Raman spectra presented in this paper are obtained with the normal thermal factor $[1 + n(\omega,T)]$. (b), (c) and (d): Raman spectra of the T$_{2g}$, A$_{1g}$ and E$_g$ optical phonon modes, measured with 532 nm excitation at 300 K and 4 K. In (b), (c) and (d), the spectral resolution is 2.8 cm$^{-1}$ for the high temperature data and 1.3 cm$^{-1}$ for the low temperature data. (e) The schematic vibration patterns for the three optical phonon modes. Because the cerium ions are at the inversion centers, Raman-active phonon modes only involve vibrations of the boron octahedrons.
Figure 3.10: Temperature dependence of the energy (in red) and FWHM (in black) of (a) the $A_{1g}$ component of the second-order acoustic phonon scattering peak, and (b) the $A_{1g}$ optical phonon mode. The solid lines are fitting curves of an anharmonic decay model assuming decay into two optical modes, or an optical plus an acoustic modes [141, 142]. The error bars represent one standard deviation of the Lorentzian fit.

peak at 1158 cm$^{-1}$, which was not reported previously. This peak might correspond to the summation mode of the 373 cm$^{-1}$ CF excitation and the $T_{2g}$ phonon mode. Such coupling has been observed in another $f$-electron system UO$_2$ [140].

In Fig. 3.10 we show the temperature dependence of the energy and FWHM of the $A_{1g}$ contribution of the second-order acoustic mode, and the $A_{1g}$ optical mode. The spectral parameters of the phonon modes were obtained by fitting the measured spectral peaks with a Lorentzian lineshape.

Temperature dependence of the phonon energy and FWHM is usually described by anharmonic effects. In most cases, the three-phonon processes renders the fastest relaxation, and higher-order processes can be neglected. Furthermore, the $A_{1g}$ optical mode at $\Gamma$ point has the highest frequency among all the phonon branches of CeB$_6$ [143]; hence we only need to consider processes in which one $A_{1g}$ optical mode at $\Gamma$ point decays into two
phonon modes satisfying conservation of energy and momentum \(^6\). We use a generalized anharmonic decay model assuming multiple decay channels; for every channel, the decay products can be two acoustic modes, an optical plus an acoustic modes, or two acoustic modes \([141, 142]\) \(^7\):

\[
\omega(T) = \omega_0 - \sum_i \omega_{\delta(i)} \left[1 + \frac{1}{e^{\hbar\omega_{1(i)}/k_B T} - 1} + \frac{1}{e^{\hbar\omega_{2(i)}/k_B T} - 1}\right],
\]

\[
\Gamma(T) = \Gamma_0 + \sum_i \Gamma_{\delta(i)} \left[1 + \frac{1}{e^{\hbar\omega_{1(i)}/k_B T} - 1} + \frac{1}{e^{\hbar\omega_{2(i)}/k_B T} - 1}\right],
\]

where the subscript \((i)\) indicates the decay channel. \(\omega_{\delta(i)}\) and \(\Gamma_{\delta(i)}\) are factors reflecting the relative importance of the various decay channels. \(\hbar\omega_{1(i)}\) and \(\hbar\omega_{2(i)}\) are the energy of the decay products in the decay channel labelled by \((i)\). \(\hbar(\omega_0 - \sum_i \omega_{\delta(i)})\) and \(\Gamma_0 + \sum_i \Gamma_{\delta(i)}\) correspond to the zero-temperature phonon energy and the FWHM, respectively. \(\Gamma_0\) accounts for the temperature-independent part of the FWHM originating not from anharmonic decay processes, but from, for example, imperfection of the sample.

Both \(\omega_{\delta(i)}\) and \(\Gamma_{\delta(i)}\) are proportional to

\[
\sum_{\mathbf{k}_{1(i)}, \mathbf{k}_{2(i)}} |\alpha(\mathbf{k}_{1(i)}, \mathbf{k}_{2(i)})|^2 \delta[\omega_{A_{1g}} - \omega_{1(i)}(\mathbf{k}_{1(i)}) - \omega_{2(i)}(\mathbf{k}_{2(i)})],
\]

where \(\alpha\) is the anharmonic coefficient; \(\mathbf{k}_{1(i)}\) and \(\mathbf{k}_{2(i)}\) are the wavevector of the decay products in the decay channel labelled by \((i)\); \(\delta\) represents the Dirac \(\delta\)-function.

Referring to the calculated phonon dispersion \([143]\), we expect two decay channels for the 1278 cm\(^{-1}\) \(A_{1g}\) phonon: (1) decay into one 684 cm\(^{-1}\) optical phonon and one 594 cm\(^{-1}\) optical phonon with opposite momenta; (2) decay into one 1178 cm\(^{-1}\) optical phonon near \(+R\) point and one 100 cm\(^{-1}\) acoustic phonon near \(-R\) point.

The two phonon branches involved in the decay channel (1) is essentially flat over the whole Brillouin zone; hence a large number of states are available for the decay to happen.

---

\(^6\)There are other constraints which the decay processes must satisfy. For example, the spontaneous decay of a phonon by anharmonic processes of any order into a set of phonons of higher phase velocity is impossible \([144]\).

\(^7\)Because in CeB\(_6\) the maximum acoustic phonon frequency is around 100 cm\(^{-1}\), for the high-frequency \(A_{1g}\) mode decay into two acoustic modes is impossible.
Table 3.3: The fitting parameters for the energy and FWHM of the $A_{1g}$ optical phonon mode. Units are cm$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$</td>
<td>1309.0±0.1</td>
<td>28.12±0.05</td>
<td>2.664±0.003</td>
</tr>
<tr>
<td>$\Gamma_0$</td>
<td>1.07±0.08</td>
<td>8.4±0.2</td>
<td>1.76±0.01</td>
</tr>
</tbody>
</table>

On the contrary, for the two phonon branches of the decay channel (2), only states near R point simultaneous satisfy the requirements of energy and momentum conservation. Therefore, the decay channel (1) would dominate if the anharmonic coefficient is not significantly different for the two channels.

The fitting results of the anharmonic decay model are summarized in Table 3.3. Indeed, $\omega_\delta(1) > \omega_\delta(2)$ and $\Gamma_\delta(1) > \Gamma_\delta(2)$. The temperature-independent $\Gamma_0$ is much smaller than $\Gamma_\delta(1) + \Gamma_\delta(2)$, indicating not only that the lineshape broadening mainly results from the anharmonic decay, but also that the sample is of excellent quality. In contrast to the behavior of the $A_{1g}$ optical mode, the second-order scattering of acoustic modes in the $A_{1g}$ channel shows decreasing energy on cooling [Fig. 3.10(a)]. The 2% softening might be a prelude to the AFQ ordering.

We attribute the apparent asymmetric lineshape of the $T_{2g}$ and $E_g$ optical phonon modes to the coupling between these phonons and the low-frequency fluctuations [SubSection 3.1.6]. The observed spectral lineshapes are resulted from convolution of the phononic Lorentzian and Drude-like function describing the low-lying fluctuations. We use the following expression to fit modes’ lineshape at 4 K:

$$\chi''(\omega, 4K) = \sum_i \left\{ \frac{A_{(i)}^2 \gamma L(i)}{(\omega - \omega L(i))^2 + \gamma L(i)^2} + \frac{A_{(i)}^2 v(i) \theta(\omega - \omega L(i)) \gamma D(i)}{(\omega - \omega L(i))^2 + (\gamma L(i) + \gamma D(i))^2} + \frac{A_{(i)}^2 v(i) \theta(\omega L(i) - \omega) n(\omega L(i) - \omega)}{(\omega L(i) - \omega)^2 + (\gamma L(i) + \gamma D(i))^2} \right\} \right. \right.$$ (3.11)

In Eq. (3.11), the first term describes the bare phonon part, while the second and third terms correspond to the Stokes and anti-Stokes of the phonon assisted electronic scattering.
Table 3.4: The fitting parameters for the T\textsubscript{2g} and E\textsubscript{g} composite modes by Eq. (3.11) for CeB\textsubscript{6}.

\begin{center}

\begin{tabular}{lcc}
Parameter (Units) & T\textsubscript{2g} Mode & E\textsubscript{g} Mode \\
\hline
A\textsubscript{(Γ)} (a.u.) & 20.29±0.03 & 7.4±0.4 \\
γ\textsubscript{L(Γ)} (cm\textsuperscript{-1}) & 5.67±0.02 & 8.5±0.5 \\
ω\textsubscript{L(Γ)} (cm\textsuperscript{-1}) & 682.73±0.02 & 1138.4±0.3 \\
A\textsubscript{(R)} (a.u.) & 7.0±0.8 & \\
γ\textsubscript{L(R)} (cm\textsuperscript{-1}) & 10±1 & \\
ω\textsubscript{L(R)} (cm\textsuperscript{-1}) & 1155.0±0.5 & \\
v (cm\textsuperscript{-1}) & 0.691±0.005 & 2.2±0.2 \\
\end{tabular}
\end{center}

The summation runs over all the k-points in the Brillouin zone. Referring to the calculated phonon dispersion [143], the T\textsubscript{2g} mode belongs to a flat branch over the Brillouin zone, while the E\textsubscript{g} mode belongs a dispersive branch which has high DOS at Γ and R points [143]. Therefore, for the latter case we only consider coupling at Γ and R points. In this equation, A\textsubscript{(i)} is the phonon light-scattering vertex; ω\textsubscript{L(i)} is the phonon frequency; 2γ\textsubscript{L(i)} is the FWHM of the bare phonon Lorentzian function; γ\textsubscript{Di} measures the relaxation rate of the Drude function; v\textsubscript{(i)} represents the electron-phonon coupling strength; and θ(ω) is the Heaviside step function.

For the T\textsubscript{2g} mode, we choose γ\textsubscript{D(Γ)} to be 3.0 cm\textsuperscript{-1}, which is consistent with the measured value of the T\textsubscript{1g} quasi-elastic fluctuations at 16 K. For the E\textsubscript{g} mode, we choose both γ\textsubscript{D(Γ)} and γ\textsubscript{D(R)} to be 11 cm\textsuperscript{-1}, which is consistent with the measured value of the A\textsubscript{1g} quasi-elastic fluctuations at 16 K. We further require that v\textsubscript{(Γ)} and v\textsubscript{(R)} are the same.

The fitting results of the T\textsubscript{2g} and E\textsubscript{g} composite modes are shown in Fig. 3.11 and summarized in Table 3.4. The dip of the fitting curve in Fig. 3.11(b) results from the negligence of the contributions at k-points between Γ and R points. The FWHM of the bare T\textsubscript{2g} phonon mode (∼11 cm\textsuperscript{-1}) is similar to that of the A\textsubscript{1g} phonon mode (∼12 cm\textsuperscript{-1}), while the FWHM of the bare E\textsubscript{g} phonon mode (∼17 cm\textsuperscript{-1}) is larger. This large E\textsubscript{g} FWHM, again, is an artifact caused by negligence of the contributions from remaining k-points. The energy difference between the E\textsubscript{g} mode at Γ and R points is ∼17 cm\textsuperscript{-1}, which is comparable to the calculated difference of ∼30 cm\textsuperscript{-1} [143].
Figure 3.11: The measured with 532 nm excitation at 4 K Raman response function (black points with one standard deviation error bars) fitted with the model of Eq. (3.11) for (a) the $T_{2g}$ and (b) the $E_g$ optical phonons coupled to low-frequency electronic excitations.

3.1.6 Quasi-Elastic Excitations

In Fig. 3.12 we show the symmetry-decomposed Raman response measured with 752 nm excitation at 300 K and 16 K. The low-energy Raman response shows quasi-elastic features which can be described by a Drude lineshape:

$$
\chi''(\omega, T) \propto \frac{\alpha^2 \omega}{\omega^2 + \gamma^2},
$$

(3.12)

where $\alpha$ is the light-scattering vertex and $\gamma$ measures the fluctuation rate.

The Raman response gets enhanced in all the channels on cooling. Especially, the $T_{1g}$ Raman response changes qualitatively and develops into a strong quasi-elastic feature at low temperature. The basis functions of the $T_{1g}$ representation in $O_h$ group transform as the three components of angular momentum, which behave as a pseudovector [107]. This transformation property indicates that the observed quasi-elastic peak in $T_{1g}$ channel may have a magnetic origin.
Figure 3.12: Raman response $\chi''(\omega, T)$ in the four Raman-active symmetry channels measured with 752 nm excitation at (a) 300 K and (b) 16 K. The solid lines are Drude fits [Eq. (3.12)]. The error bars represent one standard deviation.

We measured the temperature dependence of Raman response in the XY scattering geometry, in which $T_{1g} + T_{2g}$ symmetry components are probed. Since $T_{2g}$ signal at low-temperature is nearly constant [Fig. 3.12(b)], we fit the Raman response with the sum of Drude and constant terms, and then remove the constant part to obtain the desired $T_{1g}$ component. The $T_{1g}$ Raman response obtained this way is shown in Fig. 3.13(a). The quasi-elastic excitation in $T_{1g}$ symmetry channel becomes significant below 20 K, and its intensity increases on further cooling. The static Raman susceptibility, $\chi(0, T)$, plotted in Fig. 3.13(b) is obtained from the Raman response by virtue of Kramers-Kronig relation: $\chi(0, T) = \frac{2}{\pi} \int_{0}^{50 \text{ cm}^{-1}} \frac{\chi''(\omega, T)}{\omega} d\omega$. Drude function in Eq. (3.12) is used to extrapolate $\chi''(\omega, T)$ below 4 cm$^{-1}$. In Fig. 3.13(b) and (c), the temperature dependence of the static Raman susceptibility is compared with that of the magnetic susceptibility [145]. The fact that the temperature dependence of both quantities follows the same trend further supports the magnetic origin of the quasi-elastic peak in $T_{1g}$ symmetry channel [27].

In zero magnetic field, Raman scattering data cannot determine whether the observed $T_{1g}$ quasi-elastic response is of FM or AFM origin. Nevertheless, the Raman-measured
Figure 3.13: The Raman response in the T$_{1g}$ channel measured with 752 nm excitation, and comparison between the temperature dependence of the static Raman susceptibility and that of the magnetic susceptibility [145] for CeB$_6$. (a) Temperature dependence of the Raman response $\chi''(\omega, T)$ in the T$_{1g}$ symmetry channel measured with 752 nm excitation. The solid lines are Drude fits [Eq. (3.12)]. (b) Comparison between the temperature dependence of the static Raman susceptibility $\chi(0, T)$ (black) and that of the magnetic susceptibility $\chi_{mag}$ (purple) [145]. (c) Comparison between the temperature dependence of the inverse static Raman susceptibility (black) and that of the inverse magnetic susceptibility (purple) [145]. The blue arrow indicates the magnetic ordering temperature while the red one indicates the orbital ordering temperature. The error bars represent one standard deviation.
$T_{1g}$ quasi-elastic response is consistent with the FM correlations studied by INS: without external magnetic field and above $T_Q$, the magnitude of the INS-measured zone-center quasi-elastic peak decreases on warming [101]. We note by passing that a first-principle calculation for CeB$_6$ indicates that the expected values of both 4$f$-orbital occupancy and total angular momentum exhibit an obvious anomalies around 20 K [146]. This is the same temperature around which the $T_{1g}$ quasi-elastic Raman response starts to develop.

The mechanism responsible for the FM correlations can be understood as follows [98]. Consider the two electrons at neighboring Ce$^{3+}$ sites. In the staggered orbital-ordering phase, the orbital part of the total wavefunction of these two electrons is antisymmetric. Due to the resulting exchange interaction, the spins at neighboring Ce$^{3+}$ sites are FM correlated.

The $\Gamma_8$ CF ground state of O$_h$ group has zero quadrupole moment. If the site symmetry is reduced from O$_h$ group to D$_{4h}$ group, the $\Gamma_8$ state of O$_h$ group would be split into the $\Gamma_6$ and $\Gamma_7$ states of D$_{4h}$ group. The $\Gamma_6$ and $\Gamma_7$ states can only have quadrupole moments of $x^2-z^2$ or $y^2-z^2$ type, rather than the proposed $xy$, $yz$, and $zx$ type. Hence, only when the site symmetry is reduced to D$_{2h}$ group, and the $\Gamma_8$ state of O$_h$ group is split into two $\Gamma_5$ states of D$_{2h}$ group, can the CF ground state carries finite quadrupole moments of $xy$, $yz$, and $zx$ type. However, in a continuous second-order phase transition, the symmetry of the system cannot be directly reduced from cubic to orthorhombic, which violates Landau theory [147]. Theories which claim an AFQ phase with O$_{xy}$-type moments using a localized picture should address this difficulty. Inconsistency of the AFQ description has also been suggested based on magnetic-susceptibility anisotropy and magnetostriction measurements [148].

3.1.7 Conclusion

In summary, we have employed optical secondary-emission spectroscopy to study the spin-orbital coupling (SOC), electronic crystal-field (CF) excitations, electron-phonon interaction and long-wavelength magnetic fluctuations in the heavy-fermion metal CeB$_6$. 
Ce$^{3+}$ ions have a single electron in the 4$f$-shell. The SOC splits the degenerate 4$f$ levels into a lower-energy $^2F_{5/2}$ multiplet and a higher-energy $^2F_{7/2}$ multiplet, with a separation of around 2000 cm$^{-1}$, from which we estimate the SOC strength $\xi = 610$ cm$^{-1}$.

The two multiplets are further split into five Kramers-degenerate CF states by the cubic CF potential. The $^2F_{5/2}$ multiplet is composed of one quartet $\Gamma_8$ ground state and one doublet $\Gamma_7$ excited state, and the $^2F_{7/2}$ multiplet consists of $\Gamma_6^*$ and $\Gamma_7^*$ doublets, and a $\Gamma_8^*$ quartet states. We resolve all four electronic CF transitions: 380 cm$^{-1}$ for the intra-multiplet excitation, and 2060, 2200 and 2720 cm$^{-1}$ for the three inter-multiplet transitions.

On cooling, the FWHM for the $\Gamma_8 \rightarrow \Gamma_7$ and $\Gamma_8 \rightarrow \Gamma_7^*$ transitions first decreases from 300 K to 80 K, but then increases below 80 K. We relate the decrease of the FWHM to lattice vibration driven fluctuations of the electrostatic potential at Ce sites, which diminish on cooling. The increase of the FWHM below 80 K results from the Kondo effect, an electron-correlation effect which increases the self-energy of the excited CF states. We apply a single-ion Hamiltonian model to obtain the eigenvalues and eigenfunctions of the 4f-electron CF states. Using the Fermi Golden Rule, we also calculate the intensity of the four Raman active CF transitions and compare the calculation to the experimental data.

We study the lattice dynamics of CeB$_6$ and analyze the temperature dependence of all Raman active phonon modes. In the phonon spectra, we interpret the asymmetric lineshape of $E_g$ and $T_{2g}$ optical phonons as manifestation of electron-phonon interaction. We also identify a composite CF plus phonon excitation at 1158 cm$^{-1}$.

We acquire temperature dependence of the low-energy Raman response for all Raman-allowed symmetry channels, and uncover the development of a quasi-elastic Raman response in the magnetic-dipolar $T_{1g}$ symmetry channel below 20 K. The corresponding static Raman susceptibility shows similar temperature dependence as the magnetic susceptibility data, which supports the interpretation of its magnetic origin. By comparing the quasi-elastic Raman scattering data with electron spin resonance and inelastic neutron scattering results, we relate this $T_{1g}$ spectral feature to ferromagnetic correlations.
Additionally, we detect photo-luminescence emission centered at 1.95 eV at room temperature. We relate this emission to recombination of the electron-hole excitations between the 5d- and 4f-bands.

The experimental methods, models, and analyses demonstrated in this study can be applied to a range of systems, especially for rare-earth materials containing localized f-electrons of Ce$^{3+}$ or Yb$^{3+}$ ions at high-symmetry crystallographic sites [2]. The approach could enable us to probe ferroquadrupolar (FQ) fluctuations in TmAg$_2$ ($T_{FQ} = 5.0$ K) [84] or TmAu$_2$ ($T_{FQ} = 7.0$ K) [85] systems, to name a few examples. Also, magnetic correlation induced by quadrupolar ordering could be probed in antiferroquadrupolar (AFQ) systems, for instance in UPd$_3$ (multiple AFQ phases, with the highest $T_{AFQ} = 7.6$ K) [149], NpO$_2$ ($T_{AFQ} = 25.0$ K) [87], or DyB$_2$C$_2$ ($T_{AFQ} = 24.7$ K) [86].

3.1.8 Analysis of Raman Spectra

Subtraction of Photo-Luminescence

The measured secondary-emission intensity $I(\omega, T)$ is related to the Raman response $\chi''(\omega, T)$ by $I(\omega, T) = [1 + n(\omega, T)]\chi''(\omega, T) + L(\omega, T)$, where $n$ is the Bose factor, $\omega$ is energy, $T$ is temperature, and $L(\omega, T)$ represents photo-luminescence. Spectra taken with 752 nm excitation are subtracted by a constant [Fig. 3.14 (a)], while those taken with 532 and 476 nm excitations are subtracted by a linear function of frequency [Fig. 3.14 (b) and (c)].

Thermal Factor for Second-Order Acoustic-Phonon Scattering

For first-order scattering processes, the scattering intensity is given by the expression $[1 + n(\omega, T)]\chi''(\omega, T)$ [9], where $n$ is the Bose factor, $\chi''$ is the response function, $\omega$ is excitation energy and $T$ is temperature. However, for the second-order acoustic-phonon scattering process observed in our study, assuming the two constitute acoustic phonons have the same energy, the expression should be modified to $[1 + n(\omega/2, T)]^2\chi''(\omega, T)$.

The reason for the modification is as follows. Second-order Raman scattering can result
Figure 3.14: Illustration of subtracting photo-luminescence (PL) for spectra taken with three different excitation energy at 300 K. Secondary-emission intensity $I(\omega)$ (red line) shown together with a constant PL (a) or a linear PL (b) and (c) (blue line) to be subtracted. The resulting Raman response $\chi''(\omega)$ is shown in (d), (e), and (f), respectively.
Figure 3.15: Temperature dependence of the integrated intensity of the $A_{1g}$ component of the second-order acoustic phonon scattering peak. The intensity obtained with two different thermal factors is normalized to their respective value at 300 K. The error bars represent one standard deviation of the Lorentzian fit.

from either two successive first-order interactions, or one second-order interaction [150]. In the first case, the thermal factor $[1 + n(\omega/2, T)]$ should be used. However, it is essential that first-order scattering should be allowed for the two constituent excitations individually. Because the wavevector of visible light is much smaller than the Brillouin-zone size, first-order scattering of acoustic modes at the Brillouin-zone boundary is not allowed. The second-order Raman scattering of acoustic modes observed in our study, therefore, originates from the scattering process in which the light interacts with a pair of excitations in a single event. Wavevector conservation is effectively satisfied when the wavevectors of the constituent excitations are equal and opposite. In this case, assuming the two constituent excitations have the same energy, the thermal factor $[1+n(\omega/2, T)]^2$ should be used [9, 151, 152]

Using thermal factor $[1+n(\omega, T)]$ for the second-order acoustic-phonon scattering process in CeB$_6$ would lead to unreasonable decreasing intensity on cooling [Fig. 3.15]. The energy and FWHM of the peak, on the contrary, is insensitive to which thermal factor is used.
3.2 Quadrupolar fluctuations and crystal-field excitations in YbRu$_2$Ge$_2$

Multipolar interactions and related ordering phenomena have attracted great interest because, unlike commonly-known long-range orders of electric or magnetic dipole moments, multipoles are often related to more exotic phases which are difficult to probe directly by conventional methods [16, 23]. For systematic investigation of the collective behavior of multipole moments, \( f \)-electron systems are suitable choices since the strong coupling between spin and orbital degrees of freedom of \( f \)-electrons facilitates multipole formation. Indeed, the actinide dioxides with 5\( f \)-electrons exhibit a variety of multipolar ordering phenomena [23]. For lanthanides with 4\( f \)-electrons, multipolar, and especially quadrupolar orders, have been discovered for different systems [82, 86, 87, 153, 154].

YbRu$_2$Ge$_2$, a heavy-fermion metal with tetragonal structure (space group I4/mmm, No. 139; point group D$_{4h}$), has been suggested to hold a ferroquadrupolar (FQ) order at low temperature [155–162]. It undergoes a second-order phase transition at \( T_Q=10 \) K, before entering into an antiferromagnetic (AFM) phase below \( T_{N1}=6.5 \) K [155, 160]. At \( T_{N2}=5.5 \) K, there may exist a small change in the magnetic structure [158, 160]. Early studies show that the transition at \( T_Q \) is not magnetic, and \( T_Q \) increases when magnetic field is applied along the easy direction [155, 160]. This behavior at \( T_Q \) is similar to that of TmAu$_2$ at its FQ ordering temperature [34], hence suggesting a FQ phase in YbRu$_2$Ge$_2$.

The existence of a FQ order is further supported by recent elastoresistivity studies where above \( T_Q \) the elastoresistivity in the quadrupolar symmetry channels displays a Curie-Weiss behavior [161]. Below \( T_Q \), an orthorhombic structural distortion is observed by X-ray diffraction, which confirms that the FQ state breaks \( B_{1g} (x^2 - y^2) \) symmetry [161].

The FQ order, namely the ordering of Yb$^{3+}$ 4\( f \)-electron charge distribution at zero wavevector, can be probed indirectly by studying the lattice dynamics and crystal-field (CF) excitations. In a FQ arrangement, aligned charge quadrupoles uniformly distort the lattice via a coupling between the quadrupole moment and the strain field with the same
symmetry. The induced distortion reduces the point-group symmetry of the lattice system, splitting degenerate phonon modes; the distortion also modifies the energy and lifetime of the phonon modes of the same symmetry. Such anomalies can be revealed by investigating the phonon spectra. Besides, the quadrupolar moments are carried by the CF ground state of Yb$^{3+}$. The tetragonal CF potential splits the $^2F_{7/2}$ ground multiplet into two $\Gamma_6$ and two $\Gamma_7$ Kramers doublets. The magnetic entropy right above $T_Q$ is nearly $R \ln 4$ [155], suggesting that the CF ground state is a quasi-quartet consisting of two quasi-degenerate Kramers doublets. The quasi-quartet ground state was recently confirmed by angle-resolved photo-emission spectroscopy studies [162]. This quasi-quartet near degeneracy is essential for forming a quadrupolar ground state and deserves a detailed study.

Raman spectroscopy is a conventional tool for studying phonon modes [163] and CF excitations [113]. Here we study the lattice dynamics, low-energy quadrupole fluctuations, and CF excitations in YbRu$_2$Ge$_2$. We assign four Raman-active phonon modes, and reveal an anomalous intensity enhancement of two phonon modes on cooling. The three CF transitions within the $^2F_{7/2}$ ground multiplet are identified and a CF level scheme is in turn established. We demonstrate that low-energy Raman response undergoes remarkable enhancement on cooling towards $T_Q$ and that the static electronic Raman susceptibility in the corresponding quadrupole channels follows nearly perfect Curie behavior, signifying that the relatively strong coupling to the lattice in the $B_{1g}$-symmetry channel enhances by about 10 K the vanishingly small electronic Weiss temperature to the FQ transition temperature $T_Q$.

3.2.1 Experimental

Single crystals of YbRu$_2$Ge$_2$ were grown by flux method; details of the growth can be found in Ref [161]. Two samples were used in this study: one was cleaved in ambient condition to expose its xy crystallographic plane, the other had a clean as-grown xz crystallographic plane. The xy crystallographic plane was examined under a Nomarski microscope to find
Table 3.5: The relationship between the scattering geometries and the symmetry channels.

For scattering geometry $E_i E_s$, $E_i$ and $E_s$ are the polarizations of incident and scattered light; $X$, $Y$, $X'$, $Y'$ and $Z$ are the [100], [010], [110], [1\bar{1}0] and [001] crystallographic directions; R and L are right and left circular polarizations. $A_{1g}$, $A_{2g}$, $B_{1g}$, $B_{2g}$ and $E_g$ are the irreducible representations of the $D_{4h}$ group.

<table>
<thead>
<tr>
<th>Scattering Geometry</th>
<th>Symmetry Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>$A_{1g} + B_{1g}$</td>
</tr>
<tr>
<td>XY</td>
<td>$A_{2g} + B_{2g}$</td>
</tr>
<tr>
<td>X'X'</td>
<td>$A_{1g} + B_{2g}$</td>
</tr>
<tr>
<td>X'Y'</td>
<td>$A_{2g} + B_{1g}$</td>
</tr>
<tr>
<td>XZ</td>
<td>$E_g$</td>
</tr>
<tr>
<td>RR</td>
<td>$A_{1g} + A_{2g}$</td>
</tr>
<tr>
<td>RL</td>
<td>$B_{1g} + B_{2g}$</td>
</tr>
</tbody>
</table>

about 200×200 $\mu$m$^2$ strain-free area.

Raman scattering measurements were performed in a quasi-back scattering geometry from sample placed in a continuous helium-gas-flow cryostat. We used 476.2, 647.1 and 752.5 nm lines from a Kr$^+$ ion laser for excitation. Incident light with no more than 14 mW power was focused to a 50×100 $\mu$m$^2$ spot. Particularly, for measurements below 10 K, the power of the incident light was reduced to 2 mW. The temperatures reported in this paper were corrected for laser heating, which was estimated to be $0.75 \pm 0.25$ K/mW.$^8$

Seven polarization configurations were employed to probe excitations in different symmetry channels. The relationship between the scattering geometries and the symmetry channels \cite{9} is given in Table 3.5.

We used a custom triple-grating spectrometer with a liquid-nitrogen-cooled charge-coupled device (CCD) detector for analysis and collection of the scattered light. The data were corrected for the spectral response of the system. The measured secondary-emission intensity $I(\omega, T)$ is related to the Raman response $\chi''(\omega, T)$ by $I(\omega, T) = [1 + n(\omega, T)]\chi''(\omega, T) + L(\omega, T)$, where $n$ is the Bose factor, $\omega$ is energy, $T$ is temperature. $L(\omega, T)$ represents the far tail of photo-luminescence, which in the narrow spectral window

---

$^8$Optical absorption coefficient and thermal conductivity data for YbRu$_2$Ge$_2$, which are required for a model estimation of the laser heating \cite{117}, are currently unavailable. Hence, we base the estimate of laser heating at low temperatures on comparison with other heavy-fermion metals with comparable electrical conductivity \cite{161}: CeB$_6$ \cite{89} and URu$_2$Si$_2$ \cite{164}, for which laser heating for the same experimental set-up was established in the range of 0.5~1.0 K/mW.
Figure 3.16: Raman response $\chi''(\omega, T)$ of four Raman-active optical phonon modes at low temperature measured with the 647.1 nm excitation. The XX and XZ spectra are offset by 1.5 and 3 arbitrary units (arb. units), respectively. The spectral resolution is 1.0 cm$^{-1}$.

Table 3.6: Summary of the energy of the phonon and crystal-field (CF) modes for YbRu$_2$Ge$_2$. Results of this work are compared to inelastic neutron scattering (INS) study [165]. Units are cm$^{-1}$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>This work</th>
<th>INS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_6^{(1)} \rightarrow \Gamma_7^{(1)}$</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>$\Gamma_6^{(1)} \rightarrow \Gamma_7^{(2)}$</td>
<td>95</td>
<td>89</td>
</tr>
<tr>
<td>$\Gamma_6^{(1)} \rightarrow \Gamma_6^{(2)}$ (c)</td>
<td>239</td>
<td>–</td>
</tr>
<tr>
<td>$A_{1g}$ (c)</td>
<td>268</td>
<td>260</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>168</td>
<td>170</td>
</tr>
<tr>
<td>$E_g^{(1)}$</td>
<td>138</td>
<td>–</td>
</tr>
<tr>
<td>$E_g^{(2)}$ (c)</td>
<td>301</td>
<td>–</td>
</tr>
</tbody>
</table>

of interest was approximated by a linear frequency dependence.

3.2.2 Lattice Dynamics

The spectra of phonon modes are presented in Fig. 3.16. By group theory, four Raman-active optical phonon modes are expected for YbRu$_2$Ge$_2$ structure: $A_{1g} \oplus B_{1g} \oplus 2E_g$. $A_{1g}$ and $B_{1g}$ modes are accessible in XX geometry and $E_g$ modes in XZ geometry. The phonon energies at 13K are tabulated in Table 3.6.

In Fig. 3.17 we show the temperature dependence of the spectral parameters (energy, FWHM, and integrated intensity) of the phonon modes. The spectral parameters were
Table 3.7: The fitting parameters for the energy and FWHM of the four Raman-active optical phonon modes of YbRu$_2$Ge$_2$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega_0$</th>
<th>$\omega_2$</th>
<th>$\Gamma_0$</th>
<th>$\Gamma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g^{(1)}$</td>
<td>138.4±0.1</td>
<td>0.70±0.03</td>
<td>1.7±0.5</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>167.92±0.01</td>
<td>0.212±0.002</td>
<td>6.08±0.02</td>
<td>0.094±0.005</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>270.15±0.04</td>
<td>2.27±0.02</td>
<td>3.6±0.1</td>
<td>1.71±0.07</td>
</tr>
<tr>
<td>$E_g^{(2)}$</td>
<td>303.32±0.02</td>
<td>2.67±0.01</td>
<td>2.98±0.05</td>
<td>0.75±0.03</td>
</tr>
</tbody>
</table>

obtained by fitting the measured spectral peaks with Lorentzian lineshapes.

The temperature dependence of both frequency and FWHM of the phonon modes [Fig. 3.17(a) and (b)] is in accordance with a simple model assuming anharmonic decay into two phonons with identical frequencies and opposite momenta [166, 167]:

$$\omega(T) = \omega_0 - \omega_2 [1 + \frac{2}{e^{\hbar\omega_0/2k_BT} - 1}],$$

(3.13)

and

$$\Gamma(T) = \Gamma_0 + \Gamma_2 [1 + \frac{2}{e^{\hbar\omega_0/2k_BT} - 1}].$$

(3.14)

The fitting results are summarized in Table 3.7. Small deviations between the measured energy and the fitting curve for the $B_{1g}$ mode could be due to an additional decay channels, for example decay into one acoustic and one optical mode.

The integrated intensity of the $A_{1g}$ and $E_g^{(2)}$ phonon modes has more than 50% increase on cooling, in contrast to the behavior of the $B_{1g}$ phonon mode, whose integrated intensity is nearly temperature-independent [Fig. 3.17(c)]. The increase of the integrated intensity on cooling suggests a coupling of a CF transition to these two phonon modes [168]. This coupling is enhanced when the energies of the CF splitting and the phonon modes are close. Indeed, such a CF excitation, 239 cm$^{-1}$ at 13 K, exists. The mechanism of this coupling will be discussed in Subsection 3.2.4.

Because the FQ order parameter is of $B_{1g}$ symmetry [161], the energy and lifetime of the $B_{1g}$ phonon mode are expected to exhibit anomalies across $T_Q$ due to electron-phonon coupling. Moreover, breaking of the four-fold rotational symmetry should split the two $E_g$ phonon modes [169]. However, as shown in the insets of Fig. 3.17, $B_{1g}$ and $E_g$ phonon
Figure 3.17: Temperature dependence of (a) the energy, (b) the FWHM and (c) the integrated intensity of the Raman-active optical phonon modes. The energy and integrated intensity are normalized to their respective value at 304 K. The integrated intensity of the very weak $E_g^{(1)}$ phonon mode is not shown. The solid lines in (a) and (b) represent the fits to anharmonic decay model [166, 167], while the solid lines in (c) represent the fits to Eq. (3.26). Insets: zoom-in of the low-temperature data points showing how the physical properties change across the phase-transition temperature $T_Q=10$ K. The dashed line in the insets indicate $T_Q$. The vertical error bars are derived from Lorentzian fits and represent one standard deviation; the horizontal error bars are derived from the uncertainty of laser heating estimation.
modes do not exhibit significant anomaly across $T_Q$. $E_g$ phonon modes do not show notable splitting at 4.5 K, either [Fig. 3.16]. The splitting of the $E_g^{(1)}$ phonon mode is challenging to observe due to its weak intensity. Because the FWHM of the $E_g^{(2)}$ phonon mode is 4 cm$^{-1}$ at 4.5 K, we set the upper limit of the splitting of the $E_g$ phonon modes to be about 4 cm$^{-1}$ at 4.5 K.

### 3.2.3 Quadrupolar fluctuations

In the tetragonal phase above $T_Q$, the four-fold rotational symmetry along the z-axis is preserved and the CF ground state supports no static xy-plane quadrupole moment. However, dynamical quadrupolar fluctuations with zero time average quadrupolar moment are allowed $^9$.

In Fig. 3.18 we show the spectra of low-energy quadrupolar fluctuations. They are present in RL geometry yet absent in RR geometry [Fig. 3.18(a)]. By group theory, the absence of $A_{1g}$ and $A_{2g}$ components indicates that the CF ground state is a quasi-quartet composed of one $\Gamma_6$ and one $\Gamma_7$ doublets.

The static Raman susceptibility $\chi_\mu(0,T)$ in the symmetry channel $\mu$ ($\mu = B_{1g}$ or $B_{2g}$) can be obtained from the Raman response $\chi''_\mu(\omega,T)$ by virtue of the Kramers-Kronig relation [170, 171]:

$$\chi_\mu(0,T) = \frac{2}{\pi} \int_{0}^{\omega_{max}} \frac{\chi''_\mu(\omega,T)}{\omega} d\omega,$$

in which we choose the upper cutoff for the spectra of fluctuations at $\omega_{max} = 40$ cm$^{-1}$, see Fig. 3.18.

We use Drude lineshape

$$\chi''_\mu(\omega,T) \propto \frac{Q^2_\mu \omega}{\omega^2 + \gamma^2_\mu}$$

(3.16)

to extrapolate the Raman response below the instrumental cutoff 5 cm$^{-1}$. In Eq. (3.16), $Q_\mu$ is the magnitude of the quadrupolar moment, and $\gamma_\mu$ reflects the decay rate. In the Raman

$^9$ Detailed discussion of the symmetry breaking and the wavefunction mixing can be found in Subsection 3.2.4
Figure 3.18: Raman response $\chi''(\omega, T)$ for (a) RR and RL scattering geometries with the 647.1 nm excitation, (b) X'Y' geometry with the 752.5 nm excitation, and (c) XY geometry with the 752.5 nm excitation. The solid lines are Drude fits, Eq. (3.16). The error bars represent one standard deviation.
Figure 3.19: Temperature dependence of the static electronic Raman susceptibility $\chi(0, T)$ for $B_{1g}$ (red) and $B_{2g}$ (blue) quadrupole channels derived from Raman response shown in Fig. 3.18. Inset: temperature dependence of $1/\chi(0, T)$. The solid lines are Curie-Weiss fits, Eq. (3.17). The vertical error bars represent one standard deviation; the horizontal ones are derived from the uncertainty of laser heating estimation.

scattering process light couples to the system’s charge quadrupole moment.

Theoretically, the low-energy Raman response in the quadrupolar channels contains both the lattice and the electronic contributions [170, 171]. However, the energy of lattice fluctuations is much lower than the instrumental cutoff (5 cm$^{-1}$), and Eq. (3.16) only takes into account of the electronic contribution. Thus, only electronic quadrupole fluctuations are included in the derived susceptibility $\chi_\mu(0, T)$.

The obtained temperature dependence of the static electronic Raman susceptibilities for both $B_{1g}$ and $B_{2g}$ quadrupole channels are shown in Fig. 3.19. The static Raman susceptibility $\chi_\mu(0, T)$ obeys Curie-Weiss temperature dependence

$$\chi_\mu(0, T) \propto \frac{Q^2_\mu}{T - T_{W}^\mu}, \quad (3.17)$$

where $T_{W}^\mu$ is the Weiss temperature:

$$T_{W}^\mu = \kappa_\mu Q^2_\mu, \quad (3.18)$$

in which $\kappa_\mu$ measures the strength of the electronic intersite quadrupolar interactions.

By fitting the data, the ratio of $Q_{B_{1g}}$ to $Q_{B_{2g}}$ is determined to be nearly 1.4. The derived Weiss temperatures, $T_{W}^{B_{1g}} \sim -2$ and $T_{W}^{B_{2g}} \sim +2$ K. The nearly exact Curie law is

\[ \text{Figure 3.19: Temperature dependence of the static electronic Raman susceptibility } \chi(0, T) \text{ for } B_{1g} (\text{red}) \text{ and } B_{2g} (\text{blue}) \text{ quadrupole channels derived from Raman response shown in Fig. 3.18. Inset: temperature dependence of } 1/\chi(0, T). \text{ The solid lines are Curie-Weiss fits, Eq. (3.17). The vertical error bars represent one standard deviation; the horizontal ones are derived from the uncertainty of laser heating estimation.} \]
not surprising because both direct-exchange and super-exchange between local quadrupolar moments are expected to be vanishingly weak due to compactness of the f-orbitals. Although itinerant electrons provide effective coupling between the local magnetic dipole moments at Yb$^{3+}$ sites, and the resulting RKKY interaction\footnote{See Ref. \cite{172} and the references therein.} leads to AFM order below $T_{N1}=6.5$ K, these itinerant electrons do not provide a significant effective coupling between the local electric quadrupole moments at Yb$^{3+}$ sites. 

The true B$_{1g}$-symmetry FQ order develops at $T_Q=10$ K \cite{161}, about 10 K above the Weiss temperature $T_{W}^{B_{1g}}$. Because YRu$_2$Ge$_2$, the non-magnetic analog of the same structure, has no orthorhombic transition \cite{161,173}, the quadrupolar fluctuations of YbRu$_2$Ge$_2$ lattice themselves should have little tendency towards a structural instability. Nevertheless, coupling between the lattice strain fields and the local electronic quadrupole moments of the same symmetry enhances the transition temperature \cite{170,171,174,175}:

$$T_{Q}^{\mu} = T_{W}^{\mu} + \left(\lambda_{\mu}^2/C_{\mu}\right)Q_{\mu}^2 = \left(\kappa_{\mu} + \lambda_{\mu}^2/C_{\mu}\right)Q_{\mu}^2,$$

(3.19)

where $\lambda_{\mu}$ measures the coupling between the local charge quadrupole moments on Yb$^{3+}$ sites and the lattice strain fields, and $C_{\mu}$ is the symmetrized elastic constant, which is $(C_{11}-C_{12})/2$ for the B$_{1g}$ channel or $C_{66}$ for the B$_{2g}$ channel \cite{176}. The true quadrupolar transition temperature $T_Q$ equals to the largest of two $T_{Q}^{\mu}$. Because the FQ order in YbRu$_2$Ge$_2$ has B$_{1g}$ symmetry, the $T_{Q}^{B_{1g}}=T_Q$ and non-realized $T_{Q}^{B_{2g}}<T_Q$.

Tuning an additional parameter (magnetic field, pressure or doping, for instance) may affect the electron-lattice coupling and induce a transition from B$_{1g}$ FQ ordering to B$_{2g}$ FQ ordering. Indeed, although $T_Q$ stays constant up to application 9 GPa pressure with zero magnetic field \cite{158} and increases with in-plane magnetic field at ambient pressure \cite{155}, experimental results do show suppression of $T_Q$ by Si \cite{159} or Rh \cite{162} doping, and by applying magnetic field under 1.23 GPa pressure \cite{158}. These results suggest a competition
between $B_{1g}$- and $B_{2g}$-symmetry FQ order.

### 3.2.4 Crystal-Field Excitations

Within the $^2F_{7/2}$ multiplet, there are three CF excitations corresponding to transitions from the CF ground state to the three CF excited states. From group theoretical considerations \[107\], the CF transitions between levels of the same symmetry (i.e. $\Gamma_6 \rightarrow \Gamma_6$ or $\Gamma_7 \rightarrow \Gamma_7$) contain $A_{1g}$, $A_{2g}$ and $E_g$ representations, whereas those between levels of different symmetry (i.e. $\Gamma_6 \rightarrow \Gamma_7$ or $\Gamma_7 \rightarrow \Gamma_6$) contain $B_{1g}$, $B_{2g}$ and $E_g$ symmetry representations. The Raman intensities in different symmetry channels may vary due to matrix element effect.

The lowest-energy CF transition, namely the transition between the two quasi-degenerate Kramers doublet does not clearly exhibit itself in the low-energy Raman spectra \[Fig. 3.18\]. The CF excitations from the ground state to the remaining two higher energy states are shown in \textit{Fig. 3.20} at 95 cm$^{-1}$ and 239 cm$^{-1}$. These two transitions are expected to appear in all Raman-active symmetry channels, because the two low-lying doublets within the quasi-quartet have roughly the same population at 11 K. With the 476.2 nm excitation, the 95 cm$^{-1}$ transition indeed appears as a weak peak for four linear polarizations, while the 239 cm$^{-1}$ transition overlaps with the strong $A_{1g}$ phonon mode. With the 647.1 nm excitation, instead, the 95 cm$^{-1}$ transition becomes weaker, but the 239 cm$^{-1}$ transition is identifiable, manifesting itself as a peak in the RL spectrum and a shoulder in the RR spectrum.

The symmetry of the CF levels are assigned by the following argument: because YbRh$_2$Si$_2$ and YbIr$_2$Si$_2$, which have the same lattice structure as YbRu$_2$Ge$_2$, both have a $\Gamma_6$ CF ground state \[177, 178\], we suggest that the CF ground state of YbRu$_2$Ge$_2$ is also of $\Gamma_6$ symmetry (denoted as $\Gamma_6^{(1)}$). The other Kramers doublet within the quasi-quartet, in turn, is of $\Gamma_7$ symmetry (denoted as $\Gamma_7^{(1)}$).

The small difference of the excitation energy measured in RR and RL geometries near
Figure 3.20: Raman response $\chi''(\omega)$ of the CF excitations from the quasi-quartet to the remaining two CF levels at low temperature. The dashed lines indicate the position of the two CF transitions. (a) The spectra for four linear polarizations measured at 11 K with the 476.2 nm excitation. The XX and X'X' spectra are offset by 0.5 arbitrary units (arb. units). The spectral resolution is $3.5 \text{ cm}^{-1}$. (b) The spectra for two circular polarizations measured at 15 K with the 647.1 nm excitation. The RR spectrum is offset by 0.5 arbitrary unit. The spectral resolution is $2.5 \text{ cm}^{-1}$. 
239 cm\(^{-1}\) [Fig. 3.20(b)] serves as an estimation of the quasi-quartet splitting. Using the Lorentzian fits, we find that the excitation energy measured in RR geometry is higher by \(2 \pm 1 \text{ cm}^{-1}\) than that in RL geometry at 25 K and 15 K. Therefore, the symmetry of the CF state at 239 cm\(^{-1}\) is defined to be \(\Gamma_6\) (denoted as \(\Gamma_6^{(2)}\)), and the quasi-quartet splitting is estimated to be \(2 \pm 1 \text{ cm}^{-1}\). Because there are only two \(\Gamma_6\) and two \(\Gamma_7\) states within the \(^2F_{7/2}\) multiplet, the CF state at 95 cm\(^{-1}\) can only be of \(\Gamma_7\) symmetry (denoted as \(\Gamma_7^{(2)}\)).

The energies of the CF excitations at 15 K are summarized in Table 3.6\(^{12}\).

In an inelastic neutron scattering study of YbRu\(_2\)Ge\(_2\), excitations at 89 cm\(^{-1}\), 170 cm\(^{-1}\) and 260 cm\(^{-1}\) are resolved at 5 K with the magnitude of momentum transfer being \(\sim 1.9\text{Å}^{-1}\) (Ref. [165]). Their data well match our assignments; the comparison is shown in Table 3.6. This consistency not only supports our assignments, but also suggests that the CF excitations and optical phonon modes have little dispersion.

**Angular Electron-Cloud Distribution of the Crystal-Field States**

We use the following single-ion Hamiltonian to calculate the angular electron-cloud distribution at Yb sites:

\[
H = H_{\text{CF}} + H_{B_{1g}}.
\]  
(3.20)

The first term in Eq. (3.20)

\[
H_{\text{CF}} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^1 \hat{O}_4^1 + B_6^0 \hat{O}_6^0 + B_6^1 \hat{O}_6^1
\]  
(3.21)

is the general expression for a CF potential of tetragonal site symmetry [179]. The \(\hat{O}_2^0\), \(\hat{O}_4^0\), \(\hat{O}_4^1\), \(\hat{O}_6^0\), and \(\hat{O}_6^1\) operators are Stevens operators [131]. The five \(B\)'s are the CF coefficients.

From the CF level diagram, we cannot uniquely determine the CF Hamiltonian and wavefunctions if we assume tetragonal site symmetry. Hence, we approximate the real tetragonal CF potential with a dominating cubic CF potential [130] plus a small \(\hat{O}_2^0\) axial

\(^{12}\)We note that would the CF ground state be \(\Gamma_7\) symmetry, the symmetry of the CF states at 2 cm\(^{-1}\), 95 cm\(^{-1}\) and 239 cm\(^{-1}\) should instead be \(\Gamma_6\), \(\Gamma_6\) and \(\Gamma_7\), respectively.
Figure 3.21: Schematic energy diagram of the CF states (red horizontal lines) and the phonon modes (blue horizontal lines). The coupled CF transition and phonon modes are circled in purple. On the left are the angular electron-cloud distributions of the four CF states; on the right are the vibration patterns of the phonon modes.
term:

\[ H_{Tetra} = B_2^0 \hat{O}_2^0 + B_4 (\hat{O}_4^0 + 5 \hat{O}_4^1) + B_6 (\hat{O}_6^0 - 21 \hat{O}_6^1) \]  

(3.22)

A cubic CF potential would split the \(^2F_{7/2}\) multiplet into one quartet \(\Gamma_8\), one doublet \(\Gamma_7\), and one doublet \(\Gamma_6\) states of \(O_h\) group. Reducing the cubic symmetry to the tetragonal symmetry, the quartet \(\Gamma_8\) state of \(O_h\) group would be split into one \(\Gamma_7\) and one \(\Gamma_6\) states of \(D_{4h}\) group. Because YbRu\(_2\)Ge\(_2\) has a quasi-quartet CF ground state, it is possible that this quasi-quartet is induced by a small tetragonal perturbation to a large cubic CF potential. This small perturbation is represented by the first term in Eq. (3.22). We cannot rule out an alternative scenario that the quasi-quartet CF ground state of YbRu\(_2\)Ge\(_2\) is of accidental degeneracy, rather than derived from the quartet \(\Gamma_8\) state of cubic symmetry. Nevertheless, the Hamiltonian \(H_{Tetra}\) preserves the 4-fold rotational symmetry along z-axis, and is sufficient to provide qualitative insights. In Appendix 3.2.6 we show that based on our assumption, the ratio of \(Q_{B_{1g}}\) to \(Q_{B_{2g}}\) is calculated to be 1.34, close to the experimentally determined ratio of 1.4 [Subsection 3.2.3]. This consistency supports our choice of Eq. (3.22). Experimentally, the wavefunction of the CF ground state could be determined by core-level non-resonant inelastic X-ray scattering, which has been used for Ce-based heavy fermion systems [180].

The second term in Eq. (3.20)

\[ H_{B_{1g}} = \frac{V}{2} (\hat{j}_x^2 - \hat{j}_y^2) = \frac{V}{2} (\hat{j}_+^2 + \hat{j}_-^2) \]  

(3.23)

represents the effective quadrupole-field (QF) potential of \(B_{1g}\) symmetry. \(V\) measures the strength of the QF potential.

Above \(T_Q\), there is no static \(B_{1g}\) QF potential and we define \(H = H_{Tetra}\). We diagonalize \(H_{Tetra}\) in the basis of \(|J, m_J\rangle\), where \(J = 7/2\) and \(m_J\) are the quantum numbers of \(\hat{J}\) and \(\hat{J}_z\), respectively. After diagonalization, the CF transition energies can be expressed in terms of \(B_2^0\), \(B_4\), and \(B_6\). We fit the experimentally determined CF level diagram by these three adjustable parameters. There are four sets of parameters which reproduce the level
diagram, and we choose the set with the smallest $B_{2}^{0}$ value. The fitting results thus are $B_{2}^{0}=-0.164 \text{ cm}^{-1}$, $B_{4}=0.0518 \text{ cm}^{-1}$, and $B_{6}=-0.00442 \text{ cm}^{-1}$. The corresponding angular electron-cloud distribution of the CF states is plotted in Fig. 3.21.

Below $T_Q$, there is a finite static $B_{1g}$ QF potential, here we define $H = H_{Tetra} + H_{B_{1g}}$. We assume that the values of $B_{2}^{0}$, $B_{4}$, and $B_{6}$ do not change. We diagonalize $H$ in the basis of $|J,m_J\rangle$, and after diagonalization, the CF transition energies can be expressed in terms of $V$. We find that $V=0.523 \text{ cm}^{-1}$ renders an additional $2 \text{ cm}^{-1}$ splitting of the ground quartet. In Fig. 3.22, we plot the angular electron-cloud distribution of the ground quartet for $V=0.523 \text{ cm}^{-1}$. The charge distribution looks different from [100] and [010] directions because the $\Gamma_{5}^{(1)}$ and $\Gamma_{5}^{(2)}$ doublets carry $B_{1g}$ quadrupole moment. Furthermore, the quadrupole moment carried by $\Gamma_{5}^{(1)}$ state and that carried by $\Gamma_{5}^{(2)}$ state have approximately same magnitude but an opposite sign.

The FQ phase transition reflects the competition between the entropy and energy terms in the Helmholtz free energy of the system. Above $T_Q$, the entropy term dominates and the system prefers a quasi-degenerate CF ground state. Below $T_Q$, instead, the system pursues lowest possible energy, and an orthorhombic quadrupolar field fulfills the goal: this field mixes the wavefunctions of the quasi-degenerate $\Gamma_{6}^{(1)}$ and $\Gamma_{7}^{(1)}$ states, increasing their separation and in turn reducing the ground state energy. In view of group-theoretical considerations, the $\Gamma_{6}$ and $\Gamma_{7}$ irreducible representations of the $D_{4h}$ group become the $\Gamma_{5}$ representation of the $D_{2h}$ group. Correspondingly, the $\Gamma_{6}^{(1)}$ and $\Gamma_{7}^{(1)}$ states of the $D_{4h}$ tetragonal phase are mixed by the Hamiltonian $H_{B_{1g}}$, and become the $\Gamma_{5}^{(1)}$ and $\Gamma_{5}^{(2)}$ states of the $D_{2h}$ orthorhombic phase.

There are two obvious choices for the macroscopic order parameter of the $B_{1g}$-symmetry FQ phase. First is the quadrupole moment per unit volume:

$$
\Psi \propto (n_{\Gamma_{5}^{(1)}} - n_{\Gamma_{5}^{(2)}})Q_{B_{1g}},
$$

13Strictly speaking, the quadrupole moments have the same magnitude only if we ignore the contribution by higher energy CF states.
Figure 3.22: The effect of the $B_{1g}$ quadrupole-field potential on the ground quasi-quartet, and the angular electron-cloud distribution of the $\Gamma_5^{(1)}$ and $\Gamma_5^{(2)}$ doublets for YbRu$_2$Ge$_2$. (a) The effect of the $B_{1g}$ quadrupole-field potential on the ground quasi-quartet. The $\Gamma_6^{(1)}$ and $\Gamma_7^{(1)}$ doublets of the $D_{4h}$ group are mixed to form the $\Gamma_5^{(1)}$ and $\Gamma_5^{(2)}$ doublets of the $D_{2h}$ group. The wavefunctions are expressed in the basis of $|J = 7/2, m_J\rangle$. (b) The angular electron-cloud distribution of the $\Gamma_5^{(1)}$ and $\Gamma_5^{(2)}$ doublets viewed from three orthogonal directions.
where \( n_{\Gamma_{5}^{(1)}} \) and \( n_{\Gamma_{5}^{(2)}} \) are the occupancy for the \( \Gamma_{5}^{(1)} \) and \( \Gamma_{5}^{(2)} \) states, respectively. The second choice is the lattice orthorhombicity, which couples to the quadrupolar order:

\[
\Psi \propto \frac{a - b}{a + b},
\]

(3.25)

where \( a \) and \( b \) are the in-plane lattice constant. The orthorhombicity as a function of temperature has been measured by X-ray diffraction [161].

**Coupling between the Crystal-Field Transition and the Phonon Modes**

The coupling between the \( \Gamma_{6}^{(1)} \rightarrow \Gamma_{6}^{(2)} \) CF transition and the \( A_{1g} \) and \( E_{g}^{(2)} \) phonon modes originates from the modulation of the electron-cloud distribution of CF states by lattice vibration [Fig. 3.21]. Such coupling is allowed by group theory because \( \Gamma_{6} \otimes \Gamma_{6} = A_{1g} \oplus A_{2g} \oplus E_{g} \). We note that the phonon energy and linewidth can be well accounted for by the anharmonic decay model [Fig. 3.17(a) and (b)], suggesting that renormalization due to electron-phonon coupling is small. In the Appendix 3.2.6 we show that for small coupling strength, the temperature dependence of the integrated intensity of the phonon modes, \( I.I.(T) \), has the following phenomenological expression:

\[
I.I.(T) = Af_{(1)}(T)[1 - f_{(2)}(T)] + B,
\]

(3.26)

where \( A \) and \( B \) are two constants; \( f_{(1)}(T) = 2/Z(T) \) measures the occupancy of the \( \Gamma_{6}^{(1)} \) CF state, and \( f_{(2)}(T) = 2e^{-E_{4}/k_{B}T}/Z(T) \) measures the occupancy of the \( \Gamma_{6}^{(2)} \) CF state. \( Z = 2 \sum_{i=1}^{4} e^{-E_{i}/k_{B}T} \) is the partition function; \( E_{1}=0 \text{ cm}^{-1}, E_{2}=2 \text{ cm}^{-1}, E_{3}=95 \text{ cm}^{-1} \) and \( E_{4}=239 \text{ cm}^{-1} \) are the energies of the CF levels [Table 3.6].

In Eq. (3.26), the constant \( B \) represents the temperature-independent spectral weight of the phonon mode. Without the interaction \( v \) and in the absence of a phase transition, the integrated intensity of the phonon modes is expected to be temperature-independent. The first term, which is temperature-dependent, can be interpreted as the spectral weight transferred from the CF mode to the phonon mode. This transferred spectral weight is proportional to the occupancy of the ground CF state \( \Gamma_{6}^{(1)} \), and the un-occupancy of the
excited CF state $\Gamma_6^{(2)}$. The constant $A$ is a measure of the transferred spectral weigh at zero-temperature $^{14}$.

Because of the phase transition at $T_Q = 10$ K, Eq. (3.26) is only valid above 10 K. In addition, group theory allows the $\Gamma_7^{(1)} \rightarrow \Gamma_6^{(2)}$ CF mode to couple to the $E_g^{(2)}$ phonon mode, which is not considered by simplified Eq. (3.26). Because the splitting between the $\Gamma_6^{(1)}$ and $\Gamma_7^{(1)}$ states is only 2 cm$^{-1}$, including the contribution from the $\Gamma_7^{(1)} \rightarrow \Gamma_6^{(2)}$ CF mode will only influence the fitting curve at temperature much lower than $T_Q$, a temperature range where Eq. (3.26) is invalid.

We use Eq. (3.26) to fit the phonon intensity data above 10 K in Fig. 3.17(c). For the $A_{1g}$ phonon mode, $A = 3.14 \pm 0.08$ and $B = 0.06 \pm 0.03$; for the $E_g^{(2)}$ phonon mode, $A = 2.08 \pm 0.05$ and $B = 0.35 \pm 0.02$. These values show that at low-temperature, the integrated intensity of the $A_{1g}$ and $E_g^{(2)}$ modes is mainly contributed by the transferred spectral weight. The fitting curves match the data well, which further supports our CF level scheme.

**3.2.5 Conclusion**

In summary, the Raman scattering study of YbRu$_2$Ge$_2$ focuses on the origin of the ferro-quadrupolar transition, as well as on the spectroscopy of phonons and CF excitations within the $^2F_{7/2}$ ground multiplet of Yb$^{3+}$ ion.

The deduced CF level scheme verifies the proposed quasi-quartet ground state, and we estimate that the splitting between two quasi-degenerate Kramers doublets is about 2 cm$^{-1}$. The static electronic Raman susceptibilities in both $B_{1g}$ and $B_{2g}$ quadrupole channels essentially exhibit Curie law, signifying relatively strong coupling to the lattice in the $B_{1g}$-symmetry channel that enhances the vanishingly small electronic Weiss temperature to the temperature of quadrupole phase transition at 10 K.

The temperature dependence of the energy and FWHM of the observed phonon modes

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$^{14}$ We note that there is no general sum rule for Raman spectroscopy.
are described by anharmonic decay model. The integrated intensities of the $A_{1g}$ and $E_{g}^{(2)}$ phonon modes show more than 50% enhancement on cooling, which is explained by strong coupling between these phonons and the CF transitions with similar energies.

### 3.2.6 Theoretical details

#### The effect of the $B_{2g}$ quadrupole-field potential

For completeness, we analyze here the effect of the $B_{2g}$ QF potential on the ground quasi-quartet. Following the treatment in Subsection (3.2.4), we take $H = H_{Tetra} + H_{B_{2g}}$, where

$$H_{B_{2g}} = \frac{V^*}{2} (\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x) = \frac{V^*}{4i} (\hat{J}_+^2 - \hat{J}_-^2). \quad (3.27)$$

We find that for $B_{2g}$ potential, $V^* = 0.668 \text{ cm}^{-1}$ renders a 2 cm$^{-1}$ additional splitting of the ground quartet. On the contrary, for $B_{1g}$ potential $V = 0.523 \text{ cm}^{-1}$ renders a 2 cm$^{-1}$ additional splitting of the ground quartet. Hence smaller $B_{1g}$ QF potential is needed to induce the same additional splitting of the quasi-quartet. This result is consistent with the conclusion that the coupling between the local quadrupole moments and the lattice strain field is stronger in the $B_{1g}$ channel than in the $B_{2g}$ channel.

In Fig. 3.23, we plot the angular electron-cloud distribution of the ground quartet for $V^* = 0.668 \text{ cm}^{-1}$. The charge distribution looks different from [110] and [1\bar{1}0] directions because the $\Gamma_5^{(1)*}$ and $\Gamma_5^{(2)*}$ doublets carry $B_{2g}$ quadrupole moment.

The traceless tensor of the electric quadrupole moments [181], written in Cartesian coordinate with arbitrary units, for the $\Gamma_5^{(1)}$ wavefunction generated by the $B_{1g}$ field, Eq. (3.23), has the following values:

$$
\begin{pmatrix}
0.655 & 0 & 0 \\
0 & -0.346 & 0 \\
0 & 0 & -0.309
\end{pmatrix}
$$

(3.28)

\footnote{Asterisks are used to distinguish the symbols used for $H_{B_{2g}}$ from those used for $H_{B_{1g}}$.}
Figure 3.23: The effect of the $B_{2g}$ quadrupole-field potential on the ground quasi-quartet, and the angular electron-cloud distribution of the $\Gamma_5^{(1)\ast}$ and $\Gamma_5^{(2)\ast}$ doublets for YbRu$_2$Ge$_2$. (a) The effect of the $B_{2g}$ quadrupole-field potential on the ground quasi-quartet. The $\Gamma_6^{(1)}$ and $\Gamma_7^{(1)}$ doublets of the $D_{4h}$ group are mixed to form the $\Gamma_5^{(1)\ast}$ and $\Gamma_5^{(2)\ast}$ doublets of the $D_{2h}$ group. The wavefunctions are expressed in the basis of $|J = 7/2, m_J\rangle$. (b) The angular electron-cloud distribution of the $\Gamma_5^{(1)\ast}$ and $\Gamma_5^{(2)\ast}$ doublets viewed from three orthogonal directions.

Hence the magnitude of the $B_{1g}$-symmetry electric quadrupole moment $Q_{B_{1g}}$ of the charge distribution of the $\Gamma_5^{(1)\ast}$ wavefunction has a value of 1.00 when $V = 0.523$ cm$^{-1}$.

The same tensor for the $\Gamma_5^{(1)\ast}$ wavefunction generated by the $B_{2g}$ field, Eq. (3.27) has the following values:

$$
\begin{pmatrix}
0.176 & -0.748 & 0 \\
-0.748 & 0.176 & 0 \\
0 & 0 & -0.352
\end{pmatrix}
$$

(3.29)

The magnitude of the $B_{2g}$-symmetry electric quadrupole moment $Q_{B_{2g}}$ of the charge distribution of the $\Gamma_5^{(1)\ast}$ wavefunction is 0.748 when $V^* = 0.668$ cm$^{-1}$.

Therefore, for the same additional splitting of the ground quasi-quartet, the calculated ratio of $Q_{B_{1g}}$ to $Q_{B_{2g}}$ is 1.34. We recall that the experimentally determined ratio of $Q_{B_{1g}}$
to $Q_{B2g}$ is 1.4. This consistency supports the assumptions made in Eq. (3.22), and shows that the wavefunctions we use are close to the real wavefunctions.

**Derivation of Eq. (3.26)**

The Hamiltonian of the coupled CF transition and phonon mode can be written in second-quantization form as

$$H = \omega_1 \hat{a}_1^\dagger \hat{a}_1 + \omega_2 \hat{a}_2^\dagger \hat{a}_2 + \omega_p \hat{b}_1^\dagger \hat{b}_1 + v (\hat{a}_2^\dagger \hat{a}_1 - \hat{a}_1^\dagger \hat{a}_2) (\hat{b}_1 + \hat{b}_2) ,$$

(3.30)

where $\hat{a}_1^\dagger$ and $\hat{a}_1$ are fermionic creation and destruction operators; $\hat{b}_1^\dagger$ and $\hat{b}_1$ are bosonic creation and destruction operators. The first and second terms describe respectively the energy of the lower and upper CF level; the third term is the phonon energy; and the last term is the coupling between the CF transition and phonon mode. Coefficient $v$ measures the strength of the coupling, which we take as a real number.

The CF transition corresponds to a bubble-shape Feynman diagram of electron-hole pair. Neglecting self-energy, the propagator has the following form:

$$P(\omega, T) = \frac{f_1(T)[1 - f_2(T)]}{\omega - \omega_e + i\epsilon} - \frac{[1 - f_1(T)]f_2(T)}{\omega + \omega_e + i\epsilon} ,$$

(3.31)

where $f_1(T)$ and $f_2(T)$ are respectively the temperature-dependent occupancy of the lower and upper CF level; $\omega_e = \omega_2 - \omega_1$ is the energy of the CF transition; and $\epsilon$ is an infinitesimal positive value.

The phonon propagator is

$$D(\omega, T) = \frac{1 + n(\omega_p, T)}{\omega - \omega_p + i\epsilon} - \frac{n(\omega_p, T)}{\omega + \omega_p + i\epsilon} ,$$

(3.32)

where $n(\omega_p, T)$ is the Bose distribution function.

The experimentally-measured scattering rate, $I(\omega, T)$, has the form

$$I(\omega, T) \sim \frac{1}{\pi} \text{Im} T^\dagger G(\omega, T) T ,$$

(3.33)
where \( T^\dagger = \begin{pmatrix} T_p & T_e \end{pmatrix} \) is the vertex of the light scattering, and \( G(\omega, T) \) is the Green’s function of the Hamiltonian in Eq. (3.30). \( G \) can be obtained by solving Dyson equation:

\[
G(\omega, T) = \frac{1}{1 - P(\omega, T)vD(\omega, T)v} \left( \begin{array}{cc} D(\omega, T) & D(\omega, T)vP(\omega, T) \\ P(\omega, T)vD(\omega, T) & P(\omega, T) \end{array} \right). \tag{3.34}
\]

In the following derivation, we assume \( v \) is small so that the prefactor in the above expression can be replaced by unity. Then the approximated form of \( I(\omega, T) \) is

\[
\frac{1}{\pi} \text{Im} \left[ T_p^2D(\omega, T) + 2T_pT_eD(\omega, T)vP(\omega, T) + T_e^2P(\omega, T) \right]. \tag{3.35}
\]

By virtue of Sokhotsky’s formula

\[
\lim_{\epsilon \to 0^+} \frac{1}{\omega \pm \omega_0 + i\epsilon} = \text{p.v.} \frac{1}{\omega \pm \omega_0} - i\pi \delta(\omega \pm \omega_0), \tag{3.36}
\]

where p.v. stands for principal value, we derive from Eq. (3.35) the Stokes part of the scattering rate:

\[
I(\omega, T) \sim T_p^2[1 + n(\omega_p, T)]\delta(\omega - \omega_p) + T_e^2f_1(T)[1 - f_2(T)]\delta(\omega - \omega_e) + 2T_pT_ev[1 + n(\omega_p, T)]f_1(T)[1 - f_2(T)]\delta(\omega - \omega_p) + \frac{\delta(\omega - \omega_p)}{\omega_p - \omega_e} + \frac{\delta(\omega - \omega_e)}{\omega_e - \omega_p}. \tag{3.37}
\]

Therefore, the phonon scattering rate, \( I_p(\omega, T) \), is

\[
I_p(\omega, T) \sim T_p^2[1 + n(\omega_p, T)]\delta(\omega - \omega_p) + 2T_pT_ev[1 + n(\omega_p, T)]f_1(T)[1 - f_2(T)]\delta(\omega - \omega_p), \tag{3.38}
\]

which can be arranged into

\[
T_p^2[1 + n(\omega_p, T)] \{ 1 + 2\frac{T_e}{T_p}\frac{v}{\omega_p - \omega_e}f_1(T)[1 - f_2(T)] \} \delta(\omega - \omega_p). \tag{3.39}
\]

The phonon response function, \( \chi''_p(\omega, T) \), in turn, is

\[
\chi''_p(\omega, T) \sim T_p^2 \{ 1 + 2\frac{T_e}{T_p}\frac{v}{\omega_p - \omega_e}f_1(T)[1 - f_2(T)] \} \delta(\omega - \omega_p), \tag{3.40}
\]

and integration of \( \chi''_p(\omega, T) \) yields the integrated intensity of the phonon mode \( I.I.(T) \):

\[
I.I.(T) \sim T_p^2 \{ 1 + 2\frac{T_e}{T_p}\frac{v}{\omega_p - \omega_e}f_1(T)[1 - f_2(T)] \}. \tag{3.41}
\]
Eq. (3.41) can be cast in a phenomenological form:

\[ I.I.(T) = A f_1(T) [1 - f_2(T)] + B, \]  

(3.42)

where \( A \sim \frac{T_v T_p v}{\omega_p - \omega_e} \) and \( B \sim T_p^2 \) are two constants. Eq. (3.42) is the same as Eq. (3.26) used in the Main Text to fit the experimentally-measured temperature-dependence of the integrated intensity of the \( A_{1g} \) and \( E_{g}^{(2)} \) phonon modes.
3.3 Crystal-field excitations and vibronic modes in triangular-lattice spin-liquid candidate TbInO$_3$

Interplay between electron correlation and spin-orbit coupling (SOC) gives rise to a variety of emergent quantum phases and transitions [182]. Especially, because of the compactness of $f$ orbits and the heaviness of $f$ elements, $f$-electron systems are in both the strong Mott regime and the strong SOC regime [183]. For these materials, exotic spin-liquid (SL) and multipolar-ordered ground states were predicted [83, 184]. The multipolar interactions and the resulting ordering phenomena have also been studied [16, 23]. However, rare-earth-based SL systems still remain to be explored, especially from the experimental side; many of the candidate materials are not widely accepted as hosting SL ground state due to absence of convincing experimental evidence.

It has been recently proposed that ferroelectric insulator TbInO$_3$ could harbor a 2D spin-liquid ground state [185–187]. In the ferroelectric phase this material has a hexagonal structure [188] (space group $P6_3cm$, No. 185; point group $C_{6v}$), as shown in Fig. 3.24(a). The magnetic Tb$^{3+}$ ions form a slightly distorted triangular lattice, separated by non-magnetic layers of corner-sharing [InO$_5$]$^{7-}$ polyhedra. The Tb$^{3+}$ ions possess two different site symmetries: Tb2 sites form a hexagonal plane, while Tb1 sites reside at the hexagonal centers and buckle slightly out of the hexagonal plane [Fig. 3.24(b-c)]. Hence the site symmetry is $C_{3v}$ for Tb1 sites and $C_3$ for Tb2 sites. The distortion from ideal triangular lattice is weak because the buckling of Tb1 is only 0.38 Å, around one tenth of the in-plane Tb2-Tb2 distance (3.65 Å) [185]. The fluctuating magnetic moment is shown to be confined to the triangular-lattice plane [186]. Magnetic susceptibility of polycrystalline samples obeys Curie-Weiss law above 10 K, with the Weiss temperature being -17.2 K; however, no magnetic ordering or spin freezing occurs down to 0.1 K [185], indicating strong magnetic frustration.

The classification of the proposed spin-liquid state in TbInO$_3$, though, remains unclear.
Figure 3.24: Crystal structure of ferroelectric TbInO$_3$. (a) The black frame indicates the unit cell. (b) The Tb layer viewed from X direction. The Tb2 sites form a hexagonal lattice while the Tb1 sites slightly buckle out of the plane. (c) The Tb layer viewed from Z direction. The Tb1 sites at the hexagonal centers are labeled by “1”.

The inelastic neutron-scattering (INS) study by L. Clark et al. suggests a singlet crystal-field (CF) ground state for Tb1, and a doublet for Tb2 ions [185]. At low temperature, then, Tb1 ions become nonmagnetic, and a honeycomb lattice of magnetic Tb2 ions emerges. In this scenario a Kitaev $Z_2$-symmetry SL is likely realized [67]. This CF level scheme was supported by analysis of the low-temperature specific heat [187]. On the contrary, the observations of another INS study by M.G. Kim et al. are consistent with a SL state based on triangular lattice [186]. Such a scenario implies that the CF ground states of Tb1 and Tb2 are the same, and the SL state might have a continuous symmetry. Interestingly, if the CF ground states of Tb1 and Tb2 are both non-Kramers doublets, on a triangular lattice spin-orbit-entangled multipolar phases are predicted to emerge [189]. It is therefore vital to identify the ground state of the Tb$^{3+}$ ions in this system, because this is the principal step to construct the spin Hamiltonian and to elaborate on emergent low-energy physics.

Moreover, in rare-earth compounds vibronic modes, namely coupled vibrational and CF electronic excitations, have been observed [190–192]. Thus, the lattice may play a pivotal role in defining the electronic ground state. Therefore, we explore electron-phonon interactions and such hybrid modes in TbInO$_3$. 
Here we present spectroscopic study of the electronic and phononic excitations in TbInO$_3$. We measure the inter- and intra-multiplet excitations, and establish the CF level scheme within the lowest-energy multiplet. We find that the ground state of the Tb$^{3+}$ ions is a non-Kramers doublet, and show that the derived CF level scheme is consistent with the entropy data. We determine the energy of the 38 allowed Raman-active phonon modes at low temperature. In addition, we observe hybrid vibronic excitations resulting from strong coupling between the CF and phonon modes. The coupling originates from the modulation of the electron-cloud distribution of the CF states by lattice vibration.

### 3.3.1 Experimental

Single crystals of TbInO$_3$ were prepared using laser-floating-zone method, and characterized by Laue diffraction to confirm single phase [187]. Two samples were used for Raman study: one cleaved to expose its (001) crystallographic plane and the other polished to expose its (010) plane. The samples were then examined under a Nomarski microscope to find a strain-free area. Raman-scattering measurements were performed in a quasi-back-scattering geometry from the samples mounted in a continuous helium gas flow cryostat.

We used a custom fast f/4 high resolution 500/500/660 mm focal lengths triple-grating spectrometer for data acquisition. All the data were corrected for the spectral response of the spectrometer.

For acquisition of the low-frequency Raman response, we used 1800 mm$^{-1}$ master holographic gratings; the 647 and 676 nm lines from a Kr$^+$ ion laser were used for excitation: 647 nm laser line combined with 100 µm slit width provides 0.19 meV spectral resolution; 676 nm laser line combined with 25 µm slit width provides 0.05 meV spectral resolution. For the high-frequency Raman response, we used 150 mm$^{-1}$ ruled gratings; the 476 and 568 nm lines from the same Kr$^+$ ion laser were used for excitation: 476 nm laser line combined with 100 µm slit width provides around 4 meV spectral resolution; 568 nm laser line combined with 100 µm slit width provides around 3 meV spectral resolution.
For polarization optics, a Glan-Taylor polarizing prism (Melles Griot) with a better than $10^{-5}$ extinction ratio to clean the laser excitation beam and a broad-band 50 mm polarizing cube (Karl Lambrecht Corporation) with an extinction ratio better than 1:500 for the analyzer was used. To perform measurements with circularly-polarized light, we use a Berek polarization compensator (New Focus) after the polarizing prism to convert the incoming linearly-polarized light into circularly-polarized light for excitation, and a broad-band 50 mm-diameter quarter wave retarder (Melles Griot) before the polarizing cube to convert the outgoing circularly-polarized light into linearly-polarized light for the analyzer. Experiments involving circular polarization geometry are performed from the (001) crystallographic plane.

Incident light was focused to a $50 \times 100 \mu m^2$ spot. For the spectra at 5 K, 2 mW laser power was used; for other data, 5 mW laser power of was used. The reported temperature values were corrected for laser heating: 1 K/mW laser heating rate was assumed.

The measured secondary-emission intensity $I(\omega, T)$ is related to the Raman response $\chi''(\omega, T)$ by $I(\omega, T) = [1 + n(\omega, T)]\chi''(\omega, T)$, where $n$ is the Bose factor, $\omega$ is energy, and $T$ is temperature.

In Fig. 3.25 we show an overview spectrum to illustrate the relevant energy scales. Below 15 meV, energy proximity between the CF state of the lowest-energy multiplets and the phonon modes leads to vibronic spectral features. From 15 meV to 80 meV, phononic features dominate. Above 80 meV, the spectrum is composed of the inter-multiplet excitations on top of a broad photo-luminescence continuum.

### 3.3.2 Inter-multiplet excitations

In this section we present the inter-multiplet excitations within the $^7F$ term of Tb$^{3+}$ ions. The electronic configuration of Tb$^{3+}$ ion is $4f^8$. According to Hund’s rules, the $^7F$ term has the lowest energy. In Fig. 3.26 we show the inter-multiplet excitations within the $^7F$ term. They are on top of a broad photo-luminescence continuum centered at 2.05 eV [Fig. 3.26(a)].
Figure 3.25: An overview of the low-temperature secondary-emission intensity $I$ measured in XY geometry at 20 K with 476 nm excitation in semi-log scale. The top scale is the absolute energy of the secondary-emission photons; the bottom scale shows the Raman shift: the energy loss, or the laser-photon energy minus the scattered-photon energy. The region below 15 meV features coexistence of CF and phononic excitations, and the resulting hybrid vibronic modes. The region between 15 and 80 meV is dominated by phonon modes. The region above 80 meV contains the inter-multiplet excitations on top of a broad photoluminescence continuum (shaded in blue).

This luminescence features could be attributed to the dipole-allowed $^5D \rightarrow ^7F$ transition [193–195].

The lowest-lying multiplet should have the largest possible total angular momentum, namely $J = 6$. The other multiplets of the $^7F$ term, with total angular momentum from $J = 5$ to $J = 0$ in integer step, have increasing energy in order: 0.30, 0.43, 0.48, 0.56, 0.63 and 0.70 eV, respectively [Fig. 3.26(b)]. The energies of the multiplets measured in this study are consistent with those measured in TbMnO$_3$ [193], TbAl$_3$(BO$_3$)$_4$ [194], and Tb-doped LaF$_3$ [195].

These multiplets are further split by the CF potential, resulting in sharp spectral features clustered within a particular energy range. Fine intra-multiplet CF structures are revealed at low temperature [Fig. 3.26(b)]. Because the degeneracy of each multiplet is $2J + 1$, the number of CF levels within each multiplet decreases with $J$. 
Figure 3.26: The inter-multiplet excitations within the $^7F$ term of Tb$^{3+}$ ions in TbInO$_3$. Secondary-emission intensity $I$ in XY scattering geometry is measured. (a) Secondary-emission intensity measured at 300 K as a function of outgoing photon energy. (b) Secondary-emission intensity measured at 300 and 20 K as a function of Raman shift.
Table 3.8: The basis functions of the A\(_{1}\)-, A\(_{2}\)- and E-symmetry CF eigenfunctions, respectively. These basis functions are expressed as combinations of \(| m_j \rangle\) with J=6.

\[
\begin{array}{ccc}
A_1 & A_2 & E \\
\frac{1}{\sqrt{2}}(|+3\rangle - |-3\rangle) & \frac{1}{\sqrt{2}}(|+3\rangle + |-3\rangle) & \frac{1}{\sqrt{2}}(|+1\rangle \pm |-1\rangle) \\
\frac{1}{\sqrt{2}}(|+6\rangle + |-6\rangle) & \frac{1}{\sqrt{2}}(|+6\rangle - |-6\rangle) & \frac{1}{\sqrt{2}}(|+2\rangle \pm |-2\rangle) \\
|0\rangle & |0\rangle & \frac{1}{\sqrt{2}}(|+4\rangle \pm |-4\rangle) \\
& & \frac{1}{\sqrt{2}}(|+5\rangle \pm |-5\rangle)
\end{array}
\]

3.3.3 Crystal-field excitations

In this section we discuss the intra-multiplet excitations, between the CF levels, within the lowest-lying \( ^7F_6 \) multiplet. The general expression for a CF potential of C\(_{3v}\) site symmetry can be written as \[132\]

\[H_{CF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6, \quad (3.43)\]

where \( \hat{O} \)'s are Stevens operators \[131\] and the \( B \)'s are the CF coefficients. The C\(_{3v}\)-symmetry CF potential splits the 13-fold degenerate \( ^7F_6 \) multiplet, resulting in 3 A\(_{1}\) singlets, 2 A\(_{2}\) singlets and 4 E doublets. The CF wavefunctions can be expressed in the \(| J, m_j \rangle\) bases; by group theory we can identify the basis functions of the CF eigenfunctions of each symmetry. These basis functions are given in Table 3.8. The A\(_{1}\) and A\(_{2}\) singlets are non-magnetic, while the E doublets allow a finite magnetic dipole moment. On the site symmetry reduction from C\(_{3v}\) to C\(_{3}\), the A\(_{1}\) and A\(_{2}\) states of C\(_{3v}\) group merge into the A states of C\(_{3}\). Therefore, the C\(_{3}\)-symmetry CF potential splits the \( ^7F_6 \) multiplet into 5 A singlets and 4 E doublets. Due to the mirror symmetry breaking, both the A singlets and E doublets of C\(_{3}\) group could carry magnetic moment.

In Fig. 3.27 we present the high-resolution spectra of the CF excitations within the \( ^7F_6 \) multiplet. The relationship between the scattering geometries and the symmetry channels is given in Table 3.9: the singlet-to-singlet transitions (A symmetry) appear in ZZ geometry; the doublet-to-singlet transitions (E symmetry) appear in XZ and RL geometries; the doublet-to-doublet transitions (A and E symmetries) appear in all these three geometries. We note that if Tb1 and Tb2 have different CF level scheme, at least 6 CF modes
should appear in ZZ geometry, however, only 3 CF modes are resolved. Hence both sites have essentially the same CF level scheme \(^{16}\), consistent with the weakness of ferroelectric distortion.

First, we fit the XZ spectrum with Lorentzian functions to determine the energy and linewidth of the CF excitations [Fig. 3.27(a)]. Because we find eight CF modes in XZ spectrum, the ground state must be a doublet: otherwise there would be only four CF modes in XZ spectrum.

Next, we turn to the ZZ spectrum. Because the CF transitions at 0.8, 2.5 and 3.7 meV are absent in the ZZ spectrum [Fig. 3.27(b)], we assign the states as singlets (the doublet-to-singlet transitions should not appear in ZZ geometry). For the remaining CF transitions, there are two in 5-7 meV range and three in 8-12 meV range. We find that to fit the A\(_1\)-symmetry spectrum, one mode in 5-7 meV interval and two modes in 8-12 meV interval are required. These three modes must be doublets, and there are only three doublets to be assigned. Hence, the two modes in 5-7 meV interval must be a singlet and a doublet. Among them, we assign the 6.3 meV mode as a doublet to better fit the A\(_1\)-symmetry spectrum \(^{17}\). For the same reason, we assign the 8.7 and 11.5 meV modes in 8-12 meV range as doublets.

The CF energies and transition widths are given in Table 3.10.

\(^{16}\) The same CF level scheme for both Tb1 and Tb2 is further confirmed by the fact that d2, d3 & d4 modes each has the same energy and linewidth in XZ and ZZ scattering geometries [Fig. 3.27], and the temperature dependence of CF entropy [Fig. 3.32(b)]

\(^{17}\) The energy and width of a CF mode are intrinsic properties of the system which is same for all symmetry channels. This requirement puts a constraint on the fitting process.

Table 3.9: Relationship between the scattering geometries and the symmetry channels. Each geometry is represented by E\(_i\)E\(_s\), where E\(_i\) and E\(_s\) are the polarizations of incident and scattered light; X, Y, and Z are the [100], [010], and [001] crystallographic directions; R and L represent right and left circular polarizations. The symmetry of the phonon modes is classified by the irreducible representations of C\(_{6v}\) group; the symmetry of the CF transitions at Tb1 and Tb2 sites is classified by those of C\(_{3v}\) group and C\(_3\) group, respectively.

<table>
<thead>
<tr>
<th>Scattering geometry</th>
<th>RL</th>
<th>XZ</th>
<th>ZZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phophon modes (C(_{6v}))</td>
<td>E(_2)</td>
<td>E(_1)</td>
<td>A(_1)</td>
</tr>
<tr>
<td>CF transition (C(_{3v}))</td>
<td>E</td>
<td>E</td>
<td>A(_1)</td>
</tr>
<tr>
<td>CF transition (C(_3))</td>
<td>E</td>
<td>E</td>
<td>A</td>
</tr>
</tbody>
</table>
Figure 3.27: The low-energy crystal-field (CF) transitions in TbInO$_3$, measured at 5 K with 647 nm excitation in (a) XZ and (b) ZZ scattering geometries. The Raman data are represented by black dots. The red lines represent the fits by Lorentzian lineshapes. The blue lines show doublet-to-singlet CF oscillators labeled by the final singlet state, and the green lines show doublet-to-doublet CF transitions; the phonon modes, labeled by their symmetry, are shown in purple. The Raman data and fitting curves below 7 meV are multiplied by a factor of 5 for clarity.

Table 3.10: The crystal-field (CF) level scheme for the $^7F_6$ multiplet of Tb$^{3+}$ ions in TbInO$_3$. The ground state, not listed in the table, is a doublet (d1); the excited states include five singlets (s1-s5) and three doublets (d2-d4). The energy and half width at half maximum (HWHM) are determined from Raman spectra measured at 5 K. Units are meV.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>s1</th>
<th>s2</th>
<th>s3</th>
<th>s4</th>
<th>d2</th>
<th>d3</th>
<th>s5</th>
<th>d4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>0.8</td>
<td>2.5</td>
<td>3.7</td>
<td>5.7</td>
<td>6.3</td>
<td>8.7</td>
<td>10.8</td>
<td>11.5</td>
</tr>
<tr>
<td>HWHM</td>
<td>0.25</td>
<td>0.4</td>
<td>0.4</td>
<td>0.65</td>
<td>0.65</td>
<td>0.7</td>
<td>0.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>
By now the low-energy CF level scheme is established [Table 3.10], and we can relate our results to the two excitation branches measured in the INS study [186]: their gapless excitation extending to 1.4 meV likely corresponds to the Raman-measured 0.8 meV singlet with 0.5 meV width; their broad excitation between 1.6 and 3.0 meV matches well the Raman-measured 2.5 meV singlet with 0.7 meV width.

Low-temperature CF excitations in insulators are expected to be sharp [113]. However, the linewidths of the low-energy CF excitations in TbInO$_3$ are much broader than the typical. To identify the reason for this broadening, first we exclude the effect of thermal fluctuations: the observed widths measured by INS and Raman are consistent even though the INS data are taken at 0.2 K while the Raman data are acquired at 5 K; moreover, the Raman linewidth of the s4 and d2 CF modes remains essentially same between 5 and 15 K. Second, the same excitation branches measured by INS in TbIn$_{0.95}$Mn$_{0.05}$O$_3$ have very similar linewidth [186], indicating that the broadening is not due to structural imperfection; in addition, the fact that the CF modes exhibit a Lorentzian lineshape indicates lack of inhomogeneous broadening. Third, the three lowest-lying CF modes are well separated in energy from the phonon modes. As the effective coupling to phonons depends on the energy separation between the CF and phonon modes, the large linewidth of these CF modes cannot be attributed to coupling to phonons. We suggest that the anomalously large CF linewidth of TbInO$_3$ is caused by magnetic fluctuations near the SL ground state: the dynamics of the correlated yet non-ordered magnetic moments manifests itself through the width of CF excitations.

Thus, in this section we have shown that both Tb1 and Tb2 ions have essentially the same CF level scheme within the lowest-lying $^7F_6$ multiplet; particularly, their ground state is a non-Kramers doublet. Such a doublet ground state allows a finite magnetic moment, and the same CF level scheme for all Tb$^{3+}$ ions further supports the scenario of triangular magnetic lattice. We have suggested that the broad CF linewidth is related to the magnetic fluctuations resulting from the SL dynamics.
3.3.4 Phonon modes

In this section we identify the Raman-active phonon modes from the low-temperature spectra. We start from group-theoretical analyses to count the number and symmetries of Raman modes. In the high-temperature paraelectric phase (space group $P6_3/mmc$, No. 194; point group $D_{6h}$), TbInO$_3$ has 10 atoms in one unit cell, and 5 Raman-active optical phonon modes: $1A_{1g} \oplus 1E_{1g} \oplus 3E_{2g}$; in the low-temperature ferroelectric phase (space group $P6_3cm$, No. 185; point group $C_{6v}$), TbInO$_3$ has 30 atoms in one unit cell, and 38 Raman-active optical phonon modes: $9A_1 \oplus 14E_1 \oplus 15E_2$.

The spectra of phonon modes at low temperature are presented in Fig. 3.28 with both linear and semi-log scale. Unlabelled spectral features below 15 meV are related to crystal-field modes; some weak features at higher energy, for example those in between $A_1^{(8)}$ and $A_1^{(9)}$ modes, result from second-order phonon scattering. In such scattering process, two phonons of zero total momentum are excited simultaneously; because the resulting spectral feature depends on the phonon dispersion and density of states, it does not have Lorentzian lineshape and commonly exhibits broad linewidth [1, 151].

The energies of the phonon modes at 20 K are summarized in Table 3.11. The energy of 9 phonon modes was identified by unpolarized Raman measurements of a series of hexagonal rare-earth (RE) REInO$_3$ compounds [196]; these energy values are consistent with the result of this study.

The atomic displacements of a Raman-active optical phonon mode modulate the macroscopic polarizability. The stronger the induced polarizability, the stronger the intensity of the corresponding Raman mode. For TbInO$_3$, the paraelectric to ferroelectric transition not only causes some Raman-inactive modes in the paraelectric phase to become Raman-active in the ferroelectric phase, but also results in new Raman-active modes in the ferroelectric phase which have no correspondence to the modes in the paraelectric phase. Because the ferroelectric structure differs by only small distortions from the paraelectric structure, these
Figure 3.28: Raman response $\chi''(\omega, 20\, K)$ of the (a) A$_1$-symmetry, (b) E$_1$-symmetry and (c) E$_2$-symmetry phonon modes measured at 20 K with 647 nm excitation, plotted in linear scale. (d-f) The respective plots in semi-log scale. Unlabelled spectral features below 15 meV are related to crystal-field modes; weak features at higher energy result from second-order scattering.
Table 3.11: The energies of the $A_1$-symmetry, $E_1$-symmetry and $E_2$-symmetry Raman-active optical phonon modes at 20K. Units are meV.

<table>
<thead>
<tr>
<th>Number</th>
<th>$A_1$ modes</th>
<th>$E_1$ modes</th>
<th>$E_2$ modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.9</td>
<td>10.2</td>
<td>8.1</td>
</tr>
<tr>
<td>2</td>
<td>23.1</td>
<td>13.8</td>
<td>9.6</td>
</tr>
<tr>
<td>3</td>
<td>26.8</td>
<td>18.3</td>
<td>15.2</td>
</tr>
<tr>
<td>4</td>
<td>30.1</td>
<td>21.4</td>
<td>17.4</td>
</tr>
<tr>
<td>5</td>
<td>36.2</td>
<td>23.1</td>
<td>29.0</td>
</tr>
<tr>
<td>6</td>
<td>39.7</td>
<td>30.2</td>
<td>32.0</td>
</tr>
<tr>
<td>7</td>
<td>46.7</td>
<td>36.2</td>
<td>36.1</td>
</tr>
<tr>
<td>8</td>
<td>52.6</td>
<td>40.2</td>
<td>40.3</td>
</tr>
<tr>
<td>9</td>
<td>75.6</td>
<td>44.9</td>
<td>44.0</td>
</tr>
<tr>
<td>10</td>
<td>47.0</td>
<td>46.7</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>52.5</td>
<td>52.2</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>64.3</td>
<td>60.1</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>67.8</td>
<td>64.1</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>75.5</td>
<td>68.0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>75.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

additional Raman-active modes are expected to render only weak modulation of polarizability and in turn have weak intensity. On the contrary, the $A_1^{(9)}$, $E_1^{(10)}$, $E_2^{(2)}$, $E_2^{(10)}$ and $E_2^{(15)}$ modes have much stronger intensity than the other modes. These modes correspond to the 5 Raman-active modes of the paraelectric phase:

$$A_1^{(9)} \rightarrow A_{1g};$$

$$E_1^{(10)} \rightarrow E_{1g};$$

$$E_2^{(2)}, E_2^{(10)}, E_2^{(15)} \rightarrow 3E_{2g}. \quad (3.44)$$

Hitherto, we have characterized the symmetry and measured the energy of all 38 Raman-active phonon modes at 20K. Moreover, we have interpreted the relative intensity of these modes in view of the structural change between the paraelectric and ferroelectric phases: the modes which are Raman-active in the paraelectric phase have strong intensity in the ferroelectric phase, while other modes have weak intensity.

### 3.3.5 Vibronic modes in $E_2$ symmetry channel

After presenting the CF and phonon spectra respectively in Sec. 3.3.3 and Sec. 3.3.4, we examine the hybrid vibronic spectral features resulting from the coupling between the CF
and phonon modes. In Fig. 3.29 we present the temperature dependence of the $E_{2}^{(1)}$ and $E_{2}^{(2)}$ phonon modes. The apparent linewidth of the two modes anomalously increase on cooling. Moreover, the energy and HWHM of the CF modes, determined from XZ and ZZ spectra, cannot be directly used to fit the modes between 8 and 12 meV in the RL spectrum. These two phenomena indicate presence of coupling between the two phonon modes and three CF modes in the 8-12 meV energy range. Even above 100 K, when the CF modes become very broad, the coupling effects remain noticeable, as it seen from the asymmetric lineshape of the $E_{2}^{(2)}$ mode [Fig. 3.29(b)].

Because of the close proximity of CF transitions to phonon modes, vibronic excitations have been observed in several rare-earth compounds, e.g. in Ce$_2$O$_3$ [190], NdBa$_2$Cu$_3$O$_7$ [191], and Ho$_2$Ti$_2$O$_7$ [192]. In these cases, one CF transition interacts with one phonon mode, resulting in two vibronic states [197].

The $E_2$-symmetry spectra of TbInO$_3$ are more involved, because three CF transitions
and two phonon modes are close in frequency, leading to complex spectra structure. Before analyzing this multi-mode problem, we consider a simplified case in which one phonon mode interacts with one CF mode. We model the bare response of the CF and phonon modes, in the absence of interaction, by Lorentzian function 18:

$$\chi''_{e,p}(\omega) = \frac{t_{e,p}^2 \gamma_{e,p}}{(\omega - \omega_{e,p})^2 + \gamma_{e,p}^2},$$

(3.45)

where the subscript “e” and “p” label the CF and phononic responses respectively; $t_{e,p}$ is the light-scattering vertex, $\omega_{e,p}$ is the mode’s bare frequency, and $\gamma_{e,p}$ is the bare half width at half maximum (HWHM).

The interaction between the phonon and CF modes couples these dynamical responses; as a result, not only are the bare responses [Eq. (3.45)] renormalized, but also an interference term appears in the total Raman response. The full Raman response in turn can be broken into three contributions:

$$\chi''(\omega) = \chi''_{pv}(\omega) + \chi''_{ev}(\omega) + \chi''_{int}(\omega),$$

(3.46)

in which the subscript “v” indicates presence of the interaction. The first two terms correspond to the phonon response proportional to square of light coupling vertex $t_p^2$ and the CF response proportional to $t_e^2$, respectively, while the third one, that is proportional to the $t_pt_e$ combination, is the interference term appearing due to the exciton-phonon coupling with strength $v$.

The exact expressions for the three contributions are given in the Appendix 3.3.8. To illustrate the essential features, we consider the weak-coupling limit $v/\Delta \omega \ll 1$ with $\Delta \omega = \omega_p - \omega_e$ being the frequency difference between the phonon and CF modes. In this limit, the renormalized phonon response can be written in a Lorentzian form:

$$\chi''_{pv}(\omega) = \frac{t_{pv}^2 \gamma_{pv}}{(\omega - \omega_{pv})^2 + \gamma_{pv}^2}.$$

(3.47)

18We note that a proper Raman response should satisfy the requirement $\chi''(\omega = 0) = 0$; only for $\omega \ll 0$ Eq. (3.45) can be used as an approximation.
The renormalization shifts the phonon frequency from \( \omega_p \) to \( \omega_{pv} = \omega_p + v^2 \Delta \omega / (\gamma_e^2 + \Delta \omega^2) \), and broadens the phonon HWHM from \( \gamma_p \) to \( \gamma_{pv} = \gamma_p + v^2 \gamma_e / (\gamma_e^2 + \Delta \omega^2) \). The simultaneous change of both frequency and HWHM is consistent with the general effect of interaction on the self energy of a state: the interaction influences both the real part of the self energy, which shifts the frequency, and the imaginary part of the self energy, which broadens the linewidth.

Because the bare responses of the phonon and CF modes have the same form [Eq. (3.45)], the renormalized CF response also has a Lorentzian form, as required by symmetry. The energy is shifted to \( \omega_{ev} = \omega_e - v^2 \Delta \omega / (\gamma_p^2 + \Delta \omega^2) \), and the HWHM is broadened to \( \gamma_{ev} = \gamma_e + v^2 \gamma_p / (\gamma_p^2 + \Delta \omega^2) \). If \( \omega_e > \omega_p \), \( \Delta \omega \) is negative; the maximum of CF response is moved to higher energy and that of phononic response is moved to lower energy, characteristic of the conventional level-repulsion behavior.

The interference term has the following expression in the weak-coupling limit:

\[
\chi''_{int}(\omega) = \frac{-2t_p t_e v[\gamma_p(\omega - \omega_e) + \gamma_e(\omega - \omega_p)]}{[(\omega - \omega_e)^2 + \gamma_e^2][(\omega - \omega_p)^2 + \gamma_p^2]}.
\] (3.48)

The sign of this term depends not only on \( v \), but also on phase difference between the CF and phonon oscillators. The phase of a light-driven oscillator flips to the opposite sense at the resonant frequency. Hence, the sign of the interference term changes in the range between the bare CF oscillator frequency \( \omega_e \) and the bare phonon frequency \( \omega_p \); this crossover happens closer to the frequency of the oscillator which has smaller bare linewidth, see Fig. 3.30(b) and (e).

After discussing the basic properties of the coupling effect, we fit the \( E_2 \)-symmetry spectra of TbInO\(_3\) with the model described in Appendix 3.3.8. We use the energy and HWHM in Table 3.10 for the three CF transitions; the energy of the two phonon modes is constrained to be no less than their values at 300 K, and the HWHM is constrained to be no more than their values at 300 K. From the fitting we obtain the values of the coupling constants listed in Table 3.12.
Table 3.12: The coupling strength ($v$), frequency difference ($\Delta \omega$), and dimensionless coupling constant ($v/\Delta \omega$) for interactions between $E_2^{(i)}$ phonons ($i=1,2$) and the CF transitions to the states $d_3$, $s_5$ and $d_4$. Values are obtained by fitting the vibronic excitations.

<table>
<thead>
<tr>
<th>Pair</th>
<th>$E_2^{(1)}$-d3</th>
<th>$E_2^{(1)}$-s5</th>
<th>$E_2^{(1)}$-d4</th>
<th>$E_2^{(2)}$-d3</th>
<th>$E_2^{(2)}$-s5</th>
<th>$E_2^{(2)}$-d4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ (meV)</td>
<td>-0.31</td>
<td>-0.35</td>
<td>-0.46</td>
<td>-0.60</td>
<td>-0.68</td>
<td>-0.91</td>
</tr>
<tr>
<td>$\Delta \omega$ (meV)</td>
<td>-0.44</td>
<td>-2.59</td>
<td>-3.24</td>
<td>1.38</td>
<td>-0.77</td>
<td>-1.42</td>
</tr>
<tr>
<td>$v/\Delta \omega$</td>
<td>0.69</td>
<td>0.13</td>
<td>0.14</td>
<td>-0.44</td>
<td>0.89</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Figure 3.30: Illustration for coupling between (a-c) the $E_2^{(1)}$ phonon and $d_3$ CF modes; (d-f) the $E_2^{(2)}$ phonon and $s_5$ CF modes. (a) and (d): The Raman response functions for bare $\chi''_{e,p}(\omega)$ (dashed lines) and renormalized by interaction $\chi''_{ev,pe}(\omega)$ (solid lines). The shift of frequency is labeled by horizontal arrows; the anti-resonant feature of $\chi''_{ev}(\omega)$ at the bare phonon frequency is labeled by vertical arrows. (b) and (e): The interference term $\chi''_{int}(\omega)$. The bare phonon frequency, at which $\chi''_{int}(\omega)$ changes sign, is labelled by a small circle. (c) and (f): The total Raman response $\chi''(\omega)$ [Eq.(3.46)], corresponds to the sum of the renormalized responses and the interference term.
From Table 3.12, we notice that the $E_2^{(1)}$ phonon mainly couples to the d3 CF transition, and the $E_2^{(2)}$ phonon has the strongest dimensionless coupling to the s5 CF transition. We study these two pairs separately in Fig. 3.30. First we discuss the renormalization effect. Because $v/\Delta \omega \approx 1$, the weak-coupling limit does not apply to these two pairs and the renormalized responses do not have a Lorentzian lineshape [Fig. 3.30(a) and (d)]. However, the level-repulsion behavior and the broadening of lineshape seen in the weak-coupling case still applies in the strong-coupling case. At the bare phonon frequency, the renormalized CF response exhibit an anti-resonant spectral feature, which arises due to the destructive interference of the two modes. The new local maximum near the anti-resonance results instead from constructive interference. Second, we consider the interference term, which changes sign essentially at the bare phonon frequency [Fig. 3.30(b) and (e)] because the phonon mode is much sharper than the CF mode, consistent with discussion for the weak-coupling case. Third, we examine the total response, the sum of the renormalized responses and the interference term [Fig. 3.30(c) and (f)]. Because of the much smaller relative intensity of the $E_2^{(1)}$ mode, it is “absorbed” into a broad composite vibronic feature [Fig. 3.30(c)]. The $E_2^{(2)}$ phonon, on the contrary, has a much larger relative to CF transitions intensity; therefore it remains identifiable in the vibronic spectra [Fig. 3.30(f)].

In Fig. 3.31 we present the overall effect of the coupling between three CF modes and two phonon modes. Although the $E_2^{(1)}$ phonon mainly couples to the d3 CF transition, the whole effect of coupling to three CF modes [Fig. 3.31(a)] is similar to Fig. 3.30(c), except for the disappearance of the weak dip near 8.1 meV. However, for the $E_2^{(2)}$ phonon, the coupling to the d3 and d4 CF modes is not negligible; hence the whole effect is different from what is shown in Fig. 3.30(f), especially the intensity.

Summing-up, in this section we identified the hybrid vibronic features from the temperature dependence of the $E_2^{(1)}$ and $E_2^{(2)}$ phonon modes. These two phonon modes couple to three CF modes in the same energy range. Such coupling results from the modulation of the electron-cloud distribution of the CF states by lattice vibration, and is facilitated by
3.3.6 Specific heat and entropy

In this section we demonstrate that the specific heat and entropy data are consistent with the CF level scheme determined in Sec. 3.3.3. We use four components to model the specific heat of TbInO$_3$: the nuclear, CF, acoustic-phonon, and optical-phonon contributions [Appendix 3.3.8]. In particular, based on the Raman results we use Lorentzian lineshapes with the energy and width given in Table 3.10 for the CF states. The CF contribution to
the specific heat can be expressed in the following form:

\[ C_E = \frac{R}{(k_B T)^2} \left\{ \frac{1}{Z_E} \sum_i L_i(\epsilon) e^2 e^{(-\epsilon/k_B T)} d\epsilon - \left[ \frac{1}{Z_E} \sum_i L_i(\epsilon) e^{-\epsilon/k_B T} d\epsilon \right]^2 \right\}, \quad (3.49) \]

which is a generalization of the formula for CF levels with Dirac \( \delta \) function as lineshape [198].

In Eq. (3.49), \( Z_E = \sum_i \int L_i(\epsilon) \exp(-\epsilon/k_B T) d\epsilon \) is the partition function for the CF levels; \( i \) (from 1 to 8) labels the individual CF energy levels, and \( L_i(\epsilon) \) is the normalized Lorentzian function for energy level \( i \).

In Fig. 3.32(a) we compare calculated and measured specific heat data [187]. The specific heat below 0.5 K can be accounted for by nuclear Schottky contribution, and the high-temperature specific heat is mostly contributed by phonon modes. In particular, the CF contribution agrees well with the data between 0.5 K and 10 K.

In the previous study [187], the low-temperature specific heat was fitted by assuming a singlet ground state for Tb1 ions and a doublet one for Tb2 ions. As a result, a large residual specific heat between 1 and 4 K was shown after subtracting the nuclear and CF contributions. In [187] authors model the CF states by Dirac \( \delta \)-function in energy, while we consider the finite width of these excitations. We propose that the contribution from magnetic fluctuations, which correspond to SL dynamics near the ground state, is effectively treated in the width of the CF states. Hence no residual specific heat should appear in our analysis.

Regarding the entropy corresponding to the CF excitations, if the ground state is a doublet, the entropy should saturate at \( R[\ln(2J + 1) - \ln 2] = 1.9R \) (\( R \) is the ideal gas constant); and if it is a singlet, the entropy should saturate at \( R \ln(2J + 1) = 2.6R \). The entropy change \( \Delta S \) from \( T_1 \) to \( T_2 \) can be calculated from the specific heat \( C \) by integration:

\[ \Delta S = \int_{T_1}^{T_2} \frac{C}{T} dT. \quad (3.50) \]

We first subtract the nuclear and phononic contributions from the experimental specific-heat data, and then use Eq. (3.50) to find the entropy corresponding to the CF excitations. The fact that the entropy at 300 K is very close to 1.9\( R \) further supports the assignment to
Figure 3.32: The specific heat and electronic entropy of TbInO$_3$. (a) Log-log plot of the specific heat data from Ref. [187] (open black circles), and the calculated curves. The total specific heat composes of the nuclear, crystal-field, acoustic-phonon and optical-phonon contributions. (b) Semi-log plot of the entropy corresponding to the CF excitations (solid gray circles), and the calculated curves. The unit of entropy is the ideal gas constant $R = 8.314$ J/(mol K). The blue curve corresponds to the crystal-field level scheme in Table 3.10; the cyan curve assumes that the ground state is a singlet and the first excited state is a doublet; the pink curve in middle assumes that Tb1 has a singlet ground state and Tb2 has a doublet one.
doublet ground state [Fig. 3.32(b)]. Moreover, an assumption that Tb1 and Tb2 both have a doublet ground state describes the entropy much better than an assumption that Tb1 has a singlet ground state and Tb2 has a doublet one.

In this section, we described the specific heat by the nuclear, CF, and phononic contributions. In particular, we have accounted the finite linewidth of the CF states as determined by spectroscopic data. We demonstrated that the temperature dependence of the CF entropy is consistent with a doublet ground state for both Tb$^{3+}$ ion sites.

3.3.7 Conclusions

In this work, we study the electronic and phononic excitations of TbInO$_3$ by polarization resolved Raman spectroscopy. We establish that TbInO$_3$ is hosting a triangular magnetic lattice of the non-Kramers doublet ground states. Specifically, we discuss inter-multiplet excitations within the $^7F$ term, intra-multiplet excitations within the lowest-lying $^7F_6$ multiplet, Raman-active phonon modes, specific heat data, and discover hybrid vibronic modes.

We observe the $^5D \rightarrow ^7F$ luminescence continuum centered around 2 eV, and the $^7F$ inter-multiplet Raman excitations. The energy of the $^7F$ multiplets is between 0.3 and 0.7 eV. These multiplets exhibit at low temperature fine intra-multiplet CF structures which are clustered within their respective particular energy range.

We measure the CF excitations and in turn establish the CF level scheme for the lowest-lying $^7F_6$ multiplet. We show that both Tb1 and Tb2 ions, though having slightly different crystal environment, have essentially the same CF level scheme. In particular, they both exhibit a non-Kramers doublet ground state. This result supports the scenario of triangular magnetic lattice, which could support U(1)-symmetry SL ground state. Moreover, the orbital-degenerate ground state could result in spin-orbit-entangled multipolar phases. These possibilities renders TbInO$_3$ as a suitable platform to explore the SL physics. The enhanced linewidth of the CF states further serves as an indirect evidence for the magnetic fluctuations originating from SL dynamics.
We determine the energies of all 38 Raman-active phonon modes: $9A_1 \oplus 14E_1 \oplus 15E_2$ and identify the five modes which remain Raman-active in the high-temperature paraelectric phase.

We discover hybrid vibronic excitations composed of coupled CF and phonon modes in the quadrupolar $E_2$ symmetry channel. Such coupling results from the modulation of the electron-cloud distribution of the CF states by lattice vibration, and is facilitated by the energetic overlap between the CF and phonon modes. We use a simple model, with one CF mode and one phonon mode, to illustrate the physics associated with this type of interaction, including level repulsion, linewidth broadening, and spectral interference effect. We use a model fit to the $E_2$-symmetry spectrum and derive the electron-phonon coupling strength. Because the energetic proximity of CF and phonon modes is common in rare-earth compounds, the developed method for decomposing Raman spectra of strongly-coupled phononic and CF excitations may have wide applicability.

We also fit the specific-heat data by the sum of nuclear, CF and phononic contributions consistent with obtained spectroscopic parameters. The temperature dependence of the CF entropy further supports the CF level scheme determined from Raman measurements, therefore, may be of interest for further exploration of SL physics.

### 3.3.8 Theoretical details

**Multiplet splitting induced by crystal-field potential**

The multiplets of the $^7F$ term are split by the CF potential. In Table 3.13 we classify the symmetry of the resulting fine levels by the irreducible representations of $C_{3v}$ group. On reducing the site symmetry from $C_{3v}$ to $C_3$, the $A_1$ and $A_2$ states of $C_{3v}$ group mix into the $A$ states of $C_3$. 
Table 3.13: Splitting of the $^7F_J$ multiplet by the $C_{3v}$-symmetry CF potential. The symmetry of the CF states is classified by the irreducible representations of $C_{3v}$ group.

<table>
<thead>
<tr>
<th>$J$ value</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$E$</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Allowed transitions for different crystal-field ground state

In Fig. 3.33 we illustrate the allowed CF transitions in XZ and ZZ scattering geometries. If the CF ground state is a doublet, there are 8 CF transitions allowed in XZ geometry and 3 allowed in ZZ geometry; if the CF ground state is a singlet, there are 4 CF transitions allowed in XZ geometry and 4 allowed in ZZ geometry.

We note that in the case of a doublet ground state, the 3 transitions appearing in both XZ and ZZ geometries must have the same energy and linewidth; on the contrary, for a singlet ground state the 4 transitions in XZ geometry are independent from those 4 in ZZ geometry. The fact that the d2, d3, and d4 modes have the same energy and linewidth in both XZ and ZZ geometries therefore support the doublet ground state assignment.

Classification of the Γ-point phonons

In Fig. 3.34 we compare the paraelectric and ferroelectric phases of TbInO$_3$. We first discuss the high-temperature paraelectric phase [Fig. 3.24(a)], with space group $P6_3/mmc$ and point group $D_{6h}$. Although high-temperature Raman measurements were not performed in this study, considering the paraelectric phase is helpful for understanding many aspects of the Raman-active phonons, particularly the large intensity difference for different modes. The unit cell contains two formula units, having two in-equivalent oxygen sites (O$_{apex}$ and O$_{plane}$) and only one site for Tb and In. The Tb site is the center of inversion and Tb atoms therefore cannot participate in Raman-active lattice vibrations. The Γ-point phonons are classified in Table 3.14; there is a total of 5 Raman-active phonon modes.

The low-temperature ferroelectric phase [Fig. 3.24(b)], with space group $P6_3cm$ and
Figure 3.33: Cartoon showing the allowed transitions in (a) XZ scattering geometry and (b) ZZ scattering geometry for the singlet versus doublet crystal-field (CF) ground state assignments. The red and blue lines represent singlet and doublet CF levels, respectively. The vertical black arrows indicates the Raman allowed CF transitions for given scattering geometry.
Figure 3.34: Crystal structure for (a) paraelectric and (b) ferroelectric phases of TbInO$_3$. The oxygen, indium and terbium atoms are shown in red, pink, and purple colors, respectively. The black frame indicates the unit cell. The oxygen sites of different symmetry are labelled in each case. Two Tb sites of different symmetry are labelled in panel (b).

point group C$_{6v}$, can be obtained from the paraelectric phase by tilting the InO$_5$ bi-pyramids and buckling the Tb layers [199]. Because of the tilting, the apex oxygen sites O$_{(1)}$ and O$_{(2)}$, and the planer oxygen sites O$_{(3)}$ and O$_{(4)}$ become non-equivalent; as a result of the buckling, Tb$_{(1)}$ site becomes slightly out of the plane formed by Tb$_{(2)}$. The unit cell contains six formula units. We note that the number of Raman-active modes should increase for two reasons: (i) the absence of central inversion symmetry renders the Raman- and infrared (IR)-active modes not mutually exclusive; (ii) the larger volume of the unit cell leads to new phonon modes at $\Gamma$ point, some of which are Raman-active. From Table 3.15, the number of Raman-active phonon modes increase from 5 to 38.

Table 3.14: Classification of the $\Gamma$-point phonons for the high-temperature paraelectric TbInO$_3$ (space group $P6_3/mmc$, No. 194; point group D$_{6h}$; Z=2).

<table>
<thead>
<tr>
<th>Wyckoff Site</th>
<th>Irreducible symmetry representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom notation</td>
<td>symmetry</td>
</tr>
<tr>
<td>Tb</td>
<td>2(a)</td>
</tr>
<tr>
<td>In</td>
<td>2(c)</td>
</tr>
<tr>
<td>O$_{\text{plane}}$</td>
<td>2(b)</td>
</tr>
<tr>
<td>O$_{\text{apex}}$</td>
<td>4(f)</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Gamma_{\text{Raman}} &= A_{1g} + E_{1g} + 3E_{2g} \\
\Gamma_{\text{IR}} &= 3A_{2u} + 3E_{1u} \\
\Gamma_{\text{acoustic}} &= A_{2u} + E_{1u} \\
\Gamma_{\text{silent}} &= 3B_{1g} + 2B_{2u} + 2E_{2u}
\end{align*}
\]
Table 3.15: Classification of the Γ-point phonons for the low-temperature ferroelectric TbInO$_3$ (space group $P6_3cm$, No. 185; point group $C_{6v}$); $Z=6$.

<table>
<thead>
<tr>
<th>Wyckoff Site</th>
<th>Irreducible Symmetry Representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$_{(1)}$</td>
<td>2(a) $C_{3v}$ $A_1+B_1+E_1+E_2$</td>
</tr>
<tr>
<td>Tb$_{(2)}$</td>
<td>4(b) $C_3$ $A_1+A_2+B_1+B_2+2E_1+2E_2$</td>
</tr>
<tr>
<td>In</td>
<td>6(c) $C_s$ $2A_1+A_2+2B_1+B_2+3E_1+3E_2$</td>
</tr>
<tr>
<td>O$_{(1)}$</td>
<td>6(c) $C_s$ $2A_1+A_2+2B_1+B_2+3E_1+3E_2$</td>
</tr>
<tr>
<td>O$_{(2)}$</td>
<td>6(c) $C_s$ $2A_1+A_2+2B_1+B_2+3E_1+3E_2$</td>
</tr>
<tr>
<td>O$_{(3)}$</td>
<td>2(a) $C_{3v}$ $A_1+B_1+E_1+E_2$</td>
</tr>
<tr>
<td>O$_{(4)}$</td>
<td>4(b) $C_3$ $A_1+A_2+B_1+B_2+2E_1+2E_2$</td>
</tr>
</tbody>
</table>

Mathematical expressions for the coupling between one phonon and one crystal-field mode

In Sec. 3.3.5 we consider a simplified case in which one phonon mode interacts to one CF mode; the weak-coupling limit is taken in order to illustrate the essential features. In this section, we present the exact expressions for the three contributions in Eq.(3.46).

The renormalized phonon response:

$$\chi''_{pv}(\omega) = t_p^2 \{\gamma_p[(\omega - \omega_e)^2 + \gamma_e^2] + \gamma_e v^2\}/D.$$  (3.51)

The renormalized CF response:

$$\chi''_{ev}(\omega) = t_e^2 \{\gamma_e[(\omega - \omega_p)^2 + \gamma_p^2] + \gamma_p v^2\}/D.$$  (3.52)

The interference term:

$$\chi''_{int}(\omega) = -2t_p t_e v[\gamma_p(\omega - \omega_e) + \gamma_e(\omega - \omega_p)]/D.$$  (3.53)

We note that $\chi''_p(\omega)$ and $\chi''_e(\omega)$ are related by the exchange of subscript $p \leftrightarrow e$ in their respective expressions, as required by symmetry. For the same reason, the interference term is invariant under the exchange of subscript $p \leftrightarrow e$. The three expressions have the same denominator $D$, which is

$$[\gamma_e^2 + (\omega - \omega_e)^2][\gamma_p^2 + (\omega - \omega_p)^2] - 2v^2[\gamma_e \gamma_p + (\omega - \omega_e)(\omega - \omega_p)] + v^4.$$  (3.54)
The fitting model for the vibronic features

The apparent spectral linewidth of the $E_2^{(1)}$ and $E_2^{(2)}$ phonon modes anomalously increases on cooling [Fig. 3.29], indicating existence of interaction between the phonon modes and the CF excitations. Such interaction originates from the modulation of the electron-cloud distribution of CF states by lattice vibration. We use a Green’s function formalism to construct a model describing this physics [7]. In essence, the Raman response of the coupled system is calculated from the interacting Green’s function:

$$\chi'' \sim \text{Im} T^T G T , \quad (3.55)$$

in which $T$ denotes the vertices for light scattering process and $G$ is the Green’s function for the interacting phononic and CF excitations. The Green’s function $G$ can be obtained by solving the Dyson equation:

$$G = (G_0^{-1} - V)^{-1} , \quad (3.56)$$

where $G_0$ is the bare Green’s function and $V$ represents the interaction. To proceed, we first need to consider which phonon and CF modes are involved, and the way they couple to each other.

For $C_{3v}/C_3$ groups, the doublet-to-singlet transitions appear only in E symmetry channel; the doublet-to-doublet transitions appear both in $A_1/A$ and in E symmetry channels. The E-symmetry component of the CF excitations can interact with the $E_1$- and $E_2$-symmetry phonon modes; the $A_1/A$-symmetry component of the CF excitations interacts with the $A_1$-symmetry phonon modes.

From the measured Raman spectra, we identify three CF modes in the energy range between 8 and 12 meV: the first one is at 8.6 meV (a peak in both XZ and RL spectra), the second one at 10.8 meV (a peak in XZ spectrum), and the third one at 11.4 meV (a peak in RL spectrum). Two of them are doublets and the remaining one is a singlet. The three E-symmetry components of the CF excitations interact with two $E_1$-symmetry and two $E_2$-symmetry phonon modes; the two $A_1/A$-symmetry component of the CF excitations
interact with one $A_1$-symmetry phonon mode.

For the $E$-symmetry components of the CF excitations, the bare Green’s function $G_{E_0}$ and the coupling interaction $V_E$ are

$$G_{E_0} = \begin{pmatrix} G_{p_1} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & G_{p_2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & G_{p_3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{p_4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{e_1} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{e_2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & G_{e_3} \end{pmatrix}, \quad (3.57)$$

$$V_E = \begin{pmatrix} v_{11} & v_{12} & v_{13} \\ v_{21} & v_{22} & v_{23} \\ v_{31} & v_{32} & v_{33} \\ v_{41} & v_{42} & v_{43} \\ v_{11} & v_{21} & v_{31} & v_{41} & 0 & 0 & 0 \\ v_{12} & v_{22} & v_{32} & v_{42} & 0 & 0 & 0 \\ v_{13} & v_{23} & v_{33} & v_{43} & 0 & 0 & 0 \end{pmatrix}. \quad (3.58)$$

The phononic Green’s function $G_{pi}$ ($i=1,2$) corresponds to the $E_{1}^{(1)}$ and $E_{1}^{(2)}$ phonon modes; $G_{pi}$ ($i=3,4$) corresponds to the $E_{2}^{(1)}$ and $E_{2}^{(2)}$ phonon modes. The electronic Green’s function $G_{ej}$ ($j=1,2,3$) has increasing energy in order; $G_{e1}$ and $G_{e3}$ are doublet-to-doublet CF excitations, and $G_{e2}$ is a doublet-to-singlet CF excitation. These Green’s functions have a Lorentzian form: $-1/\left(\omega - \omega_0 + i\gamma_0\right)$, in which $\omega_0$ is bare frequency and $\gamma_0$ is half width at half maximum (HWHM). The parameters $v_{ij}$ ($i=1,2,3,4; j=1,2,3$) represents the coupling strength between the phononic excitation $G_{pi}$ and electronic excitation $G_{ej}$.

We can describe the coupling in an alternative way to reduce the number of free parameters. We define the effective electric field $f_i$ ($i=1,2,3,4$) for each of the four phonon modes, and the effective electric moment $q_{jk}$ ($j=1,2,3; k=1,2$) for each of the three CF transitions.
For $q_{jk}$, the first index $j$ labels the three CF transitions; the second index $k$ labels the symmetry of the corresponding electric moment: $k=1$ corresponds to $E_1$ symmetry and $k=2$ corresponds to $E_2$ symmetry. We then have $v_{ij} = f_i q_{j1}$ ($i=1,2$) and $v_{ij} = f_i q_{j2}$ ($i=3,4$). In this way, we reduce the number of needed coupling constants to ten from twelve.

The interacting Green’s function $G_E$ for the $E$-symmetry components of the CF excitations is

$$G_E = (G_{E0}^{-1} - V_E)^{-1}.$$  \hspace{1cm} (3.59)

And the Raman responses in the XZ and RL scattering geometries are calculated in the following way:

$$\chi''_{XZ} \sim \text{Im} T_{XZ}^\dagger G_E T_{XZ},$$  \hspace{1cm} (3.60)

$$\chi''_{RL} \sim \text{Im} T_{RL}^\dagger G_E T_{RL}.$$  \hspace{1cm} (3.61)

In these two expressions, $T_{XZ}^\dagger$ and $T_{RL}^\dagger$ are the vertex of light scattering process in the XZ and RL scattering geometries, respectively:

$$T_{XZ}^\dagger = \begin{pmatrix} t_{p1} & t_{p2} & 0 & 0 & t_{e1XZ} & t_{e2XZ} & t_{e3XZ} \end{pmatrix},$$  \hspace{1cm} (3.62)

$$T_{RL}^\dagger = \begin{pmatrix} 0 & 0 & t_{p3} & t_{p4} & t_{e1RL} & t_{e2RL} & t_{e3RL} \end{pmatrix}.$$  \hspace{1cm} (3.63)

For the $A_1/A$-symmetry components of the CF excitations, the bare Green’s function $G_{A0}$ and the coupling interaction $V_A$ are

$$G_{A0} = \begin{pmatrix} G_{p5} & 0 & 0 \\ 0 & G_{e1} & 0 \\ 0 & 0 & G_{e3} \end{pmatrix},$$  \hspace{1cm} (3.64)

$$V_A = \begin{pmatrix} 0 & v_{51} & v_{53} \\ v_{51} & 0 & 0 \\ v_{53} & 0 & 0 \end{pmatrix}.$$  \hspace{1cm} (3.65)
Here the phononic Green’s function $G_{p5}$ represents the $A_1$-symmetry phonon modes. Similar to the E-symmetry case, we have

$$G_A = (G_{A0}^{-1} - V_A)^{-1}, \quad (3.66)$$

$$\chi''_{ZZ} \sim \text{Im} \ T_{ZZ}^\dagger G_A T_{ZZ}, \quad (3.67)$$

$$T_{ZZ}^\dagger = \begin{pmatrix} t_{p5} & t_{e1ZZ} & t_{e3ZZ} \end{pmatrix}. \quad (3.68)$$

In practice, we find that the XZ and ZZ spectra can be fitted without any coupling between CF excitations and phonon modes. This fact suggests that the coupling in $E_1$ and $A_1$ symmetry channels is weak, and in turn significantly simplifies the model because the fitting of the XZ and RL spectra are now decoupled. As the CF modes have the same energy and linewidth in different symmetry channels, we first fit the XZ spectrum and then use the obtained energy and linewidth for the fitting of RL and ZZ spectra.

For the XZ spectrum, we have

$$\chi''_{xz} \sim \text{Im} \ T_{xz}^\dagger G_{xz} T_{xz}, \quad (3.69)$$

in which

$$G_{xz} = \begin{pmatrix} G_{p1} & 0 & 0 & 0 & 0 \\ 0 & G_{p2} & 0 & 0 & 0 \\ 0 & 0 & G_{e1} & 0 & 0 \\ 0 & 0 & 0 & G_{e2} & 0 \\ 0 & 0 & 0 & 0 & G_{e3} \end{pmatrix}, \quad (3.70)$$

and

$$T_{xz}^\dagger = \begin{pmatrix} t_{p1} & t_{p2} & t_{e1xz} & t_{e2xz} & t_{e3xz} \end{pmatrix}. \quad (3.71)$$

The RL spectrum is fitted with

$$\chi''_{rl} \sim \text{Im} \ T_{rl}^\dagger G_{rl} T_{rl}, \quad (3.72)$$

in which

$$G_{rl} = (G_{rl0}^{-1} - V_{rl})^{-1}, \quad (3.73)$$
and

$$T_{\text{rl}}^4 = \begin{pmatrix} t_{p3} & t_{p4} & t_{e1\text{rl}} & t_{e2\text{rl}} & t_{e3\text{rl}} \end{pmatrix}.$$  \hspace{1cm} (3.74)

In Eq. (3.73), $G_{rl0}$ and $V_{rl}$ have the following expression:

$$G_{rl0} = \begin{pmatrix} G_{p3} & 0 & 0 & 0 & 0 \\ 0 & G_{p4} & 0 & 0 & 0 \\ 0 & 0 & G_{e1} & 0 & 0 \\ 0 & 0 & 0 & G_{e2} & 0 \\ 0 & 0 & 0 & 0 & G_{e3} \end{pmatrix},$$ \hspace{1cm} (3.75)

$$V_{rl} = \begin{pmatrix} 0 & 0 & f_3 * q_{12} & f_3 * q_{22} & f_3 * q_{32} \\ 0 & 0 & f_4 * q_{12} & f_4 * q_{22} & f_4 * q_{32} \\ f_3 * q_{12} & f_4 * q_{12} & 0 & 0 & 0 \\ f_3 * q_{22} & f_4 * q_{22} & 0 & 0 & 0 \\ f_3 * q_{32} & f_4 * q_{32} & 0 & 0 & 0 \end{pmatrix}. \hspace{1cm} (3.76)$$

In Eq. (3.76) we use the relationship $v_{ij} = f_i q_{j2}$ (i=3,4; j=1,2,3) to reduce the number of needed coupling constants to five from six.

For the ZZ spectrum, because the coupling is weak Eq. (3.67) is simplified to

$$\chi''_{zz} \sim \text{Im} T_{ZZ}^4 G_{A0} T_{ZZ}.$$  \hspace{1cm} (3.77)

In Fig. 3.35 we compare the fits to the experimentally measured Raman data. The fitting curves match the data well. For RL spectrum [Fig. 3.35(b)], the sum of the bare responses is rather different from the interacting response, which is significantly modulated by the couplings between pairs of phonon and CF modes. In appearance, the E$_2^{(1)}$ phonon mode and d3 CF mode “merge” into the vibronic feature at 8.5 meV; the E$_2^{(2)}$ phonon mode and s5 CF mode exhibit level-repulsion behavior.

The fitting parameters can be found in Table 3.16. Using the effective electric fields and effective electric moments, we can calculate the coupling strength in unit of energy between pairs of phonon and CF modes in RL spectrum (E$_2$ symmetry channel). Considering that
Figure 3.35: The fitting results for the coupled crystal-field (CF) and phonon modes. These spectra are the same as those shown in Fig. 2 of main text. The XZ spectrum (a) is fitted with Eq. (3.69); the RL spectrum (b) with Eq. (3.72); the ZZ spectrum (c) with Eq. (3.77). The Raman data are represented by black dots. The red lines represent the fits. The blue lines show doublet-to-singlet CF oscillators labeled by the final singlet state; the green lines show doublet-to-doublet CF transitions; the phonon modes, labeled by their symmetry, are shown in purple. The dashed red line in panel (b) represents the sum of blue, green, and purple curves.
the smaller the frequency difference between one pair of modes, the stronger the coupling effect is, we can construct dimensionless coupling constants by coupling strength divided by frequency difference of the same pair of modes. The relevant values are shown in Table 3.12.

**The Specific-Heat Model**

We use four components to model the specific heat of TbInO\(_3\) from 0 to 300 K: (i) the nuclear contribution; (ii) the electronic contribution; (iii) the acoustic-phonon contribution; (iv) the optical-phonon contribution.

(i) The nuclear contribution is related to the transitions between the nuclear energy levels of Tb ions, and has the following form [198]:

\[
C_N = \frac{R}{(k_B T)^2} \left\{ \frac{1}{Z_N} \sum_i \epsilon_i^2 e^{(-\epsilon_i/k_B T)} - \left[ \frac{1}{Z_N} \sum_i \epsilon_i e^{(-\epsilon_i/k_B T)} \right]^2 \right\}, \tag{3.78}
\]

where \(R\) is the ideal gas constant; \(k_B\) is the Boltzmann constant; \(T\) is temperature; \(Z_N = \sum_i \exp(-\epsilon_i/k_B T)\) is the partition function for the nuclear levels; \(i\) (from 1 to 4) labels the individual nuclear energy levels; \(\epsilon_i\) represents the energy of level \(i\). The nuclear spin of \(^{159}\)Tb is \(I=3/2\). Assuming that its four nuclear levels are evenly spaced [200, 201], we find the splitting between each level is 0.003 meV by fitting the specific heat below 0.5 K.

(ii) The electronic contribution corresponds to the transitions between the CF states within the \(7F_6\) ground-state multiplet of Tb ions. The relevant formula has been discussed as Eq. (3.49) in Sec. 3.3.6.

(iii) We use Debye model for the acoustic-phonon contribution [198]. Because ferroelectric TbInO\(_3\) has one \(A_1\) and one \(E_1\) acoustic modes, two Debye temperatures are used:

\[
C_D = \frac{3R}{N} \left[ \left( \frac{T}{\theta_{A_1}} \right)^3 \int_0^{\theta_{A_1}/T} \frac{x^4 e^x}{(e^x-1)^2} dx + 2 \left( \frac{T}{\theta_{E_1}} \right)^3 \int_0^{\theta_{E_1}/T} \frac{x^4 e^x}{(e^x-1)^2} dx \right], \tag{3.79}
\]

in which \(N=6\) is the number of chemical units per unit cell; \(\theta_{A_1}\) is the Debye temperature for the \(A_1\) mode and \(\theta_{E_1}\) is that for the \(E_1\) mode.
Table 3.16: The values of the parameters obtained by fitting the XZ spectrum with Eq. (3.69), the RL spectrum with Eq. (3.72), and the ZZ spectrum with Eq. (3.67). Notice that although $f_i$ (i=3,4) and $q_{j2}$ (j=1,2,3) can have arbitrary units, $v_{ij}=f_iq_{j2}$ has the unit of meV.

<table>
<thead>
<tr>
<th>Parameter (Unit)</th>
<th>Value (Uncertainty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{p1}$ (arb. units)</td>
<td>2.45(0.10)</td>
</tr>
<tr>
<td>$\gamma_{p1}$ (meV)</td>
<td>0.242(0.015)</td>
</tr>
<tr>
<td>$\omega_{p1}$ (meV)</td>
<td>10.15(0.01)</td>
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<tr>
<td>$t_{p2}$ (arb. units)</td>
<td>3.83(0.01)</td>
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<tr>
<td>$\gamma_{p2}$ (meV)</td>
<td>0.184(0.001)</td>
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<tr>
<td>$\omega_{p2}$ (meV)</td>
<td>13.89(0.01)</td>
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<tr>
<td>$t_{p3}$ (arb. units)</td>
<td>1.95(0.24)</td>
</tr>
<tr>
<td>$\gamma_{p3}$ (meV)</td>
<td>0.041(0.017)</td>
</tr>
<tr>
<td>$\omega_{p3}$ (meV)</td>
<td>8.21(0.02)</td>
</tr>
<tr>
<td>f_3 (arb. units)</td>
<td>-0.50(0.21)</td>
</tr>
<tr>
<td>$t_{p4}$ (arb. units)</td>
<td>8.91(0.23)</td>
</tr>
<tr>
<td>$\gamma_{p4}$ (meV)</td>
<td>0.031(0.022)</td>
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<tr>
<td>$\omega_{p4}$ (meV)</td>
<td>10.03(0.02)</td>
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<tr>
<td>f_4 (arb. units)</td>
<td>-0.99(0.28)</td>
</tr>
<tr>
<td>$t_{p5}$ (arb. units)</td>
<td>18.25(0.12)</td>
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<tr>
<td>$\gamma_{p5}$ (meV)</td>
<td>0.223(0.003)</td>
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<tr>
<td>$\omega_{p5}$ (meV)</td>
<td>13.98(0.02)</td>
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<tr>
<td>$t_{e1xz}$ (arb. units)</td>
<td>6.93(0.04)</td>
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<tr>
<td>$t_{e1rl}$ (arb. units)</td>
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<tr>
<td>$t_{e1zz}$ (arb. units)</td>
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<tr>
<td>$\gamma_{e1}$ (meV)</td>
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<td>$\omega_{e1}$ (meV)</td>
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<tr>
<td>$q_{12}$ (arb. units)</td>
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<tr>
<td>$t_{e2xz}$ (arb. units)</td>
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<td>$t_{e2rl}$ (arb. units)</td>
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<td>$\omega_{e2}$ (meV)</td>
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<td>$t_{e3xz}$ (arb. units)</td>
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<td>$t_{e3rl}$ (arb. units)</td>
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<tr>
<td>$t_{e3zz}$ (arb. units)</td>
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<tr>
<td>$\gamma_{e3}$ (meV)</td>
<td>1.33(0.09)</td>
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<tr>
<td>$\omega_{e3}$ (meV)</td>
<td>11.45(0.12)</td>
</tr>
<tr>
<td>$q_{32}$ (arb. units)</td>
<td>0.92(0.25)</td>
</tr>
</tbody>
</table>
(iv) The optical-phonon contribution is accounted for by Einstein model [198]:

\[ C_{Ein} = \frac{R}{N} \sum_i n_i \left( \frac{\hbar \omega_i}{k_B T} \right)^2 \frac{\frac{\hbar \omega_i}{e^{\frac{\hbar \omega_i}{k_B T}}}}{\left( e^{\frac{\hbar \omega_i}{k_B T}} - 1 \right)^2}. \]  

(3.80)

In this formula, \( i \) labels the individual optical phonon modes, and \( n_i \) is the degeneracy of optical phonon mode \( i \). Ferroelectric TbInO\(_3\) has 38 Raman-active optical modes (9\( A_1 \oplus 14E_1 \oplus 15E_2 \)) and 20 silent optical modes (5\( A_2 \oplus 10B_1 \oplus 5B_2 \)). For the Raman-active optical modes, we use the experimentally determined energy listed in Table 3.11; for the silent optical modes, we assume that they are evenly spaced from 10 to 80 meV.

We subtract the nuclear, electronic, and optical-phonon contributions from the experimental specific-heat data, and then fit the subtracted data with Eq. (3.79). We find \( \theta_{A_1} = 180 \pm 50 \) K and \( \theta_{E_1} = 310 \pm 90 \) K.
Chapter 4

Electronic structure and random-singlet state of Ba$_5$CuIr$_3$O$_{12}$

In this chapter, the work on 5$d$-electron system Ba$_5$CuIr$_3$O$_{12}$ is presented. This work is relevant to two commonly-adopted concepts. The first is the $j_{\text{eff}} = 1/2$ local moment picture in discussion of the electronic and magnetic properties of iridate compounds with IrO$_6$ octahedra. The second is the belief that absence of magnetic order and large Weiss temperature points to spin-liquid phase. Interestingly, the physics of Ba$_5$CuIr$_3$O$_{12}$ serves as a counterexample for both of these concepts.

The electronic structure of Ba$_5$CuIr$_3$O$_{12}$ is discussed in Sec. 4.1. In this section we show that the $j_{\text{eff}} = 1/2$ scenario is not applicable to Ba$_5$CuIr$_3$O$_{12}$; the insulating phase of this compound is based on the molecular orbits resulting from strong covalency. The random singlet state of Ba$_5$CuIr$_3$O$_{12}$ is illustrated in Sec. 4.2. We demonstrate that absence of magnetic order and large Weiss temperature do not serve as a sufficient condition for presence of a spin-liquid phase.
4.1 The electronic structure of Ba$_5$CuIr$_3$O$_{12}$

The competition between covalency and electron correlations is a core concept in the study of the Mott physics [202]. A canonical example is the contrast between the Mott insulating and metallic behaviors of 3d and 4d transition-metal oxides (TMOs), respectively. In these systems, the Mott phases in 3d TMOs are attributed to the smaller covalency of 3d orbitals, \textit{i.e.} smaller overlap integrals and the resulting stronger Coulomb repulsion [203], while the enhanced covalency and weaker Coulomb repulsion in 4d TMOs lead to metallicity [204–206].

An interesting twist to the above simplistic picture happens in 5d TMOs, especially in iridate compounds with quasi-two-dimensional layered structures [207–210] where insulating behavior with local magnetic moments were found. The key to this puzzle was found to be the presence of the strong spin-orbit coupling (SOC) in the Ir 5d orbital. Namely, SOC introduces splitting of the broad 5d bands into narrow subbands and forms spin-orbital-entangled local moments identified with the effective total angular momentum $j_{\text{eff}} = 1/2$ [211, 212]. Since then, the $j_{\text{eff}} = 1/2$ scenario has become a cornerstone in the study of correlated phases in 5d TMOs, and various theoretical suggestions of potential novel quantum phases such as high-T$_c$ superconductivity [213, 214] or quantum spin liquid phases have been made based on this picture [183, 215, 216].

A critical necessary condition for the $j_{\text{eff}} = 1/2$ picture is the presence of (pseudo-)cubic IrO$_6$ octahedra, as shown in Fig. 4.1(a), where the Ir $t_{2g}$ orbital ($l_{\text{eff}} = 1$) splits into the $j_{\text{eff}} = 1/2$ and 3/2 subspaces. Introducing non-cubic crystal fields can mix the two $j_{\text{eff}}$ subspaces and break the $SU(2)$ symmetry of the $j_{\text{eff}} = 1/2$ pseudospin. In various iridate compounds, however, such non-cubic distortions of IrO$_6$ octahedra were found to be not strong enough to qualitatively change the $j_{\text{eff}}$ picture [217–220], except in a small number of examples where the non-cubic distortions are exceptionally huge [221]. Hence the belief for the validity of the $j_{\text{eff}}$ scenario in general iridates has become strengthened, and it has
been adopted even in situations where the applicability of the scenario is not rigorously justified [222].

In this Section, we study a material in which the local \( j_{\text{eff}} \) moment picture breaks down, and the quenching of the SOC splitting occurs not because of the non-cubic crystal fields, but because of the covalency between neighboring Ir \( d \) orbitals. The main message of this work is illustrated in Fig. 4.1, where the three representative local geometries consisting of IrO\(_6\) octahedra — corner-, edge-, and face-sharing structures — are depicted. In terms of covalency, a critical difference between the three structures is the bond length between the nearest-neighboring Ir sites, which determines the strength of the Ir \( d-d \) direct overlap integral \( t_{dd} \) [223]. While \( t_{dd} \) tends to be smaller than the size of SOC (\( \lambda_{SO} \)) for the corner- and edge-sharing geometries (Fig. 4.1(a))\(^1\), it can be stronger than \( \lambda_{SO} \) for the face-sharing structures because of the shorter Ir-Ir distance. In such cases, the neighboring Ir sites should form molecular orbitals (MO) as depicted in Fig. 4.1(b). Therefore the \( j_{\text{eff}} = 1/2 \) local moment picture in the face-sharing geometry breaks down and the effects of SOC and Coulomb interactions should be considered based on the MO description.

By combining Raman spectroscopy measurements and \textit{ab-initio} theoretical analyses, we study a mixed 3\( d \)-5\( d \) insulator Ba\(_5\)CuIr\(_3\)O\(_{12}\) for which the \( j_{\text{eff}} = 1/2 \) approach breaks down [226, 227]. In this compound, sequences of trigonal prismatic and octahedral transition metal sites run in chains parallel to the crystallographic \( z \)-axis, with Ba atoms located between the chains [Fig. 4.2]. \textit{Ab-initio} calculations and a tight-binding (TB) analysis yield a MO description of the electronic structure originating from the face-sharing geometry as depicted in Fig. 4.1(b), and predict a three-peak structure in the joint density of states (JDOS). Raman scattering, a technique successfully used to study electronic excitations in iridate compounds [228], verifies this prediction. We observe one strong and sharp excitation

\(^1\)Several recent reports of pressure-induced Ir dimerizations in layered- and hyper-honeycomb iridates [224, 225] implies that, in edge-sharing geometries, \( t_{dd} \) is almost comparable to \( \lambda_{SO} \), so that relatively small pressure of \(<5\ \text{GPa}\) is enough to enhance \( t_{dd} \) to break the \( j_{\text{eff}} = 1/2 \) states in these compounds.
Figure 4.1: Three representative local geometries consisting of IrO$_6$ octahedra and their schematic energy-level diagrams. (a) depicts corner- and edge-sharing geometries where the size of spin-orbit coupling (SOC) $\lambda_{SO}$ is larger than the covalency between neighboring Ir 5$d$-orbitals. (b) shows a face-sharing local geometry, where the Ir-O bond length is shorter compared to the other two cases so that the strength of d-d-covalency $t_{dd}$ can overcome SOC. Schematic energy level diagram for each case, the conventional atomic $j_{\text{eff}}$-picture and a trimer molecular-orbital (MO) picture for (a) and (b) respectively, are represented.

at 0.58 eV, and two weak features at 0.66 and 0.74 eV. It should be noted that such a three-peak structure is not observed in systems with well-defined $j_{\text{eff}} = 1/2$ local moments [228].

### 4.1.1 Energy diagram

We identify the structural motif for Ba$_5$CuIr$_3$O$_{12}$ to be the three face-sharing IrO$_6$ octahedra forming an Ir trimer as shown in Fig. 4.1(b) and Fig. 4.2. If the intra-Ir-trimer hybridization dominates SOC, the three Ir $t_{2g}$ orbitals at the trimer sites split into nine MOs [Fig. 4.3(a)]. Among those, the atomic $a_{1g}$ singlet at each site gives rise to the strongest $\sigma$-type overlap between neighboring Ir sites; while the other $e'_g$ doublets lead to weaker $\pi$- or $\delta$-like overlaps. Such scenario can be tested by constructing a simple TB model and comparing the results with those from DFT calculations. For the TB model, as a first-order approximation, we assume a three-fold symmetry along the $z$ direction and ignore the Cu-Ir hybridization. After this simplification, just four free parameters are left for the Ir trimer model where the parameters are tuned to fit the DFT DOS afterwards. Because this is a test for the molecular orbital picture, SOC and the on-site Coulomb interactions are not considered at

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2For the DFT calculations we employed the Vienna ab-initio Simulation Package (VASP) [229, 230].
Fig. 4.2: Ba$_5$CuIr$_3$O$_{12}$ crystal structure employed for the *ab-initio* calculations.

Fig. 4.3 presents the comparison between the TB model and the DFT results, where Fig. 4.3(a), (b), and (c) show the schematic TB energy diagram, TB DOS, and DFT DOS respectively. Both the $a_{1g}$- and $e'_{g}$-derived MO states, depicted in blue and red in Fig. 4.3, show bonding ($\sigma/\pi/\delta$), nonbonding ($\bar{\sigma}/\bar{\pi}/\bar{\delta}$), and antibonding $\sigma^*/\pi^*/\delta^*$ characters [Fig. 4.3(a)]. Remarkably, the DOS from the simple 4-parameter-model agrees quite well with the DFT DOS; features of the DOS obtained from DFT calculations are consistent with those derived from the TB analysis, especially that the nonbonding $\bar{\sigma}/\bar{\pi}/\bar{\delta}$-MOs are located only at the two ends of the trimer [Fig. 4.3(b) and (c)]. The bonding-antibonding splitting between the $\sigma$- and $\sigma^*$-MO is 2.5 eV, much larger than the strength of SOC (0.4 eV) [211]. Therefore the intra-Ir-trimer hybridization indeed dominates SOC.

Since the size of MO splitting is large, we only need to consider the effect of SOC near the Fermi level. Fig. 4.4 illustrates how SOC and the Coulomb interaction induce a spin
Figure 4.3: Energy level diagram and projected DOS for Ba$_5$CuIr$_3$O$_{12}$. (a) Energy level diagram showing the splitting of the Ir $t_{2g}$ states in an Ir trimer into MO states. Here $\sigma/\pi/\delta$, $\sigma^*/\pi^*/\delta^*$, and $\sigma^*/\pi^*/\delta^*$ denote bonding, nonbonding, and antibonding states, respectively. Electrons in fully filled states are represented by circles, while magnetically active electrons are represented by arrows. (b,c) Projected DOS from the simple tight-bonding model for Ir trimers (b), and from ab-initio calculations without SOC and magnetism (c). The color scheme for the orbital character is the same in (a-c).
polarization within the $\sigma^*/\pi^*/\delta^*$ MOs and in turn open a gap. First, because the $\pi^*/\delta^*$ MOs carry atomic orbital angular momenta $l_{\text{eff}}^z = \pm 1$, SOC functions as an orbital Zeeman field that splits the $\pi^*/\delta^*$ MOs [compare Fig. 4.4(a) and (b)]. Then the Coulomb interaction induces a ‘high-spin-like’ configuration by pushing down the unoccupied $\sigma^*$ state with $l_{\text{eff}}^z = 0$ below the Fermi level in the majority spin channel and fully spin-polarizing the $\pi^*/\delta^*$ and $\sigma^*$ states as shown in Fig. 4.4(c). Fig. 4.4(d) and (e) show the projected DOS with $U_{\text{Ir}} = 0$ and 2.8 eV respectively ($U_{\text{Ir}}$ denoting $U$ at Ir sites), where the $a_{1g}/e'_{g}$-projected DOS from the DFT+U [231] calculation with SOC included is plotted. Comparing Fig. 4.4(d) and (e) demonstrates the spin-polarizing effect of $U_{\text{Ir}}$. As a result, a three-peak structure appears in the unoccupied sector as shown in Fig. 4.4(e). The three peaks, $\alpha$, $\beta$, and $\gamma$ in the JDOS from the DFT+U result [Fig. 4.4(d)] originate from the transitions from the highest occupied MO state with $j_{\text{eff}}^z = 0$ to the unoccupied MO states with $j_{\text{eff}}^z = +1/2, 0,$ and $-3/2$, respectively. Note that the inclusion of $U_{\text{Ir}}$ tends to recover the local atomic picture by mixing MO states, as shown in Fig. 4.4(c), where there is a small mixture among the $j_{\text{eff}}^z = +1/2, 0,$ and $-3/2$ MO states. This effect, however, does not qualitatively affects the above MO description. Note also that different values of $U_{\text{Ir}}$ only changes the gap size while not affecting the three-peak structure.

4.1.2 Raman results

To confirm the predicted three-peak structure in the electronic excitation spectrum, we perform Raman-scattering measurements in a quasi-back-scattering geometry from the (001) crystallographic surface of Ba$_5$CuIr$_3$O$_{12}$ single crystal grown by flux method. We use 476.2 nm line from a Kr$^+$ ion laser for excitation. Incident light with $\sim$10 mW power is focused to a 50$\times$100 $\mu$m$^2$ spot.

Fig. 4.5 shows the Raman spectrum measured at 25 K. The sharp features at 17, 41 and 84 meV are phonon modes. The two peaks at 130 and 170 meV result from second-order phonon scattering ($41 + 84$ meV and $84 + 84$ meV, respectively). The broad feature
Figure 4.4: The MO levels, projected DOS, and joint DOS for Ba$_5$CuIr$_3$O$_{12}$. (a-c) Schematic diagram showing the MO levels (a) with both SOC and $U_{Ir}$ not included, (b) with SOC included but with no $U_{Ir}$, and (c) both SOC and $U_{Ir}$ included ($U_{Ir}$ denoting $U$ at Ir sites). The $l_{eff}^z$ and $j_{eff}^z$ eigenvalues are given. (d-e) Projected DOS from DFT+SOC+U calculations for the $a_{1g}$ and $e'_g$ states at Ir sites, where the $U$ values employed are ($U_{Ir},U_{Cu}$) = (0, 6) eV and (2.8, 6) eV for (d) and (e), respectively ($U_{Cu}$ denoting $U$ at Cu sites). (f) The joint DOS (JDOS) with ($U_{Ir},U_{Cu}$) = (2.8, 6) eV, showing a three-peak structure ($\alpha$, $\beta$, and $\gamma$).
Figure 4.5: Raman spectrum $\chi''(\omega)$ at 25 K. Sharp features below 0.1 eV are phonon modes; the two peaks at 0.13 and 0.17 eV result from second-order phonon scattering while the broad feature at 0.24 meV originates from third-order phonon scattering. The three high-energy electronic excitations at 0.58, 0.66 and 0.74 eV are labeled by $\alpha$, $\beta$, and $\gamma$ respectively, corresponding to the labeling in Fig. 4.4(d).

centered at 240 meV, weaker and broader than the second-order phonon scattering peaks, is attributed to third-order phonon scattering (84 + 84 + 84 meV).

Importantly, three high-energy electronic excitations at 0.58, 0.66 and 0.74 eV are resolved. The high-energy Raman spectrum exhibits the general trends of the JDOS from DFT+$U$. The high-energy gap in the Raman spectrum is about 0.55 eV, while it is 0.70 eV in the JDOS. The three peaks in the Raman spectrum are evenly spaced, with a separation of 0.08 eV; those in the JDOS are also evenly spaced but with a 0.2 eV separation. One possible reason for the smaller splitting in experimental spectrum compared to the DFT+$U$ JDOS peak splitting can be a stronger mixing between the $l_{\text{eff}}^z = \pm 1$ and 0 antibonding MO states near the Fermi level in the real system. This mixing reduces the expectation value of SOC energy and in turn decreases the separation. Another thing to mention is, while in the JDOS all the three peaks have similar spectral weight, in the Raman spectrum the 0.58 eV peak is much stronger than the other two. This could be attributed to the matrix element effect.
4.1.3 Effect of hybridization and implication for magnetism

The three-peak structure in the DFT+U JDOS and in the Raman measurement is a distinct feature indicating deviation from the \( \tilde{J}_{\text{eff}} = 1/2 \) picture. Simple \( \tilde{J}_{\text{eff}} = 1/2 \) picture predicts up to two high-energy transition peaks, because non-cubic crystal fields just induce splitting of the fully occupied \( \tilde{J}_{\text{eff}} = 3/2 \) quartet \[211, 218\]. On the contrary, our three-peak structure in \( \text{Ba}_5\text{CuIr}_3\text{O}_{12} \) comes from the strong Ir-Ir hybridization in the face-sharing \( \text{IrO}_6 \) octahedral geometry and the resulting formation of MOs. We note that in other compounds with similar face-sharing geometries with alternating 3\( d \) and 5\( d \) transition metal ions such as \( \text{Sr}_3\text{NiIrO}_6 \) \[232\] or \( \text{Sr}_3\text{CuIrO}_6 \) \[220\], two-peak structures are observed in their \( \tilde{J}_{\text{eff}} \)-excitation spectra \[218\]. This implies that, although the size of non-cubic distortions is large in these compounds, still the local \( \tilde{J}_{\text{eff}} = 1/2 \) moment picture remains effective because of the reduced covalency between the 3\( d \) and 5\( d \) orbitals as suggested in a recent \textit{ab-initio} study for \( \text{Sr}_3\text{NiIrO}_6 \) \[233\]. We also comment that there is another theoretical study on \( \text{BaIrO}_3 \) \[222\], consisting of the same face-sharing \( \text{Ir}_3\text{O}_{12} \) octahedral trimers like \( \text{Ba}_5\text{CuIr}_3\text{O}_{12} \). A similar three-peak structure in the upper Hubbard band (UHB) was reported therein, but it was speculated that the UHB states still retain the \( \tilde{J}_{\text{eff}} = 1/2 \) character, which seems to require a more rigorous justification.

As for possible magnetism in this compound; from the projected DOS plotted in Fig. 4.4(b) and (c), we identify three magnetically active states; a \( \sigma^* \) state with mostly \( a_{1g} \) \( (l_{\text{eff}}^z = 0) \) character mainly located at Ir 2 site, and two \( \pi^*/\delta^* \) states with the \( e'_g \) character \( (l_{\text{eff}}^z = \pm 1) \) at Ir 1 and 3 sites. The strong SOC within the Ir \( d \)-orbital then behaves as a single-ion anisotropy to the electron spins filling the \( l_{\text{eff}}^z = \pm 1 \) MO states, locking the spins parallel to the \( z \)-direction. Spin in the \( l_{\text{eff}}^z = 0 \) MO state, on the other hand, has little single-ion anisotropy due to the vanishing orbital angular momentum. The spin moments at Cu sites are also isotropic, so this compound should have three different kinds of spin moments: isotropic Cu spins, isotropic Ir spins at Ir 2 sites, and anisotropic Ir spins at Ir 1 and 3 sites locked along the \( z \)-direction. Because all the Ir spins are occupying the MO states, rather
than behaving as the $j_{\text{eff}} = 1/2$ local moments, they may show distinct low-energy magnetic properties compared to previously known magnetic iridate compounds. For future studies, interesting questions about the outcome of MO formation can be posed, for example on the form of exchange interactions and the spectrum of low-energy magnetic excitations.

4.1.4 Conclusion

Our study on the face-sharing iridate $\text{Ba}_5\text{CuIr}_3\text{O}_{12}$ demonstrates the breakdown of the SOC-based $j_{\text{eff}} = 1/2$ physics, and reveals the MO nature of the electronic structure originating from the strong intermetallic $d$-$d$ direct overlap. A similar scenario, leading to the formation of benzene-ring-shaped quasi-molecular orbitals (QMO) driven by $\pi$-like $d$-$p$ overlap, was suggested for $\text{Na}_2\text{IrO}_3$ [234]. In $\text{Na}_2\text{IrO}_3$, the $d$-$p$ overlap preserves the three-fold symmetry of the Ir $t_{2g}$ orbitals, hence the inclusion of SOC and $U$ induces a crossover from the delocalized QMO to the local $j_{\text{eff}} = 1/2$ moment picture [235]. In $\text{Ba}_5\text{CuIr}_3\text{O}_{12}$, on the contrary, the direct overlap $t_\sigma$ is not only huge but also explicitly breaks the degeneracy of the Ir $t_{2g}$ orbitals, resulting in a completely different MO description. Overall, this work suggest a peculiar relation between the crystal structure and the nature of electronic degree of freedom in $5d$ iridate and other transition metal compounds, which can be useful in search of novel correlated materials.

4.1.5 Experimental details

Material preparation

Single crystals of $\text{Ba}_5\text{CuIr}_3\text{O}_{12}$ are grown by flux method; details of growth and characterization will be published separately. This material has a trigonal structure (space group $P3c1$, No.158; point group $C_{3v}$) [226, 227]. The sample is polished with a lapping film (1 micrometer, Buehler) and is subsequently annealed at 650 °C in air to remove residual strain. Its annealed (100) crystallographic surface is then used for Raman measurements.
Raman scattering

Raman-scattering measurements are performed in a quasi-back-scattering optical setup. The 476.2 nm line from a Kr$^+$ ion laser is for excitation. Incident light with $\sim 10$ mW power is focused to a $50 \times 100 \, \mu\text{m}^2$ spot on the (100) crystallographic surface. Environmental temperature of 20 K is achieved in a helium-gas-cooled cryostat, and the laser heating is assumed to be $0.5 \, \text{K/mW}$. We use a custom triple-grating spectrometer and a liquid-nitrogen-cooled charge-coupled device (CCD) detector for collection and analysis of the scattered light. The data are corrected for the system background and the spectral response. The measured scattering intensity $I(\omega, T)$ is related to the Raman response $\chi''(\omega, T)$ by $I(\omega, T) = [1 + n(\omega, T)]\chi''(\omega, T)$, where $n$ is the Bose factor, $\omega$ is Raman shift and $T$ is temperature.

Low-energy Raman spectrum

Fig. 4.6 shows the low-energy Raman spectrum of Ba$_5$CuIr$_3$O$_{12}$ at 25 K. The sharp features at 17, 41 and 84 meV are identified as phonon modes. The 17 meV mode primarily involves motion of Ir atoms, and the 84 meV mode is derived from vibration of O atoms. The broad feature centered at 40 meV could be a bundle of phonon modes related to the motion of Ba atoms. The two weak features at 60 and 78 meV are also likely phonon modes.
4.1.6 Computational details

Ab-initio simulations

For our ab-initio simulations, we first assume a crystal structure with no disorder in Cu positions, that Cu are located at one of the three equivalent prismatic facial positions as shown in Fig. 2 in the main text. Further, no Cu-Ir intermixing is considered. The unit cell contains 6 formula units, i.e. three Ir-Cu chains. It should be commented that, for a better reproduction of the experimentally measured spectra one may need to take an average over ab-initio calculations from all possible orderings of Cu to restore the three-fold rotation symmetry along the chain direction. For a qualitative understanding of the high-energy spectra, however, the current result from the choice of Cu ordering shown in Fig. 2 in the main text seems to be enough.

The Vienna ab-initio Simulation Package (VASP), which uses the projector-augmented wave (PAW) basis set [229, 230], is employed for structural optimizations and electronic structure calculations. 400 eV and a Γ-centered 3x3x3 \( k \)-point grid are used for the plane wave energy cutoff and the \( k \)-point sampling, respectively. A revised Perdew-Burke-Ernzerhof generalized gradient approximation for crystalline solids (PBEsol) is chosen for the exchange-correlation functional [236], and \( 10^{-2} \) eV/Å of force criterion was used for the structural optimization. A simplified rotationally-invariant form of DFT+U method [231] is employed to treat the on-site Coulomb interaction both at Cu and Ir sites with the spin-orbit coupling (SOC) included.

Tight-binding model

Assuming the three-fold rotational symmetry along the chain direction (i.e. ignoring the IrO\(_6\) octahedral distortions other than the trigonal one), and also assuming the Ir-Ir hybridizations are dominating those from Ir-Cu (this choice is justified by DFT calculations which show small hybridization between Ir and Cu d-orbitals), the three-site tight-binding
model can be written as follows,

\[
H_{\text{TB}} = \begin{pmatrix}
0 & \Delta_{\text{tri}} & \Delta_{\text{tri}} & t_1 & t_2 & t_2 & 0 & 0 & 0 \\
\Delta_{\text{tri}} & 0 & \Delta_{\text{tri}} & t_2 & t_1 & t_2 & 0 & 0 & 0 \\
\Delta_{\text{tri}} & \Delta_{\text{tri}} & 0 & t_2 & t_2 & t_1 & 0 & 0 & 0 \\
t_1 & t_2 & t_2 & \epsilon_{\text{on}} & \Delta_{\text{tri}} & \Delta_{\text{tri}} & t_1 & t_2 & t_2 \\
t_2 & t_1 & t_2 & \Delta_{\text{tri}} & \epsilon_{\text{on}} & \Delta_{\text{tri}} & t_2 & t_1 & t_2 \\
t_2 & t_2 & t_1 & \Delta_{\text{tri}} & \Delta_{\text{tri}} & \epsilon_{\text{on}} & t_2 & t_2 & t_1 \\
0 & 0 & 0 & t_1 & t_2 & t_2 & 0 & \Delta_{\text{tri}} & \Delta_{\text{tri}} \\
0 & 0 & 0 & t_2 & t_1 & t_2 & \Delta_{\text{tri}} & 0 & \Delta_{\text{tri}} \\
0 & 0 & 0 & t_2 & t_2 & t_1 & \Delta_{\text{tri}} & \Delta_{\text{tri}} & 0
\end{pmatrix},
\]

where \(t_1\) and \(t_2\) are nearest-neighbor hopping integrals between the same and different kinds of Ir \(t_{2g}\) orbitals respectively, \(\Delta_{\text{tri}}\) is the on-site trigonal crystal field within the \(t_{2g}\) complexes, and \(\epsilon_{\text{on}}\) is the on-site energy difference between the central and lateral Ir. The projected density of states in Fig. 3(b) in the main text are calculated by choosing \(t_1 = -0.43\) eV, \(t_2 = -0.20\) eV, \(\Delta_{\text{tri}} = -0.12\) eV, and \(\epsilon_{\text{on}} = -0.3\) eV, which yield qualitative agreement with the \textit{ab-initio} results as discussed in the main text. If we take the unitary transform to the trigonal basis set (\(a_{1g}\) and \(e'_g\) states), the \(\sigma\)-like overlap between the \(a_{1g}\) states becomes \(t_1 + 2t_2 = -0.83\) eV, twice larger than the SOC of Ir (\(\lambda_{SO} \simeq 0.4\) eV), supporting the molecular-orbital scenario.

**\(U_{\text{Ir}}\) dependence of the electronic structure**

In the computations of projected DOS presented in the main text, a collinear magnetic configuration illustrated in Fig. 4.7(a) is employed. Note that in our calculations with various trial magnetic configurations, the Ir spin moments on a Ir trimer show a collective motion and favor the direction parallel to the Cu-Ir chain, consistent with the effect of MO formation and the role SOC discussed in the main text. Also note that the one depicted in Fig. 4.7(a) is the ground state configuration for our choice of Cu-Ir chain structure [see
Figure 4.7: The ground state magnetic configuration and projected DOS of a Cu-Ir chain. (a) The ground state magnetic configuration in a Cu-Ir chain, where the black arrows depict the size and direction of the spin moments at Cu and Ir sites. (b,c) $a_{1g}/e'_{g}$-projected DOS with (b) $(U_{Ir}, U_{Cu}) = (2, 4) \text{eV}$ and (c) $(2.8, 6) \text{eV}$. 
Fig. 1 in the main text], while the energetics and the ground state configuration may depend on a different choice of Cu order.

In our DFT+U calculations we choose $U$ value for Cu (denoted as $U_{\text{Cu}}$) to be 4~6 eV. With this choice of $U_{\text{Cu}}$ the Cu $e_g$ orbital character is almost absent near the Fermi level, so that the electronic structure near the Fermi level is mostly determined by the Ir $t_{2g}$ states. As discussed in the main text, the combination of Ir SOC and $U_{\text{Ir}}$ induces the three-peak structure as observed in the Raman measurement. In the main text we employ $U_{\text{Ir}} = 2.8$ eV, and the three peak structure does not qualitatively change in the range of $2 < U_{\text{Ir}} < 3$ eV. Fig. 4.7(b) and (c) show the projected DOS with $(U_{\text{Ir}}, U_{\text{Cu}}) = (2, 4)$eV and $(2.8, 6)$eV respectively. It can be seen that smaller value of $U_{\text{Ir}}$ induces smaller charge gap, but the three-peak structure remains almost unchanged. the spacing between the three peaks in the upper Hubbard bands can be affected in a quantitative way with a different choice of $U_{\text{Ir}}$. 
4.2 The random-singlet state of Ba$_5$CuIr$_3$O$_{12}$

Strong quantum fluctuations in insulating magnetic compounds can give rise to quantum spin liquid (QSL) ground states, where the interaction-driven ordering tendencies are thwarted completely. Devoid of long-range order, QSLs lie beyond the Landau symmetry-based classification, and are characterized instead by their unconventional entanglement properties and the presence of exotic fractionalized excitations [237, 238]. However, identifying the elusive QSL behavior in real materials has proven to be a formidable task [238–240]. The search for QSL candidate materials represents a major challenge of modern condensed matter physics.

Disorder is one of the major hindrances to identify QSL materials [241–243], as it can drive the formation of random singlet states (RSS) [244] or disordered stripe states [245] instead of a QSL. Importantly, this includes single crystal samples due to intrinsic disorder [66, 246]. A convenient reference point can be found in 1D systems, where the quantum fluctuations are dominant [247] and the effect of disorder was clarified some time ago [248, 249]. In 1D it converts the spin liquid ground state into a RSS, where the effective exchange coupling follows a broad probability distribution that has a universal form [250] at low energies. In 2D and 3D, on the contrary, the fate of disordered spin systems is still an open question. While a random singlet state with a power law distribution has been conjectured [251], the true ground state of such systems is still under debate and might not be universal [252–254]. In particular, enhanced suppression of QSL states by disorder has been found in model calculations [254, 255]. However, mechanisms for stabilization of QSL states by disorder have also been proposed [256]. Additionally, a strong spin-orbit coupling (SOC) is an important ingredient in many QSL candidates. While its effects on clean QSLs has been studied [237, 238] and particularly emphasized for the so-called Kitaev materials [57, 184], the interplay of SOC with disorder still remains to be understood. Thus, careful studies on the role of disorder and SOC in materials showing QSL-like behavior (i.e., no ordering or glassiness down to the lowest temperatures) are of the utmost importance to
Figure 4.8: The depiction of intrinsic disorder in chains of Cu and Ir in Ba$_5$CuIr$_3$O$_{12}$ lattice structure. (a) Cu-Ir chains composed of Ir$^{4+}$ trimers and Cu$^{2+}$ ions (Ba ions fill the space between the chains [4]). Disorder occurs either due to Cu-Ir site mixing or due to Cu being displaced from the prism center [226, 227]. (b) Spin degrees of freedom in a chain segment, here Ir trimers form effective $J = 1/2$ moments that interact with the Cu$^{2+}$ spins. (c) An example of disorder in the position of Cu and Ir leading to exchange disorder. Interchanging Cu and Ir sites leads to Ir clusters forming low-spin states. The Cu spins interact with each other through perturbatively generated $J'$ and $J''$ resulting in disorder in the effective magnetic exchange couplings.

confirm, or rule out, the QSL state.

In this Section, we study magnetic and thermodynamic properties of the insulating iridate Ba$_5$CuIr$_3$O$_{12}$, which features a quasi-1D arrangement of alternating Cu$^{2+}$ ions and Ir$^{4+}$ trimers [226, 227], see Fig. 4.8. This iridate is of particular interest for the following reasons. Firstly, previous studies [226] have shown that no magnetic ordering occurs in Ba$_5$CuIr$_3$O$_{12}$ down to 4 K despite a Curie temperature of $-98$ K, which suggests a possible QSL ground state. Moreover, a related compound Ba$_4$NbIr$_3$O$_{12}$ has recently been proposed to be a QSL candidate material [257]. Second, the nature of the Ir magnetic moments in this system is quite peculiar. The 5$d$ Ir ions have a strong spin-orbit coupling and form face-sharing Ir$^{4+}$ trimers, which renders the usual local $J_{\text{eff}}=1/2$ moment picture [211, 212] inapplicable due to enhanced covalency. Instead, molecular orbitals at each Ir trimer are expected to form [4, 257, 258]. Finally, the material contains intrinsic disorder due to site mixing between Cu and Ir, as well as Cu displacement from the prism center [226, 227] [see
The former can lead to randomness (i.e. disorder) in the exchange couplings. A particular scenario is shown in Fig. 4.8 (c), where interchanging Cu and Ir within a unit cell transforms two Ir trimers into a dimer and tetramer with a possible $S = 0$ ground state. As a result, the remaining Cu spins interact by means of perturbatively generated exchange couplings, that are different from the initial non-random value. All of the above makes Ba$_5$CuIr$_3$O$_{12}$ a well-suited candidate to explore the interplay of QSL physics with intrinsic disorder and strong spin-orbit coupling.

We have performed magnetic susceptibility, specific heat, and high-field magnetization measurements. We demonstrate that these data combined point unambiguously to Ba$_5$CuIr$_3$O$_{12}$ being in a random singlet state with a power-law distribution of exchange couplings, and thus ruling out QSL behavior. As such, we show how the high field magnetization measurements are essential to reveal and characterize a RSS in materials that otherwise show QSL-like behavior.

### 4.2.1 Magnetic susceptibility

In Fig. 4.9(a) we show the temperature dependence of the magnetic susceptibility for fields along the $c$-axis $\chi^c(T)$ or in the $a-b$ plane $\chi^{ab}(T)$. Both $\chi^c(T)$ and $\chi^{ab}(T)$ show a featureless monotonic increase towards low temperatures and a weak anisotropy. At high temperatures, a constant contribution $\chi_0$ in addition to the Curie behavior can be identified, which is attributed to Van Vleck paramagnetism. The effective moment that is obtained from the Curie law fit is $\mu_{\text{eff}} = 2.2\mu_B$, which is close to the value that is expected from one Cu$^{2+}$ moment ($\mu_{\text{eff}}^{\text{Cu}} = 1.9\mu_B$) and one Ir trimer ($\mu_{\text{eff}}^{\text{Ir-tr}} = 0.8\mu_B$) [257] that yield $\sqrt{(\mu_{\text{eff}}^{\text{Cu}})^2 + (\mu_{\text{eff}}^{\text{Ir-tr}})^2} \approx 2.06\mu_B$.

In an earlier study on polycrystalline samples [226], the susceptibility was analyzed using a modified Curie-Weiss model for temperatures between 150K and 300K. Using $\chi(T) = C/(T - T_W) + \chi_0$ resulted in a large negative Weiss temperature $T_W = -98$K. Analyzing our data, we have come to the conclusion that Curie-Weiss model does not
provide an adequate description. First, if the analysis is restricted to high temperatures, large uncertainties in the value of $T_W$ result. Second, at low temperatures $(\chi - \chi_0)^{-1}$ is not linear as would have been expected from the Curie-Weiss form. We demonstrate this in the inset of Fig. 4.9 (a) by showing $(T - T_W)(\chi^c - \chi_0^c)^{-1}$ for a range of $T_W$ from $-3$ K to $-5$ K. Additionally, one can see that larger or smaller values of $T_W$ would lead to even larger deviations, suggesting weak antiferromagnetic (AFM) correlations.

This is further corroborated by noting that even in the absence of order, anomalies in $\chi(T)$ are expected to arise at a temperature corresponding to the interaction scale in 1D antiferromagnetic chains [259, 260], spin glasses [261, 262] and spin liquids with AFM interactions [263]. The absence of such features in Fig. 4.9 (a) implies that the relevant interaction scale is lower than 2 K. We have also confirmed the absence of glassy behavior above 2 K by performing low-field (100 Oe) field cooled/zero field cooled (FC/ZFC) susceptibility measurements.

### 4.2.2 Specific heat

In Fig. 4.9(b) we show the temperature dependence of the specific heat $C_P(T)$. The high-temperature behavior of $C_P(T)/T$ is dominated by the phonon contribution, which freezes out as the temperature as lowered. Thus, the dramatic upturn that is observed below $\sim 10$ K must be of magnetic origin. As no Schottky-like peak is observed down to 2 K, the energy scale associated with these magnetic excitations should be below 2 K. This is consistent with the weak AFM correlations conjectured above on the basis of the $\chi(T)$ measurements.

### 4.2.3 High-field magnetization

Surprisingly, the field dependence of the magnetization $M(H)$ is in stark contrast with the expectation from weak AFM correlations, see Fig. 4.10. Namely, $M(H)$ shows a monotonic increase without saturation up to the highest fields measured, 59 T. To illustrate this, we show in Fig. 4.10 (green line) $M(H)$ that is expected for a system of two free $S = 1/2$ spins
Figure 4.9: Temperature dependence of the magnetic susceptibility and the specific heat for Ba$_5$CuIr$_3$O$_{12}$. (a) The magnetic susceptibility, data in red ($H \parallel c$) and blue ($H \perp c$). The black dashed line is a fit for $H \parallel c$ with the random singlet model $\chi_{RS} = \partial M_{RS}/\partial H$, see Eq. (4.1). Inset: $(\chi^c - \chi_0^c)$ multiplied by a function $f(T)$. For the colored points we take $f(T) = 3(T - T_W)$ for several values of $T_W$ between -3 K and -5 K, for $H \parallel c$ demonstrating the nonlinearity of the low temperature dependence. Black points are the RSS contribution $f(T) = \chi_{RS}(T)/\mu_{\text{eff}}^2$. Lines are guide to the eye. At high temperatures all curves converge to $\mu_{\text{eff}}^2$. (b) Specific heat divided by temperature. Black line is a fit to the combination of the random singlet model in Eq. (4.2) and a simplified model for phonons (see text). Inset: The specific heat divided by $T^{0.54}$; the grey band shows the confidence interval of the fit.

Figure 4.10: Magnetic-field dependence of the magnetization at 2 K for Ba$_5$CuIr$_3$O$_{12}$. The weak kink near 50 T results from the noise of the equipment. The black dashed line is a fit with the random singlet model, Eq. (4.1), using the parameters given in Table 4.1. The green line represents the magnetization of an $S = 1/2$ paramagnet. The Van Vleck contribution $H\chi_0$ has been added to both. Inset: Log-Log plot of $dM(H)/dH - \chi_0$ for the field along the c-axis, and the black line is a power law fit $0.18 H^{-0.6}$. 
per unit cell, with an effective moment $\mu_{\text{eff}}/\sqrt{2}$ each, and taking the Van Vleck contribution $M_{VV} = \chi_0 H$ into account. One can see that within such a model the magnetization would have saturated well below 59 T, implying that magnetic interactions in Ba$_5$CuIr$_3$O$_{12}$ must be rather strong. One can estimate the scale of the interactions assuming the $S = 1/2$ moments mentioned above to form singlets with an isotropic exchange energy $J$. The magnetization would then saturate when the Zeeman energy $E_Z = H g S = H \mu_{\text{eff}} \sqrt{S/(S+1)}$ for the triplet excitation reaches $J$, see Fig. 4.11. As the saturation field is at least larger than 59 T, we estimate $J \gtrsim 70$ K. On the contrary, the energy scales we have derived above from the susceptibility and specific heat measurements are below 2 K. In addition, in systems with AFM interactions the shape of the magnetization curve as a function of $H$ is usually convex [259, 264–266] at low temperatures, while the $M(H)$ curve shown in Fig. 4.10 is clearly concave, further making the interpretation of the high-field magnetization in terms of strong AFM exchange interaction problematic.

### 4.2.4 Random singlet state

We will now show that the conflict between the energy scales that we have seen in low- and high-field measurements can be resolved by assuming a distribution of energy scales in the system in the framework of a RSS. The exchange disorder driving the RSS can result from the intrinsic positional disorder between Cu and Ir observed in X-ray [226] and neutron scattering [227] experiments, as discussed above and illustrated for a particular scenario in Fig. 4.8 (c). Other possible scenarios would involve nonstoichiometric compositions within one unit cell, e.g., simply substituting one Cu for Ir.

Given the small magnetic anisotropy observed in $\chi(T)$ [see Fig. 4.9 (a)], we consider an ensemble of singlets formed by two effective $S = 1/2$ moments with total magnetic moment $\mu$, and with an isotropic random exchange coupling $J$ that is drawn from the distribution $P(J)$. The magnetization of the whole system is then an average of the magnetization of
Figure 4.11: The energy levels and the ground state of an isolated singlet, and the random singlet distribution in a magnetic field. (a) The energy levels and the ground state of an isolated singlet. The triplet \(S = 1\) of excited states at \(H = 0\) is split in the field, and a change of the ground state occurs at \(H_c(J)\), from singlet \((S = 0)\) to fully polarized \((S = 1)\). (b) The random singlet distribution in a magnetic field. Singlets with \(J < \mu H\) are broken by the field and are fully polarized, while the ones with \(J > \mu H\) remain in the singlet state, leading to a non-saturating magnetization.

Each isolated singlet, and is given by

\[
M_{RS}(H) = \int_0^\infty dJP(J) \frac{2\mu \sinh(\beta \mu H)}{2 \cosh(\beta \mu H) + 1 + e^{\beta J}},
\]

where \(\beta = 1/(k_BT)\). We account for the Van Vleck contribution as before for free spins, i.e. \(M(H) = M_{RS}(H) + H\chi_0\). Qualitatively, Eq. (4.1) allows a coexistence of almost free spins that can yield a diverging susceptibility towards \(T = 0\) and strongly bound singlets from the high-\(J\) tail of the distribution that require the applied field to be above a threshold value for the magnetization to saturate (see Fig. 4.11). Importantly, in the limit \(T \ll \mu H\) one obtains from Eq. (4.1) that \(M'(H) \approx \chi_0 + \mu^2 P(\mu H)\), allowing one to extract the functional form of the distribution \(P(J)\) directly from the experimental data. We find that \(P(\mu H)\) follows the power-law form \(P(\mu H) \sim H^{-0.6}\) for fields between 1 and 15 T (see Fig. 4.10, inset).

Let us now discuss the specific heat. Similarly to the magnetization, the contribution of the RSS is an average over specific heats of individual singlets

\[
C_{RS}(T) = k_B \int_0^\infty dJP(J) \frac{J^2}{T^2} \frac{3e^{-J/T}}{(1 + 3e^{-J/T})^2}.
\]
Table 4.1: The power-law exponents $\alpha$ and the cutoff scale $J_0$ are obtained by fitting the magnetic susceptibility, magnetization, and heat capacity data with the corresponding confidence intervals. The resulting fits are plotted in Figs. 4.9 and 4.10.

<table>
<thead>
<tr>
<th>Measured Quantity</th>
<th>$\alpha$</th>
<th>$J_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^c(T)$</td>
<td>0.62 ± 0.02</td>
<td>36 ± 1</td>
</tr>
<tr>
<td>$\chi^{ab}(T)$</td>
<td>0.66 ± 0.01</td>
<td>16.3 ± 0.4</td>
</tr>
<tr>
<td>$M_c(H)$</td>
<td>0.64 ± 0.01</td>
<td>67.8 ± 0.4</td>
</tr>
<tr>
<td>$C_p(T)$</td>
<td>0.55 ± 0.05</td>
<td>95 ± 5</td>
</tr>
</tbody>
</table>

For $P(J) \sim J^{-\alpha}$ it follows that at low temperatures $C_{RS} \sim T^{(1-\alpha)}$. Indeed, we find that below about 4 K, $C_P \sim T^{0.54}$ (see Fig. 4.9 (b), inset), that suggests the power-law exponent to be 0.46. The discrepancy of this value with the one obtained from the high-field magnetization can be attributed to $P(J)$ having a slightly different form for low and moderate $J$, as the specific heat (4.2) is most sensitive to $P(J)$ below $J \approx 4$ K, while the power law in the magnetization is extracted for larger values of $J$. Nonetheless, the discrepancy between the power law exponents is not too large.

Hence, we have attempted to fit the data from each measurement with a single form of $P(J) = \theta(J_0 - J)J^{-\alpha}$, where a cutoff scale $J_0$ has been introduced to ensure proper normalization. The results of the fits are given in Table 4.1. The parameter $\mu$ in Eq. (4.1) is related to $\mu_{\text{eff}}$ at high temperatures as $\mu = \sqrt{2/3} \mu_{\text{eff}}$. Additionally, to describe the specific heat at all temperatures, we have modeled the phonon contribution of specific heat with a combination of Debye and Einstein phonons, i.e. $C_P(T) = C_{RS}(T) + C_{\text{phon}}(T)$.

The resulting fits to the data are excellent as shown in Figs. 4.9 and 4.10. Importantly, the qualitative features of all three measurements are well captured: the susceptibility increasing nonlinearly at low-$T$ [see inset of Fig. 4.9 (a)], the upturn in the specific heat at low-$T$ where $C_{RS}$ dominates, and the non-saturating concave high-field magnetization. Moreover, the resulting power-law exponents obtained from fits across different experiments agree well with each other, see Table 4.1. The cutoff scale $J_0$, on the contrary, shows significant variations. This can be partially attributed to the deviations of $P(J)$ from the power-law form at the lowest and highest values of $J$ (as is seen in Fig. 4.10), as different
quantities are most sensitive to different ranges of $J$ values. Additionally, it can be shown that this parameter depends on the way the cutoff is implemented - e.g., implementation of a soft cutoff affects the value of $J_0$. Thus, we argue that the variations of $J_0$ reflect the approximate character of the form of $P(J)$ we use, which is nonetheless sufficient for the qualitative description of the data.

As has been mentioned above, the distribution parameters may vary between the low and intermediate energy scales. The agreement of the power law exponents in Table 4.1 with the one obtained from magnetization between 1 and 15 T suggests that these values do not concern the distribution at very low energies. Instead, we have established the presence of random singlet excitations with a unique power law form in the intermediate energy range.

4.2.5 Conclusion

By combining low- and high- magnetic field measurements we have established that Ba$_5$CuIr$_3$O$_{12}$ at low temperatures is well described as a random singlet state. We have shown that a non-saturating high-field magnetization allows one to rule out a QSL scenario and quantitatively extract the exchange coupling distribution of the random singlet state $P(J) \sim J^{-0.6}$ at intermediate energies. We find the extracted power law distribution is consistent across the magnetization, susceptibility, and specific heat measurements. Thus, we establish that a combination of high-field measurements with more conventional techniques allows one to study the role of disorder in QSL candidate materials as well as characterize strongly disordered ground states.

4.2.6 Experimental details

Single Crystal Growth

For the Ba$_5$CuIr$_3$O$_{12}$ single crystal growth, we first prepared polycrystalline material by the solid-state reaction method: a stoichiometric composition of BaCO$_3$, IrO$_2$ and CuO
Figure 4.12: Left panel: XRD measurement data (black) and intensity pattern expected from \( \text{Ba}_5\text{CuIr}_3\text{O}_{12} \) (red lines). Right panel: Laue diffraction data confirming the threefold symmetry and single-crystal nature of the sample. Inset: image of one of the samples on the Laue holder.

Powders (Alfa Aeser) were grounded, and the pelletized powder was sintered in the air at 1000 – 1200 °C with intermediate grindings. Then \( \text{Ba}_5\text{CuIr}_3\text{O}_{12} \) single crystals were grown by flux method using \( \text{K}_2\text{CO}_3 \) with added \( \text{BaCO}_3 \). The \( \text{Ba}_5\text{CuIr}_3\text{O}_{12} \) polycrystalline powder were mixed with the flux of \( \text{K}_2\text{CO}_3 \) and \( \text{BaCO}_3 \), and then were melted in alumina crucible at 1050 °C and slowly cooled down to room temperature at a cooling rate 2 °C/hr. The crystals were washed with hot water to separate from the flux.

XRD measurements of crushed single crystal powder confirm the right phase (see Fig. 4.12); the resulting lattice parameters are \( a=10.1361 \text{Å}, c=21.3561 \text{Å} \). While \( a \) agrees to within 0.1% with the previous measurements [226, 227] \( c \) is shorter by about 1.4% than the previous reported values [226, 227]. We attribute this discrepancy as well as imperfect match to the predicted intensities to the possible strains and imperfections emerging during crushing. Additionally, we have performed Laue diffraction measurements; the resulting pattern for (001) direction is presented in Fig. 4.12, right panel. It confirms the single crystal character of our samples and the threefold pattern symmetry is consistent with the \( P3c1 \) space group of \( \text{Ba}_5\text{CuIr}_3\text{O}_{12} \).
Magnetic anisotropy

In the main text we have concentrated on the data for $H \parallel c$ and generally disregarded the magnetic anisotropy. While it is indeed weak, we provide here additional information regarding this anisotropy and its dependence on the applied field and temperature. In Fig. 4.13 we show the anisotropy of (a) magnetic susceptibility (b) magnetization, as a function of temperature and magnetic field, respectively. The van Vleck contribution, subtracted form the data in the figure, is also anisotropic: $\chi_0^c = 0.0033$ emu/mol and $\chi_0^{ab} = 0.0012$ emu/mol. To account for the discrepancies in the temperature/field values of the two measurements we use the numerically interpolated values. At large fields or temperatures the anisotropy is seen to decrease. This can be attributed to the anisotropic exchange interactions, characteristic of systems with strong spin-orbit coupling [267] and Ir-based ones in particular [216, 268]. Indeed, temperature-dependent anisotropy has been observed in Ir-based systems [269] and is expected theoretically [270].

FC/ZFC measurements and glassiness

To confirm the absence of glassy behavior in Ba$_5$CuIr$_3$O$_{12}$ we have performed ZFC/FC magnetic susceptibility measurements in field of 100 Oe using a SQUID magnetometer (Quantum Design), with the results presented in Fig. 4.14. We find no signatures of spin freezing or history dependence. The relative differences between the FC and ZFC data are below 2% for both field orientations (for points measured at the same temperature) and
can be attributed to the equipment noise (especially taking into account the relatively large background signal, which has been observed to be roughly 10 times larger at this field value than that of an optimally working SQUID).

4.2.7 Theoretical details

Model of the random singlet state

The partition function of a singlet with antiferromagnetic (AFM) interaction $J$ in magnetic field $H$ is (with the singlet state energy set to zero)

$$Z_s = 1 + e^{-\beta J} [2 \cosh(\beta \mu H) + 1].$$  (4.3)

And the corresponding magnetization is

$$M_s = -\frac{\partial F}{\partial H} = \mu \frac{2 \sinh(\beta \mu H)}{2 \cosh(\beta \mu H) + 1 + e^{\beta J}}.$$  (4.4)

The magnetization of the whole system is an average of $M_s$ over a distribution $P(J)$:

$$M = \int_0^\infty dJP(J) M_s = \int_0^\infty dJP(J) \mu \frac{2 \sinh(\beta \mu H)}{2 \cosh(\beta \mu H) + 1 + e^{\beta J}}.$$  (4.5)

On the one hand, if $T \ll \mu H \& J$, $M_s$ is equal to $\mu$ for $\mu H > J$ and to 0 otherwise. In this limit, Eq.(4.5) simplifies to

$$M = \mu \int_0^{\mu H} dJP(J) + O[TP(\mu H)].$$  (4.6)

The derivative of $M$ with respect to $H$ is then

$$M'(H) = \mu^2 P(\mu H).$$  (4.7)
On the other hand, if $T \gg \mu H & J_0$, we have

$$M = \int_0^\infty dJP(J)\mu\frac{2\beta\mu H}{4} = \frac{\mu^2 H}{2T},$$  \hspace{1cm} (4.8)

and

$$M'(H) = \frac{\mu^2}{2T}. \hspace{1cm} (4.9)$$

Eq.(4.9) is simply the Curie susceptibility $\frac{(g\mu_B)^2 S(S+1)}{3T}$ of two $S=1/2$ spins with g-factor $\mu/\mu_B$. We can also calculate the zero-field specific heat from Eq.(4.3):

$$C_{RS} = -Tk_B \frac{\partial^2 F}{\partial T^2} = \int_0^\infty dJP(J)\frac{J^2}{T^2} \frac{3e^{-J/T}}{(1 + 3e^{-J/T})^2}. \hspace{1cm} (4.10)$$

Using Eq.(4.7) one can extract the distribution $P(J)$ from the low-temperature field dependence of magnetization. Using (4.9) the value of the moment $\mu$ can be extracted from the high-temperature susceptibility value.

Details of fitting the data

General remarks and choice of random coupling distribution

In main text we have used distribution $P(J) = \theta(J_0 - J)J^{-\alpha}$ for the exchange interaction in the random singlet state, motivated by the magnetization data in Fig. 3, inset. The $\theta(J_0 - J)$ factor is necessary as the integral over the distribution otherwise diverges at large $J$. While this allows us to satisfactorily describe the data qualitatively, this distribution form is only approximate and thus the values of the parameters extracted from the fits can be model-dependent. Here we show that using a different different way to implement the cutoff may strongly affect the value of $J_0$, but not $\alpha$. Namely, we attempt to fit the experimental data with the distribution $P(J, \sigma) = \frac{J^{-\alpha}}{e^{(J-J_0)\sigma} + 1}$, where $\sigma \to 0$ results in the distribution used in the main text. Indeed, the values of $J_0$ are affected by $\sigma$, especially for the observables yielding lower values of $J_0$, such as the susceptibility $\chi_c(T)$. On the other hand, the power-law exponent $\alpha$ shows a less pronounced dependence on $\sigma$ for all datasets. Additionally, the discrepancies between the fit results for different observables
can be explained as follows. While $C_p(T)$ and $\chi(T)$ are primarily sensitive to the low-energy part of the distribution, $M(H)$ probes instead the intermediate-to-high energy part most reliably. Indeed, the behavior of $C_p(T)$ at low $T$ (see Fig. 2 (b) of the main text) suggests $\alpha \approx 0.46$, different from the one extracted from $M(H)$. As we use a distribution having same form at low and intermediate energies, one may expect such discrepancies to appear. Additionally, phonons provide an important contribution to $C_p(T)$ and thus the parameters of the random-singlet model also may depend on the modeling of phonon contribution (see below).

**Susceptibility and Curie-Weiss law**

Here we provide some details regarding the deviation of $\chi^{c,ab}(T)$ from Curie-Weiss behavior. Analyzing our data in the same way as in [226], we found large uncertainties in $T_W$, e.g. for the interval between 150 K and 300 K we get $23 \pm 15 K$ along the $c$-axis and $-16 \pm 7 K$ for the in-plane (i.e. $a-b$) direction. Expanding the fitting interval to include lower temperatures (while keeping the upper bound of 300 K), we find that the uncertainties diminish, and that the value of $T_W$ for the lower bound under 40 K falls between $-3 K$ and $-5 K$ along the $c$-axis and between $-1 K$ and $-3 K$ for the in-plane direction. These results suggest weak antiferromagnetic (AFM) correlations.

In Fig. 4.15 we present $\chi - \chi_0$ multiplied by a function $f(T)$ for fields in the chain (a) and in-plane (b) directions. Colored lines are for $f(T) = 3(T - T_W)$ and black line corresponds to $f(T) = \chi_{RS}(T)/\mu_{eff}^2$. At high temperatures all curves converge to the same value (within error bars). The error bars grow with $T$ as we effectively multiply $\chi$ by $T$ at high temperature, and thus the absolute value of the error bar for is enhanced with it. At low temperatures one can see that the colored curves exhibit significant deviations from the high-temperature value. For some values of $T_W$ there is a pronounced dip, while for others it is the marked enhancement towards low $T$. However, there is no single curve that has neither. In this respect, fits with the RSS model show superior quality (see insets for low temperatures).
Figure 4.15: Details of the susceptibility data of Ba$_5$CuIr$_3$O$_{12}$. (a) $\chi^c - \chi_0^c$ multiplied by a function $f(T)$. For colored points $f(T) = 3(T - T_W)$ for several values of $T_W$ between -3 K and -5 K, for $H \parallel c$. Black points: $f(T) = \chi_{RS}(T)/\mu_{\text{eff}}^2$. Lines are guide to the eye. At high temperatures all curves converge to $\mu_{\text{eff}}^2$. (b) Same for $\chi^{ab} - \chi_0^{ab}$ and values of $T_W$ between -1 K and -2 K. Kink at around 2 K is due to the equipment noise. The units have been converted from $emu \cdot K/mol$ to $\mu_B^2$ with a prefactor $k_B[\text{erg}/K]/N_A/\mu_B^2[\text{erg}/G]$. 

\[ f(T) = \frac{\chi_{RS}(T)}{\mu_{\text{eff}}^2} \]
Table 4.2: Fitting parameters of the phonon model (4.13) for Ba$_5$CuIr$_3$O$_{12}$.

<table>
<thead>
<tr>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\theta_D$ (K)</th>
<th>$\hbar \omega_1$ (K)</th>
<th>$\hbar \omega_2$ (K)</th>
<th>$\hbar \omega_3$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36 ± 0.03</td>
<td>0.13 ± 0.04</td>
<td>0.51 ± 0.01</td>
<td>74 ± 15</td>
<td>196 ± 12</td>
<td>97 ± 9</td>
<td>567 ± 13</td>
</tr>
</tbody>
</table>

**Specific heat**

Assuming unit cell with six formula units [4], one expects $3 \cdot 126$ phonon branches in Ba$_5$CuIr$_3$O$_{12}$. At low temperatures 3 acoustic branches should dominate and we use the Debye model for their contribution

$$C_{Deb}(\theta_D, T) = 9k_B \left( \frac{T}{\theta_D} \right) \int_{0}^{\theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}. \quad (4.11)$$

For higher temperatures the contribution of optical phonons should be included; we use the Einstein model

$$C_{Ein}(\omega, T) = 3k_B \left( \frac{\hbar \omega}{T} \right)^2 \frac{e^{\frac{\hbar \omega}{T}}}{(e^{\frac{\hbar \omega}{T}} - 1)^2}. \quad (4.12)$$

We’ve found that a successful fitting can be performed using Einstein model with three different frequencies. In total, we have used (per formula unit)

$$C_{phon}(T) = C_{Deb}(\theta_D, T)/6 + 125/6(aC_{Ein}^1(\omega_1, T) + bC_{Ein}^2(\omega_2, T) + cC_{Ein}^3(\omega_3, T)), \quad (4.13)$$

where $a + b + c = 1$ and $\theta_D, \omega_{1,2,3}$ are fitting parameters. Their values resulting from the fit are $a = 0.36 \pm 0.03$, $b = 0.13 \pm 0.04$, $c = 0.51 \pm 0.01$, $\omega_1 = 196 \pm 12$ K, $\omega_2 = 97 \pm 9$ K, $\omega_3 = 567 \pm 13$ K and the ones for the random singlet part are given in Table 4.2. The confidence intervals for $a, b, c$ have been calculated without taking the constraint $a + b + c = 1$ into account.

**Magnetization**

To obtain the $\mu_{eff}$ value used in the main text, we performed magnetization measurements at 9 T by using a Vibrating Sample Magnetometer (Quantum Design Dynacool) in the temperature interval 2 K to 300 K. The data were taken from the same sample as the one used in high-field studies. In Fig. 4.16 we present $\chi_{9T} = M(H, T)/H$.

For the susceptibility, the curves become linear in $T$ above 50 K, suggesting a Van Vleck term in addition to a Curie term. Fitting the curves between 100 and 250 K with
Figure 4.16: Susceptibility at 9T field multiplied by the temperature for Ba$_5$CuIr$_3$O$_{12}$.

\[
\chi_{gT}^{ab(c)}(T) = \frac{C^{ab(c)}}{T} + \chi^{ab(c)}_0
\]

we obtain: $C^{ab} = 0.518$ emu/mol*K, $\chi^{ab}_0 = 0.0012$ emu/mol; $C^c = 0.513$ emu/mol*K, $\chi^{c}_0 = 0.00174$ emu/mol. From these values one obtains $\mu_{c_{eff}}^c = 2.025 \mu_B/f.u.$ and $\mu_{c_{eff}}^{ab} = 2.035 \mu_B/f.u.$.

These values are close to the effective moment expected from one Cu$^{2+}$ $\mu_{\text{eff}}^{\text{Cu}} = 1.9 \mu_B$ and one Ir trimer $\mu_{\text{eff}}^{\text{Ir-tr}} = 0.8 \mu_B$[257] moments per formula unit (f.u.): $\sqrt{(\mu_{\text{eff}}^{\text{Cu}})^2 + (\mu_{\text{eff}}^{\text{Ir-tr}})^2} \approx 2.06 \mu_B$.

Note that $\chi - \chi_0$ at the lowest available temperature restricts the possible low-temperature Curie contribution due to unpaired spins to less then 20 % of the high-temperature value.

Moreover, the Curie contribution is likely to be much smaller then that, as there are no signs of saturation of $T * \chi$ in Fig. 4.16 at low temperature.

The high-field measurements were calibrated with magnetization curves measured at field up to 9 T with SQUID magnetometer (Quantum Design) at 2 K. The value of pulsed-field measurement is taken to coincide with the SQUID measurement at 9 T. The resulting curves are presented in Fig. 4.17 with 10% error bars for the pulsed-field data, taken for the purpose of illustration, as the sample signal has been rather low.

One can see that the calibration curve does not fit satisfactorily the pulsed-field data for $H \parallel ab$. Furthermore, other issues appear if we proceed with magnetization along $ab$ in high-fields. In Fig. 4.18 the magnetization is presented after subtracting the Van Vleck contribution assuming it being linear in field (i.e. $M_{VV}(H) = H \chi_0$).
Figure 4.17: Pulsed-field magnetization and magnetization for Ba$_5$CuIr$_3$O$_{12}$.

Figure 4.18: Magnetization curves at $T = 2$ K for Ba$_5$CuIr$_3$O$_{12}$. 
Because the magnetization does not saturate, the maximal value of the magnetization attained, $M_{c}^{\text{max}} \approx 1.62 \mu_B/f.u.$ and $M_{ab}^{\text{max}} \approx 1.79 \mu_B/f.u.$, should be smaller than the saturation moment $\mu_{\text{sat}}$. Assuming that $\mu_{\text{eff}}$ is realized two $S = 1/2$ spins we have $\mu_{\text{eff}} = \sqrt{\mu_{\text{eff},1}^2 + \mu_{\text{eff},2}^2}$, and hence $\mu_{\text{sat}} = (\mu_{\text{eff},1} + \mu_{\text{eff},2})\sqrt{S\over S+1} = {\mu_{\text{eff},1} + \mu_{\text{eff},2} \over \sqrt{3}} \leq {\sqrt{3}\mu_{\text{eff}} \over \sqrt{3}} \approx 1.66 \mu_B/f.u$. This value is smaller than $M_{ab}^{\text{max}}$. If we use the more realistic effective moments for the $Cu^{2+}$ ions ($1.9 \mu_b$) and $Ir^{4+}$ trimers ($0.8 \mu_b$ [257]), $\mu_{\text{sat}} = 2\over\sqrt{3} \approx 1.56 \mu_B/f.u.$, which is even smaller than $M_{c}^{\text{max}}$. Such discrepancy could be attributed to the issues in the pulsed-field measurements for $H \parallel ab$ evident from Fig. 4.17.

Given the smaller magnitude of the discrepancy for $M_{c}^{\text{max}}$, we use the $H \parallel c$ data for the analysis.
Chapter 5

Excitonic physics of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family

In this chapter, the work on Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family is presented. We demonstrate that the ground state of Ta$_2$NiSe$_5$ is an excitonic insulator, by identifying the excitonic soft mode and coherent band hybridization. Sulfur doping suppresses the excitonic instability; for Ta$_2$NiS$_5$ the phase transition is purely ferroelastic.

Study of excitonic insulator state of Ta$_2$NiSe$_5$ is presented in Sec. 5.1. We identify above the phase transition temperature the overdamped excitonic soft mode in the quadrupolar symmetry channel, and below the phase transition temperature the coherent superpositions of band states at the gap edge. A systematic investigating of the lattice dynamics for Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family is in Sec. 5.2. We identify all Raman-active optical phonons of $A_g$ (fully symmetric) and $B_{2g}$ (ac-quadrupole-like) symmetries ($D_{2h}$ point group) and study their evolution with temperature and sulfur concentration. The electronic phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family is discussed in Sec. 5.3. The critical excitonic fluctuations diminish with $x$ and eventually shift to high energy, suggesting a quantum phase transition. However, a structural phase transition happens at finite temperature for all $x$, indicating a co-oprating lattice instability at large $x$. 
5.1 Excitonic insulator state of Ta$_2$NiSe$_5$

Attractive interactions between fermions are known to lead to a proliferation of bound pairs of particles at low temperatures causing a transition into superconducting or superfluid phases. In a semiconductor or a compensated semimetal, the Coulomb attraction between electrons and holes may induce a similar transition where electron-hole pairs, the excitons, develop macroscopic coherence [271–274]. The resulting state, characterized by an interaction-induced gap, has been dubbed as the excitonic insulator [275]. However, so far only a few materials have been identified as excitonic insulator candidates [276–281] - possibly because its formation requires strong attraction or matching energy dispersion of the electron- and hole-like carriers [271]. These restrictions can be overcome by creating a non-equilibrium exciton population and cooling below their degeneracy temperature, in which case the coherent state may be observable only as a transient due to the finite lifetime of the excited state [282–284]. An equilibrium excitonic phase in a bulk material, on the other hand, would allow for a far wider range of questions to be asked and answered regarding the excitonic states of matter and their formation.

As an example, controlling the bare band gap of an excitonic insulator allows one to explore a range of correlated regimes: from a weakly correlated electron-hole condensate analogous to the Bardeen-Cooper-Schrieffer (BCS) condensate in fermionic superfluids in the negative-gap (semimetallic) regime to a weakly interacting gas of tightly bound excitons in the opposite limit of a gapped (semiconductor) band structure [273, 275, 285]. In the former case, weakly bound excitons are characterized by size $\xi_{ex}$ larger than the interparticle distance $l_{eh}$ and the exciton wavefunctions overlap strongly, while in the latter one, a dilute gas of tightly bound excitons with $\xi_{ex} \ll l_{eh}$ exists also above the transition temperature, with their chemical potential going to zero at the transition, in analogy with the Bose-Einstein condensation (BEC). The “BCS” and “BEC” regimes are also characterized by a different dynamics of the excitons. In particular, for a semimetallic normal state
(as in Fig. 5.1d), the exciton, regardless of its energy, may decay into unbound particle-hole pairs (Landau damping), leading to overdamped dynamics. On the other hand, for a semiconductor-like normal state, the exciton energy is within the direct gap at $T > T_c$, such that energy conservation ensures the undamped dynamics of the excitons. Most interesting is the strongly correlated crossover regime [286, 287], where neither of the weakly-coupled bosonic or fermionic descriptions applies and the signatures of excitons above $T_c$ may coexist with the strongly coupled electron-hole plasma.

However, proving the excitonic origin of the phase transition is challenging as it is expected to be obscured by an accompanying structural transition of the crystalline lattice. Formation of a macroscopic excitonic population in a real material may break some of the lattice symmetries: translational one if the excitons are indirect (i.e. have a nonzero center-of-mass momentum) [279] or point-group ones otherwise [273]. In the latter case, the nontrivial effect on the lattice comes about due to the transformation properties of the particle and hole wavefunctions involved in forming an exciton: if those are distinct, e.g. an $s$-like electron is paired with a $d$-like hole, the exciton wavefunction would have symmetry lower than the lattice one, even if the relative motion of the particle and hole is in a fully symmetric $s$-like state. The discrete nature of the point-group symmetry broken in the excitonic insulator at the transition temperature $T_c$ bears important consequences for its properties: in particular, its excitations are expected to have a finite energy gap, in contrast to the non-equilibrium excitonic condensates, where a continuous $U(1)$ symmetry associated with approximate exciton number conservation is broken resulting in superfluidity and a gapless Bogoliubov-Goldstone mode at $T < T_c$ [282–284].

The above mentioned difficulties are pertinent to the case of Ta$_2$NiSe$_5$, a material showing a semiconducting behavior at low temperatures with a phase transition from high-temperature orthorhombic phase to a monoclinic one at $T_c = 328$ K [288], breaking two of the mirror symmetries (Fig. 5.1, a and b). Symmetry-wise, this transition corresponds to
Figure 5.1: Schematics of the excitonic insulator physics for Ta$_2$NiSe$_5$. a, Crystal structure in the high-temperature orthorhombic phase. Three unit cells in a direction are shown. b, Possible mechanisms of the phase transition: below $T_c$, the symmetry of the lattice can be reduced due to structural distortion or coherent excitonic condensation. c, Illustration of the polarization-resolved Raman process: the $aa$ scattering geometry (top) probes excitations with the full symmetry of the lattice ($A_g$), while the $ac$ scattering geometry (bottom) couples to the symmetry-breaking excitations with the symmetry of the $ac$-like quadrupole order parameter ($B_{2g}$). d and e, Excitonic transition in a semimetal: above $T_c$ d conduction (blue) and valence (red) bands cross at the Fermi level; pre-formed excitons are coupled to interband transitions forming an overdamped collective mode in the $B_{2g}$ channel. e, At low temperatures excitonic order hybridizes the bands, opening a spectral gap. At the gap edge, the eigenstates are equal-weight superpositions of the two bands, shown on the right. As a result, distinct interference effects occur for $ac$ (black arrows) and $aa$ (red/blue arrows) geometries. f, Expected Raman spectra for the $ac$ scattering geometry near $T_c$. Left: for a structural transition one of the phonon modes softens to zero energy. Right: for an excitonic insulator, the excitonic mode is overdamped and softens to zero energy at $T_c$. g, Expected Raman spectra at low temperature: due to the coherence factors e, the response at the gap edge is suppressed to zero in the $ac$ scattering geometry, but not in $aa$ (see Methods for details). On heating the features move to lower frequencies (dashed lines).
the reduction of point group symmetry from $D_{2h}$ to $C_{2h}$ with the order parameter transforming as the $B_{2g}$ irreducible representation of $D_{2h}$ ($xz$-like quadrupole). The electronic structure of Ta$_2$NiSe$_5$ has been predicted to have a small or negative (as in Fig. 5.1d) direct gap at the Brillouin zone center [289, 290], in agreement with experiments above $T_c$ [285, 291]. The two bands closest to Fermi energy have quasi-1D character and are derived from superpositions of Ta 5$d$ and Ni 3$d$ orbitals at the multiple sites of the unit cell. Hybridization between them in the $k_x = 0$ plane, forbidden by $x \rightarrow -x$ symmetry above $T_c$, can serve as the order parameter that is microscopically induced by a condensation of the resulting interband excitons [292, 293]. This points to the quadrupolar character of these excitons.

Experimentally, below $T_c$ formation of a gap has been observed in transport [285] and optical [291] measurements, and an anomalous dispersion of the hole-like band [294] has been taken as an indication for the excitonic character of the transition. Above $T_c$, a gap-like spectral weight suppression has been observed in ARPES studies [295] suggesting a BEC-like picture for the excitons, while the low values of transport gap suggest otherwise [285]. On the other hand, the changes in spectral and transport properties could also be due to the change of the lattice structure below $T_c$. While Ta$_2$NiSe$_5$ has been actively investigated since then [285, 291, 293, 295–297], a structural origin of the transition has not been excluded [298–300]. Additionally, the origin of the low-temperature spectral gap has not been directly probed: while the valence band dispersion at low temperatures is consistent with a symmetry-breaking hybridization forming below $T_c$ [294], a direct proof of hybridization (regardless of the driving force behind the transition) requires showing the states of two bands being mixed into coherent superpositions of the states at the gap edge as in Fig. 5.1d.

The questions above can be addressed directly by Raman spectroscopy that probes the excitations of the system by an inelastic two-photon process. Polarization analysis of the incoming and outgoing photons further enables one to select excitations with a specific symmetry [11, 301]. Applied to Ta$_2$NiSe$_5$ above $T_c$, $ac$ polarization geometry (Fig. 5.1c, bottom)
probes excitations with the symmetry of \textit{ac}-type quadrupole (i.e. $B_{2g}$, see Methods), the same as that of the order parameter, allowing direct observation of the soft mode expected at a second-order phase transition (Fig. 5.1d). Being even in parity, these excitations are invisible in a conventional light absorption experiment due to the dipole selection rules. The character of the soft mode reveals the origin of the transition. In an excitonic transition in a semimetal, critical fluctuations would have a broad relaxational lineshape due to the Landau damping and are enhanced at low frequencies close to $T_c$ (Fig. 5.1f, right). On the other hand, in a structural transition driven by an optical phonon, a sharp spectral peak would soften to zero energy at $T_c$ (Fig. 5.1f, left). In addition, the structural transition can also be driven by an instability of the acoustic modes (ferroelastic instability [302]), which would lead to absence of signatures in Raman scattering, as coupling to light vanishes at $q = 0$ for acoustic modes [171].

Hybridization between bands can be further revealed by studying the contribution of electron-hole excitations to Raman scattering. Above $T_c$, the \textit{ac} scattering geometry probes the interband transitions (Fig. 5.1d) between the valence (red) and conduction (blue) bands that have an \textit{ac}-type quadrupole ($B_{2g}$) character. The \textit{aa} scattering geometry, on the other hand, probes fully symmetric excitations (Fig. 5.1c, top), and is limited to intraband transitions only. Below $T_c$, hybridization mixes the states of two bands into coherent superpositions (Fig. 5.1e). This results in interference effects at the gap edge, in analogy with the effect of coherence factors in a superconductor [303]. In particular, for \textit{ac} geometry a destructive interference occurs between transitions from “red” to “blue” states and vice versa resulting in an exact cancellation (Fig. 5.1e, on the right). In contrast, for \textit{aa} geometry, the destructive interference is between two types of interband transitions which do not cancel exactly, as “red” and “blue” bands couple to light differently (Fig. 5.1e). This results in the intensity close to the gap edge being strongly suppressed in \textit{ac} geometry with respect to \textit{aa}. In Fig. 5.1g we present the spectra expected in two polarization channels based on a mean-field model of an excitonic insulator. In contrast to the above description, if hybridization
is absent and the low-temperature gap is between the conduction and valence bands, the gap edge corresponds to a purely interband transition. The intensity in \( ac \) geometry is then expected to be dominant, clearly distinct from the hybridization gap case.

In this section, we employ polarization-resolved Raman spectroscopy to prove the excitonic origin of the transition in \( \text{Ta}_2\text{NiSe}_5 \), as opposed to structural one, and the hybridization nature of the low-temperature gap. We further determine that the resulting excitonic insulator is in the strongly correlated BCS-BEC crossover regime. In particular, close to \( T_c \) we observe critical softening of overdamped quadrupolar excitations Fig. 5.2b,f) that are consistent with excitonic fluctuations in a semimetal. In contrast, we find no softening of the optical phonon modes (Fig. 5.3, Fig. 5.39b). At low temperatures, by comparing the intensities in \( aa \) and \( ac \) polarization geometries (Fig. 5.2e) we find direct evidence for hybridization-induced gap and coherent mixing of the two semimetallic bands driven by the excitonic order (as in Fig. 5.1d), i.e. spontaneously formed symmetry-breaking hybridization between the bands. With heating, the gap observed in fully symmetric channel fills in, rather than closes, characteristic of strong correlations beyond the mean-field regime. By estimating the exciton coherence length, we find that for \( \text{Ta}_2\text{NiSe}_5 \) the excitonic condensate lies within the strongly correlated BCS-BEC crossover regime, and argue that the whole body of experimental data for \( \text{Ta}_2\text{NiSe}_5 \) is consistent with this identification.

5.1.1 Overview

In Fig. 5.2a-d we present an overview of the Raman spectra. For \( ac \) geometry, probing excitations with the symmetry of \( ac \)-type quadrupole above \( T_c \), same as that of the order parameter (Fig. 5.1c, bottom), a pronounced enhancement of the low-energy response is observed around \( T_c \). This is characteristic of a soft mode development near a second order phase transition. For \( aa \) geometry, the most prominent feature is the redistribution of intensity towards higher energies below \( T_c \) with a pronounced gap-like suppression below 380 meV; at low energies conventional phonon peaks are observed (Fig. 5.2c).
Figure 5.2: Temperature dependence of Raman spectra. a and b, Raman response $\chi''_{aa}$ and $\chi''_{ac}$ in the $aa$ and $ac$ scattering geometries, respectively. The horizontal frequency (Raman shift) scales are logarithmic. To emphasize the region around $T_c = 328$ K the vertical axes are rescaled by a nonlinear transformation $\text{arctanh} [T/T_0]$, where $T_0 = 390$ K. $\chi''$ values are displayed on a logarithmic false color scale, with the strongest phononic resonances in saturation. In b, a critical enhancement at low frequencies is observed close to $T_c$. Due to broken mirror symmetries below $T_c$, “leakages” of sharp phonon features appear in both a and b. Additionally, a strong peak at 380 meV emerges in a with a weaker feature in b. c and d: Details of Raman response $\chi''_{aa}$ and $\chi''_{ac}$, for $T = 330$ K (above $T_c$) and $T = 35$ K. Shading highlights the electronic contribution (see also Fig. 5.3). e and f, $\chi''_{aa}$ and $\chi''_{ac}$ in the range enclosed by the dashed white boxes in a and b on a linear frequency scale with the resolution shown in top left corner. In e, $\chi''_{aa}(\omega,T)$ all cross at the 280 meV isosbestic point, showing intensity transfer on heating from the 380 meV peak to the low-temperature gap region. $\chi''_{ac}(\omega,T)$ is shown for intensity comparison. In f, above $T_c$ (red curve) three phonon modes are observed, with the first two showing a pronounced asymmetric Fano lineshape, pointing to an interaction with an electronic continuum. Below $T_c$ the asymmetry becomes less pronounced and additional modes appear due to mutual $aa$-$ac$ “leakage”.
The presence of a symmetry-breaking phase transition at $T_c$ is evident from the appearance of new sharp optical phonon modes in both geometries. Their appearance is related to the change in selection rules below $T_c$ (see Methods); in what follows, we will call this intensity admixture from another polarization as ‘leakage’.

This reflects that below $T_c$ the two polarization geometries are no longer orthogonal, thus all excitations may appear in both geometries. In Fig. 5.39a we further quantify this effect by showing the temperature dependence of the integrated intensity of the lowest-energy fully symmetric (above $T_c$) phonon mode in $ac$ scattering geometry, which grows substantially below 328 K. The parameters of the fully symmetric phonon modes are also consistent with a recent study of Raman scattering in $aa$ geometry [304].

5.1.2 Identification of the excitonic soft mode

We now focus on the low-energy lineshapes in the $ac$ geometry spectra close to the transition temperature, detailed in Fig. 5.2f and Fig. 5.3. Three distinct peaks are observed, which correspond to three optical phonons of $B_{2g}$ symmetry expected from the space group of Ta$_2$NiSe$_5$ ($Cmcm$), ruling the presence of other optical modes out. The striking feature of the raw data is the notably asymmetric shape of the two lowest-energy modes, that cannot be described as conventional Lorentzian oscillators. Instead, the data above $T_c$ is well described by a generalized Fano model, including three phononic oscillators interacting with a continuum of overdamped excitonic excitations described by a purely relaxational response

$$\chi_{\text{cont}}(\omega) \propto \frac{1}{-i\omega + \Omega_e(T)},$$

where its imaginary part $\chi''_{\text{cont}}(\omega)$ exhibits a maximum at $\Omega_e(T)$. This continuum is clearly distinct from the structural phonons and suggests the presence of an overdamped bosonic mode emerging from the electronic system consistent with a Landau-damped exciton in a semimetal (Fig. 5.1d). The parameter $\Omega_e(T)$ can then be represented by an analogy with an overdamped oscillator as $\Omega_e(T) \equiv \omega_0^2 / \Gamma$, $\omega_0$ being the exciton frequency (which is a
collective mode of the semimetal, similar to the collective Cooper pair mode above $T_c$ in a superconductor [305]) and $\Gamma \gg \omega_0$ — the damping rate. This form can be alternatively derived using the time-dependent Ginzburg-Landau equation. Upon cooling towards $T_c$, $\Omega_e(T)$ linearly decreases as $\Omega_e(T) \propto T - T^{el}_c$, where $T^{el}_c = 137(16)$ K, consistent with a critical softening of this excitonic collective mode. Just below $T_c$, the $ac$ Raman response is additionally enhanced at the lowest frequencies (Fig. 5.3e,f). We associate this enhancement with coupling to acoustic $B_{2g}$ modes with finite momenta, that is mediated by a quasi-periodic pattern of structural domains (which form below $T_c$) that takes the quasimomentum recoil.

Most importantly, we do not observe phonon softening: instead, the two bare lowest $B_{2g}$ mode frequencies harden on cooling, Fig. 5.39b. Consequently, an instability of a zone-center optical phonon [299] can be ruled out by our results. Away from $T_c$, the hardening on cooling is consistent with the expectations due to lowest-order phonon anharmonicity (lines in Fig. 5.39b); however, a more pronounced increase is observed close to $T_c$. We attribute this increase to a nonlinear coupling between the excitonic fluctuations and the phonons. In particular, introducing the electronic order parameter $\varphi$, the phonon frequency can be expressed as $\omega_{ph}(T, \varphi) \approx \omega_{ph}(T, 0) + \alpha_{ph} \varphi^2$. For $\alpha_{ph} > 0$ (which points to a competition between the electronic and lattice orders), below $T_c$ an additional increase of the phonon frequency is expected. In our results, the increase starts above $T_c$, where $\langle \varphi \rangle = 0$, pointing to the influence of the fluctuations beyond the mean-field; in particular, the increase starts at 350 K suggesting a fluctuation region of around 20 K for the phonon properties.

To study the effects of the exciton-phonon coupling on the transition, we analyze the static order parameter susceptibilities (Fig. 5.5). From the Fano model, one can deduce the individual susceptibilities of the excitonic continuum, optical phonons as well as the combined one, that includes the effects of the coupling between them. The purely electronic contribution to the inverse susceptibility (Fig. 5.5b) $\chi_{cont}^{-1}(0, T) = \Omega_e(T)/t_e^2$ (from Eq. (5.1)) follows the Curie-Weiss form $\propto (T - T^{el}_c)$ above $T_c$, indicating the softening of $\Omega_e(T)$. 
Figure 5.3: Temperature dependence of the low-energy Raman response in the \textit{ac} scattering geometry. \textbf{a-h}, show $\chi''_{ac}(\omega)$ data (black dots) for temperatures from 380 K to 35 K on a semilog scale. Thick red lines show the fits to the data with a generalized Fano model (see Methods) of three phonons coupled to a continuum with a relaxational response $\chi''_{\text{cont}}(\omega)$, Eq. (5.1). The deduced bare phonon and continuum responses are shown by green line and blue line with shading, respectively. Full Fano model response (red) does not equal sum of the two due to the presence of interference terms. \textbf{e-f}, Below $T_c$, an additional enhancement at low frequencies is modeled by a low-energy mode, originating from recoil scattering of acoustic phonons on the structural domains (see Methods), interacting with the continuum. Purple line shows its combined response with the continuum. \textbf{g-h}, At lower temperatures $\chi''_{\text{cont}}(\omega)$ is suppressed due to gap opening, reducing the asymmetry of the phonon modes. Spectral resolution is shown in top right corner of the panels.
Figure 5.4: Temperature dependence of the phonon parameters. **a**, The ratio between the integrated intensity of the lowest-energy $A_g^{(1)}$ phonon mode in the $ac$ and $aa$ scattering geometries. Its appearance below $T_c$ implies the onset of symmetry breaking that mixes the responses in $aa$ and $ac$ geometries. For comparison, the temperature derivative of the transport activation gap $E_{tr}(T) = k_B T \log \left[ \frac{R(T)}{R(360 \text{ K})} \right]$ is shown in black, displaying a discontinuity at $T_c$. Error bars are the standard deviation. **b**, The temperature dependence of the frequency of the two lowest-energy optical phonon modes $\omega_{ph1,2}$ in $ac$ geometry, that exhibit strong coupling with the excitonic continuum. Error bars are the 95% confidence intervals of the Fano model fit. The phonon frequencies soften on heating consistent with anharmonic decay model (solid lines) below $T_c$ and above 350 K. The more pronounced change between these regimes is attributed to a nonlinear exciton-phonon coupling, not included in the Fano model (see text).
Extrapolating this trend to $T < T_c$ suggests that a purely electronic transition would have taken place at $T_{c\text{el}} < T_c$ marked by the divergence of $\chi_{\text{cont}}(0, T_{c\text{el}})$. On the other hand, the bare optical phonon susceptibility remains almost constant and is even reduced around $T_c$.

Nevertheless, the coupling between the normal modes of the lattice and the excitonic continuum can increase the transition temperature. Extrapolating the susceptibility of the full Fano model, which includes the exciton-phonon interaction, from above $T_c$ (red line in Fig. 5.5) we obtained a transition temperature $T_{c\text{comb}} = 238(18)$ K, larger than $T_{c\text{el}}$ by about 100 K. However, $T_{c\text{comb}}$ is still smaller then the actual $T_c$, because apart from the optical phonons that we have observed, the coupling to the acoustic $B_{2g}$ strain modes has also to be considered. Such a coupling has been demonstrated to increase the temperature of an electronic nematic ordering to the actually observed one in iron-based superconductors [306, 307]. These effects can be understood within the Landau theory, where the electronic order parameter $\phi$ couples linearly to (optical) phononic and strain order parameters (denoted as $\eta_i$ and $\varepsilon_{ac}$, respectively) of the same symmetry resulting in the free energy expansion

$$F[\phi, \eta_i, \varepsilon_{ac}, T] = \chi_{\text{cont}}^{-1}(0, T) \frac{\phi^2}{2} + \sum_{i=1}^{3} \chi_{\text{opt},i}^{-1}(0, T) \frac{\eta_i^2}{2}$$

$$+ \lambda_{\text{opt},i} \phi \eta_i + \frac{\kappa \varepsilon_{ac}^2}{2} + \lambda_{ac} \phi \varepsilon_{ac} + O(\phi^4),$$

(5.2)

where $\kappa$ is the $B_{2g}$ shear modulus. Minimizing the quadratic term one obtains the condition for the transition temperature $\chi_{\text{cont}}^{-1}(0, T_c) - \lambda^2/\kappa - \sum_{i=1}^{3} \lambda_{\text{opt},i} \chi_{\text{opt},i}(0, T_c) = 0$, as opposed to $\chi_{\text{cont}}^{-1}(0, T_{c\text{el}}) = 0$ in the purely electronic case, leading to an enhanced transition temperature $T_c$. In Fig. 5.5 we illustrate this effect (dashed black line) by choosing the value of the interaction with strain such that the total susceptibility diverges at $T_c$. We find the value of the exciton-strain coupling obtained this way to be consistent with a recent study of the sound velocity renormalization above $T_c$ [308], and the Raman response from finite-momentum acoustic phonons below $T_c$ in Fig. 5.3e,f.

The analysis above leads us to the following conclusions: (a) the excitonic mode exhibits a strong tendency to soften, suggesting a purely electronic transition temperature of $T_{c\text{el}} = \ldots$
Figure 5.5: Static $B_{2g}$ susceptibility derived from the Fano fits to the Raman data shown in Fig. 5.3. a, Temperature dependence of the $ac$ quadrupole static susceptibilities $\chi_{ac}(0, T)$ derived from the decomposition of $\chi''_{ac}(\omega, T)$ (Fig. 5.3): excitonic (blue), phononic (green) and combined (red). Above $T_c$ (purple background), while the phononic susceptibility mildly decreases on cooling, the electronic and combined ones grow: lines represent an extrapolation using the Fano model parameters above 350 K. The extrapolated electronic susceptibility diverges at $T_{el}^c = 137(16)$ K (blue background below). Black dashed line illustrates the total susceptibility including the exciton-strain coupling, that diverges at the actual transition temperature $T_c$. Below $T_c$ (pink background), the electronic and combined susceptibilities are suppressed, indicating the formation of the order parameter. b, Same for inverse static susceptibilities $1/\chi_{ac}(0, T)$. Extrapolated electronic inverse susceptibility shows a linear (Curie-Weiss) behavior vanishing at $T_{el}^c$, while the combined inverse susceptibility is nonlinear and vanishes at a higher temperature, showing that the coupling to otherwise stable (green line) optical phonons can strongly enhance transition temperature. Same is true for coupling to acoustic strain, that can further enhance it to the actually observed $T_c$. Error bars in all panels are the 95% confidence intervals of the Fano model fit.
137(16) K; and (b) the transition temperature is boosted to the observed $T_c = 328$ K due to the coupling to noncritical optical phonon modes and acoustic strain.

5.1.3 Coherent factors in the excitonic insulator

Having established the excitonic origin of the transition in Ta$_2$NiSe$_5$ we now demonstrate that an interband hybridization emerges in the excitonic insulator phase. At low temperatures, an intense peak at about 380 meV in the $aa$ geometry emerges with a much subtler feature in the $ac$ geometry (Fig. 5.2e). This stark contrast cannot be attributed to the difference of the Raman coupling in two geometries: while the intensity in the $ac$ geometry is indeed weaker than in the $aa$ one at all temperatures, the evolution of the intensity in $aa$ geometry at $T < T_c$ is much more pronounced, allowing to relate this effect to the symmetry breaking. Moreover, a substantial part of the signal observed in $ac$ geometry at low temperatures can be attributed to the change in selection rules below $T_c$, making the $ac$ intensity actually related to the interband transition even smaller (see Appendix Fig. 5.8). Both band structure calculations [292] and experiments [309–311] suggest that only two bands are mostly affected by this symmetry breaking, allowing us to limit ourselves to the simplest excitonic insulator model of Fig. 5.1. The strong temperature dependence of this feature below $T_c$ (also discussed below) also precludes its attribution to transitions away from $k_x = 0$ plane, where hybridization can be present already above $T_c$. For a hybridization-induced gap in a semimetal, a suppression of interband transitions at the gap edge in the $ac$ geometry is indeed expected (Fig. 5.1e). Within a simplified two-band model of the excitonic insulator (Fig. 5.1g), a divergence of the intensity at the gap edge occurs in $aa$ geometry, but not in the $ac$ one, where interference effects lead to an exact cancellation of the intensity at the gap edge. These predictions are in agreement with the pronounced peak being observed in the $aa$ geometry only (which is further exacerbated if the leakage from $aa$ to $ac$ geometry is accounted for, see Appendix Fig. 5.8). On the other hand, in the case of a semiconductor with a large direct gap, such that hybridization effects can
be ignored, the opposite is true: the interband transition would have predominantly \textit{ac} quadrupolar character allowing its observation only in \textit{ac} geometry, in stark contrast to the data in Fig. 5.2e. Thus, the observation of an intense peak emerging at low temperatures in \textit{aa} geometry clearly favors a semimetallic band structure with a hybridization-induced gap.

Now we discuss the temperature dependence of the high-energy Raman response in \textit{aa} geometry (Fig. 5.2e). Within the mean-field theory, the energy of the peak is related to the amplitude of the order parameter, which is expected to diminish upon heating towards $T_c$ (Fig. 5.1g), and zero intensity is expected within the hybridization gap. We have observed a pronounced redistribution of intensity in a broad energy range, with intensity appearing at the lowest energies at temperatures significantly smaller than $T_c$. Such behavior appears inconsistent with the mean-field expectation, pointing to a role of correlations beyond the mean-field picture. This is further emphasized by all the curves crossing at 280 meV - the so-called “isosbestic point” \cite{11, 312, 313}, characteristic of strongly correlated systems (see also the discussion of BCS-BEC crossover effects and pseudogap below). It was previously observed in materials where spectral gap has a many-body origin, such as SmB$_6$ \cite{314} or cuprates \cite{315}. While band gap renormalization in semiconductors can be also related to electron-phonon interactions \cite{316}, the broadening of the gap edge features is expected to be rather small in that case; on the contrary, the spectral features we have observed quickly become broader than their energy on heating (Fig. 5.2e). Furthermore, the renormalization effects are expected to diminish with phonon energy \cite{317} and in our case all phonon energies are below 50 meV, suggesting the scale of the electron-phonon effects to remain below 100 meV.

5.1.4 Correlation effects

Our results unambiguously point to the excitonic physics playing a crucial role in Ta$_2$NiSe$_5$; we further found evidence for strong correlation effects beyond the mean-field expectations. The important role of correlations in the formation of excitonic order in Ta$_2$NiSe$_5$ is further
corroborated by the large ratio $\frac{2\Delta}{k_BT_c} \approx 13$, $k_B$ being the Boltzmann constant ($2\Delta \approx 380$ meV taking the energy of the spectral peak in Fig. 5.2e as an estimate for the order parameter value), well beyond the BCS prediction, but consistent with the suppression of $T_c$ occurring in BCS-BEC crossover [286]. Moreover, we can estimate the coherence length of the excitonic order using the bare electronic transition temperature with the BCS expression $\xi_{ex} = \frac{\hbar v_F}{1.76\pi k_BT_{el}}$. As the system is highly anisotropic, we use the value of $v_F$ along the most dispersive $a$ direction, where the exciton size is expected to be largest. This yields $\xi_{ex} = 32 \, \text{Å}$, while the distance between particles can be estimated in a quasi-1D system from $l_{eh} = \frac{\pi}{2k_F} \approx 16 \, \text{Å}$ ($k_F \sim 0.1 \, \text{Å}^{-1}, m^* \approx 0.37m_0$ [309]). The estimate places the excitons in Ta$_2$NiSe$_5$ in the correlated BCS-BEC crossover regime $l_{eh} \sim \xi_{ex}$.

Identification of Ta$_2$NiSe$_5$ as a correlated excitonic insulator finally allows to clarify the character of the electronic structure above $T_c$. Semimetallic character is suggested by the absence of a discernible gap in spectroscopy (Fig. 5.2e and Refs. [291, 309]) and the overdamped lineshape of the excitonic fluctuations (Fig. 5.3). A direct semiconducting gap at $T > T_c$ would further contradict the absence of a noticeable peak in $ac$ Raman intensity (Fig. 5.2e) at low temperatures that requires strong mixing of the bands as in Fig. 5.1e. On the other hand, an apparent gap feature has been observed in ARPES studies above $T_c$ [295]. It is known however, that strong fluctuations of a particle-hole order, such as a charge density wave, result in a pseudogap [318, 319] in a metallic system - a suppression of the density of states already above $T_c$, which has been experimentally observed close to charge- or spin-density wave transitions [320, 321]. In all of these cases, the pseudogap opens above the ordering transition due to the thermal order parameter fluctuations, regardless of the microscopic mechanism of the transition. Strong excitonic fluctuations in the BCS-BEC crossover regime may be expected to lead to similar effects, which explains the spectral weight suppression observed in ARPES [295]. Moreover, as the density of states in the pseudogap is finite [318], it can be reconciled with both the zero-gap behavior of the high-temperature transport [285] as well as the overdamped character of the excitonic mode.
5.1.5 Conclusion

In conclusion, by using polarization-resolved Raman spectroscopy, we have directly revealed the excitonic fluctuations driving a phase transition in Ta$_2$NiSe$_5$, shown the coherence of the low-temperature insulator by revealing the coherent band superpositions, and identified the fingerprints of strong electronic correlations, similar to the ones occurring in the BCS-BEC crossover. The strongly correlated excitonic insulator nature of Ta$_2$NiSe$_5$ accommodates for its anomalous features and provides a unified view of its electronic structure, consistent with the previous experiments [291, 294, 295]. Furthermore, as the band structure of this material can be tuned by chemical substitution or pressure [285], this opens perspectives for the exploration of different correlation regimes in excitonic insulators.

5.1.6 Experimental details

Static susceptibility

The function used to fit the finite-energy Raman response (by taking the imaginary part) can be also used to calculate the static $B_{2g}$ susceptibility by simply taking its zero-frequency limit:

$$\chi_{ac}(0,T) = \sum_{ij} T_i G_{ij}(0) T_j.$$  \hspace{1cm} (5.3)

This expression is used to calculate the combined susceptibility data for Fig. 5 in the main text. Additionally, one can define the purely electronic (continuum) and purely phononic parts of the susceptibility as:

$$\chi_{\text{cont}}(0,T) = \frac{t_2^2(T)}{\Omega_e(T)},$$

$$\chi_{\text{opt}}(0,T) = \frac{3}{2} \sum_{i=1}^{3} \frac{t_{pi}^2(T)}{2\omega_{pi}(T)}.$$ \hspace{1cm} (5.4)

The critical temperature due to excitons and optical phonons $T_{c}^{\text{comb}}$ (excluding the coupling to strain modes) can be obtained from Eq. (5.3); the condition for $\chi_{ac}(0,T)$ to diverge is
independent of the light-scattering vertex $T_i$, and is given by \( \det G^{-1}_{ij}(0) = 0 \) resulting in the following equation:

\[
\Omega_e(T_{c^{comb}}) - 3 \sum_{i=1}^{3} \frac{2v_i^2}{\omega_{pi}} = 0.
\] (5.5)

Using the values of $v_i$ and $\omega_{pi}$ above 350 K where they do not depend strongly on temperature and a linear extrapolation of $\Omega_e(T)$ one obtains $T_{c^{comb}} \approx 227$ K.

One can also include the contribution of acoustic phonons at $q \to 0$ to get the full susceptibility:

\[
\Omega_e(T_c) - 3 \sum_{i=1}^{3} \frac{2v_i^2}{\omega_{pi}} - \frac{2\beta^2_s}{c_s} = 0.
\] (5.6)

One observes that the effect of the acoustic mode on $T_c$ does not vanish in the $q \to 0$ limit despite the coupling is $\sim \sqrt{q}$. This equation allows to determine $\beta_s$ used for fitting the domain-induced low-energy upturn below $T_c$ discussed above.

**High-energy Raman spectra**

**Temperature dependence of the high-energy ac spectra**

In Fig. 2e of the main text we compare the high-energy Raman response in $aa$ and $ac$ scattering geometries on the same scale. In Fig. 5.6b below we show the enlarged $ac$ spectra where the stark contrast to the $aa$ (Fig. 5.6a) response can be better appreciated: there is no pronounced redistribution of intensity and no gap opening on cooling. The intensity actually increases on cooling below 200 meV, which can be partially attributed to “leakage” from $aa$ geometry below $T_c$ -see subSec. 5.1.6 below.

**Intensity redistribution in high-energy Raman spectra**

Here we illustrate the evolution of intensity in $aa$ and $ac$ geometries on cooling by computing the integral $I_{aa(ac)}(\omega^*) = \int_{0}^{\omega^*} \chi''_{aa(ac)}(\omega) d\omega$ (Fig. 5.7). For $\omega^* \to \infty$ this quantity is proportional to the static susceptibility in the respective geometry, while the $\omega^*$ dependence allows to understand the contribution of different frequency ranges.

For $aa$ polarization (Fig. 5.7a), one observes that at frequencies larger than 50 meV, the spectral weight gets suppressed on cooling below around 300 meV, but then recovers at
500 meV to an almost temperature-independent value. This is consistent with the absence of strong temperature dependence of the static $A_g$ susceptibility that has no instability in $\text{Ta}_2\text{NiSe}_5$. Moreover, this shows that unlike in a mean-field theory (see section S2 below) where the $A_g$ signal should vanish in the absence of the order parameter, the integral at 500 meV is roughly constant across $T_c$, consistent with the presence of signatures of the excitonic pairing (the pseudogap) well above $T_c$ observed in ARPES [295].

In $ac$ geometry, on the other hand, $I_{ac}(500\text{meV})$ is strongly dependent on temperature. However, $I_{ac}(\omega^*)$ appear to be almost parallel above around 30 meV, without any signs of redistribution as in $aa$ geometry. This suggests that the temperature dependence arises due to the contribution of the lower energies to the integral. Indeed, there is a strong enhancement at the lowest frequencies on cooling from 380 K to 310 K explained by the softening of the excitonic continuum, and a suppression on further cooling. The enhancement on cooling from 265 K to 35 K can be seen to arise from energies around 15 – 20 meV where a contribution of phonon “leakage” (which grows on cooling) from $aa$ geometry is prominent.
Overall, we have shown that the pronounced redistribution of the high-energy Raman response is characteristic of $aa$ geometry, but not $ac$ geometry, demonstrating that the emergence of the strong peak in the ordered phases, shown in Fig. 2e of the main text, is indeed specific for $aa$ geometry.

“Leakage” in high-energy Raman spectra at low temperatures

Here we demonstrate that a large part of the $ac$ Raman intensity (Fig. 2e) can be attributed to the change in the Raman selection rules below $T_c$. In analogy to the phonons, one may expect the intensity from $aa$ geometry to “leak” into $ac$ geometry and vice versa. As $aa$ intensity is significantly larger in the high-energy region than the $ac$ one, we can neglect the leakage of $ac$ into $aa$, and consider only the former effect. Consequently, we have analyzed $\chi''_{ac}(\omega) - p \cdot \chi''_{aa}(\omega)$, where $0 < p < 1$. Intriguingly, for $p = 0.07$ (Fig. 5.8), we observe the resulting intensity (shown in purple) to be featureless below around 310 meV, while for other values of $p$ a residual energy dependence in this region is observed. This coincidence of lineshapes up to a background constant below around 310 meV suggests that the “intrinsic” $ac$ intensity, corresponding to the interband transitions, is actually represented by the purple curve, Fig. 5.8. It follows then that not only the intensity in $ac$ geometry is

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Figure 5.7: The integral $\int_{0}^{\omega^*} \frac{\chi''_{ac(\omega)}(\omega)}{\omega} d\omega$ as a function of the Raman shift $\omega^*$ for $aa$ (a) and $ac$ (b) polarization geometries.
Figure 5.8: “ Leakage” analysis of the high-energy Raman data at 35 K. Blue line is the measured $ac$-polarization data; subtracting 7% of the $aa$-polarization data (red line) from the $ac$-polarization data one obtains an almost flat intensity below about 0.33 eV (purple line), suggesting that there is a 7% leakage between $aa$ and $ac$-polarized data at high-energies. The spectral resolution is 2.8 meV.

much weaker, but also that its lineshape is different, characterized by the appearance of intensity at higher energies than in $aa$ geometry. The latter observation is consistent with the prediction of the mean-field model, where the intensity in $aa$ geometry is expected to be peaked at the gap edge, while the one in $ac$ geometry only starts to grow at the gap edge and should be maximal at higher energies.

5.1.7 Theoretical details

Raman scattering in an excitonic insulator at low temperatures

We consider a model with an electron-like conduction band and hole-like valence band described by the hamiltonian

$$
\hat{H}_0 = \sum_{p, \sigma} \varepsilon_c(p) \hat{c}_{c, \sigma}^\dagger(p) \hat{c}_{c, \sigma}(p) + \varepsilon_v(p) \hat{c}_{v, \sigma}^\dagger(p) \hat{c}_{v, \sigma}(p),
$$

(5.7)

where the band operators at the $\Gamma$ point transform under irreducible representations $I_1$ and $I_2$ of the point group above $T_c - D_{2h}$, such that $I_1 \otimes I_2 \equiv B_{2g}$. The latter requires the hybridization between the two bands at the $\Gamma$ point to vanish; however, below $T_c$ the point-group symmetry is reduced to $C_{2h}$ such that $B_{2g}$ merges with the trivial $A_g$ representation into a single one, allowing for the $c - v$ hybridization at the $\Gamma$ point. Thus, the quantity
of the form $\langle \hat{c}_{c,\sigma}^{\dagger} \hat{c}_{v,\sigma'} \rangle$ may serve as the order parameter for the phase transition from $D_{2h}$ to $C_{2h}$. One needs to be make sure though, that the average does not break any additional symmetries. In particular, no spin anisotropy or magnetism have been observed in Ta$_2$NiSe$_5$, requiring $\langle \hat{c}_{c,\sigma}^{\dagger} \hat{c}_{v,\sigma'} \rangle = W \delta_{\sigma,\sigma'}$. Moreover, time-reversal symmetry that acts as a complex conjugation, if spin is ignored, requires $W$ to be real. This suggests that in contrast to true bosonic condensates, there is no $U(1)$ degeneracy of the order parameter in an excitonic insulator, that is instead reduced to $Z_2$. The general reason for that is that while there is a global $U(1)$ symmetry due to particle number conservation, the number of $c$ and $v$ electrons are not separately conserved (which would yield a $U(1) \times U(1)$ symmetry otherwise), suggesting that the exciton number is not a conserved quantity, i.e. $U(1) \times U(1)$ is initially broken to $U(1) \times Z_2$ already in the $D_{2h}$ phase. The mechanism of this breaking may be either due to pair-hopping interaction between bands, or coupling to phonons.

While most of the equations below are generic, we will use the following form of the dispersion to illustrate the results:

$$\varepsilon_c(p) \approx \frac{p_x^2 \pm p_0^2}{2m_c}; \quad \varepsilon_v(p) \approx -\frac{p_x^2 \pm p_0^2}{2m_v}, \quad (5.8)$$

where with the $+$ sign dispersion is semiconducting, while it is semimetallic for $-$ sign; here $p_0$ is equal for both bands due to the charge compensation condition. While the dispersion (5.8) is strictly one-dimensional, we assume that the transition itself would have three-dimensional character either due to terms neglected in (5.8) (corresponding to interchain hopping along $b$ and $c$ directions $t_{b,c}$), or due to the coupling to optical phonons or acoustic strain fields, that are expected to have a three-dimensional dispersion. Due to the layered structure of Ta$_2$NiSe$_5$ one may also expect that the three-dimensional character would be rather weak, with an extended 2D-like regime. However, due to discrete nature of the broken $Z_2$ symmetry, this is not expected to significantly reduce $T_c$ as even in strictly two dimensions the transition is allowed to occur.

We introduce a $2 \times 2$ “band space” and rewrite $\hat{H}_0$ using Pauli matrices $\tau_i$ and spinors
\[ \Psi_{p,\sigma} = (\hat{c}_{c,\sigma}(p), \hat{c}_{v,\sigma}(p)) : \]

\[ \hat{H}_0 = \sum_{p,\sigma} \Psi_{p,\sigma}^\dagger (E(p) + \xi(p)\tau_3)\Psi_{p,\sigma}; \]

\[ E(p) = \frac{\varepsilon_c(p) + \varepsilon_v(p)}{2}; \]

\[ \xi(p) = \frac{\varepsilon_c(p) - \varepsilon_v(p)}{2}. \]

In what follows we will omit \((p)\) in \(\xi(p), E(p)\), where that doesn’t lead to a confusion. At low temperatures, the mean field Hamiltonian including the excitonic order parameter \(W\) is

\[ \hat{H}_{MF} = \begin{bmatrix} \hat{c}_c(p) \\ \hat{c}_v(p) \end{bmatrix}^\dagger \begin{bmatrix} \varepsilon_c(p) & \ W \\ \ W & \varepsilon_v(p) \end{bmatrix} \begin{bmatrix} \hat{c}_c(p) \\ \hat{c}_v(p) \end{bmatrix}. \] (5.10)

Unlike in a superconductor \([303]\), the mean-field hamiltonian (5.10) explicitly conserves the total particle number \(N = \sum_p \hat{c}_c^\dagger p \hat{c}_c p + \hat{v}_v^\dagger p \hat{v}_v p\) and consequently vertex corrections for Raman scattering are not required to ensure it. Diagonalizing Eq. (5.10), one obtains the following eigenvalues and eigenvectors:

\[ \varepsilon_{\pm}(p) = E(p) \pm \sqrt{\xi^2(p) + W^2}; \]

\[ \Psi_{\pm}(p) = [u_{\pm}(p), v_{\pm}(p)]^T, \]

\[ u_{\pm}(p) = \pm \sqrt{\frac{1}{2} \left( 1 \pm \frac{\xi}{\sqrt{\xi^2 + W^2}} \right)} ; \] (5.11)

\[ v_{\pm}(p) = \sqrt{\frac{1}{2} \left( 1 \mp \frac{\xi}{\sqrt{\xi^2 + W^2}} \right)}. \]

The factors \(u_{\pm}, v_{\pm}\) are analogous to the BCS coherence factors in a superconductor.

We consider the Raman scattering in the non-resonant approximation, where the effective coupling of the electrons to the two-photon process is described by \(\sum_q \hat{R}^{ij} A_i(q) A_j(-q)\), where \(\hat{R}^{ij} = \sum_p \gamma^{ij}_{\alpha\beta} c_\alpha^\dagger p c_\beta(p)\) is the Raman vertex \([11]\), where we additionally neglect the momentum dependence of \(\gamma^{ij}_{\alpha\beta}\). The Raman susceptibility in the polarization geometry set by \(i\) and \(j\) is determined by the transition rate of the electronic system due to the perturbation by \(\hat{R}^{ij}\). The symmetry restricts the possible form of \(\hat{R}^{ij}\) \([11]\); for our case \(\hat{R}^{aa}\) has
to be of $A_g$ symmetry and $R^{ac} - B_{2g}$ symmetry. Taking these constraints into account the
Raman vertices take the form

\[ \hat{R}_{aa} = \sum_p g_c \hat{c}_p \hat{c}_p + g_v \hat{v}_p \hat{v}_p, \quad \hat{R}_{ac} = g_{ac} \sum_p \hat{c}_p \hat{v}_p + \hat{v}_p \hat{c}_p, \]  

(5.12)

where $\hat{R}_{aa}$ corresponds to $aa$ polarization geometry and $\hat{R}_{ac}$ to $ac$ geometry. Using Fermi’s
Golden rule we evaluate the probability to find:

\[ 2\pi \int |\langle + | \hat{R} | - \rangle|^2 \delta(\varepsilon_+(\mathbf{p}) - \varepsilon_-(\mathbf{p}) - \omega) \frac{2d\mathbf{p}}{(2\pi)^D}, \]

where we assumed that the system is fully gapped, i.e. $\varepsilon_+(\mathbf{p}) > 0 > \varepsilon_-(\mathbf{p})$ for all values of $\mathbf{p}$. Under this assumption the resulting expression does not depend on $E(\mathbf{p})$.

**Semimetallic case**

In this case the bands are assumed to cross in the normal state, similar to the Fig. 1d of
the main text. In this case, one can linearize the dispersion near the band crossing $\xi(\mathbf{p}) = 0$, such that $\frac{2d\mathbf{p}}{(2\pi)^D} \approx \nu_0 d\xi$, $\nu_0$ being the density of states. Using the definition of the Raman vertex (5.12) and the eigenvectors obtained in (5.11) one gets

\[ I_{R_{ac}} \sim \frac{4\pi g_{ac}^2 \nu_0 \sqrt{\omega^2/4 - W^2}}{\omega} \theta(\omega - 2W); \]

\[ I_{R_{aa}} \sim \frac{\pi(g_c - g_v)^2 \nu_0 W^2}{\omega \sqrt{\omega^2/4 - W^2}} \theta(\omega - 2W), \]  

(5.13)

where we used that $u_+ v_+ + u_- v_- = \frac{\xi}{\sqrt{\xi^2 + W^2}}$; $u_+ u_- + v_+ v_- = 0$; $u_+ u_- - v_+ v_- = -\frac{W}{\sqrt{\xi^2 + W^2}}$

and $\delta(2\sqrt{\xi^2 + W^2} - \omega) = \frac{\delta(\xi \pm \sqrt{\omega^2/4 - W^2})}{2\xi/\sqrt{\xi^2 + W^2}}$. In the absence of the order parameter ($W = 0$), the Hamiltonian (5.10) would respect the conservation of $c$ and $v$ particle numbers separately, leading to a zero Raman response in $aa$ geometry, which couples to densities of $c$ and $v$ fermions. Also, one notices that the $aa$ intensity vanishes when $g_c = g_v$, i.e. when the Raman vertex (5.12) becomes just the total density operator. This further shows that particle number conservation is respected in our calculation.

**Semiconducting case**

In this case there is a direct gap between the two bands without hybridization. We use
the 1D dispersion relation 5.8 with the “+” sign, such that the direct gap is $2E_0 = \frac{\mu_0}{\mu}$. 

where $\mu = 2m_cm_v/(m_c + m_v)$ is the effective mass. For the Raman intensity one gets then

$$I_{Rac} \sim 2g_{ac}^2 \int \frac{(p^2/(2\mu) + E_0)^2}{(p^2/(2\mu) + E_0)^2 + W^2} \delta(2\sqrt{(p^2/(2\mu) + E_0)^2/4 + W^2 - \omega}) dp,$$

$$I_{Raa} \sim \frac{(g_c - g_v)^2}{2} \int \frac{W^2}{(p^2/(2\mu) + E_0)^2 + W^2} \delta(2\sqrt{(p^2/(2\mu) + E_0)^2 + W^2 - \omega}) dp.$$ 

The result of the integration is:

$$I_{Rac} \sim 2g_{ac}^2 \frac{\sqrt{2\mu}}{\omega} \frac{\sqrt{\omega^2/4 - W^2 - E_0}}{\sqrt{\omega^2/4 - W^2}} \theta(\omega - 2\sqrt{W^2 + E_0^2}),$$

$$I_{Raa} \sim \frac{(g_c - g_v)^2}{2} \frac{\sqrt{2\mu}}{\omega} \frac{\sqrt{\omega^2/4 - W^2 - E_0}}{\sqrt{\omega^2/4 - W^2}} \theta(\omega - 2\sqrt{W^2 + E_0^2}).$$

Most important difference from the semimetallic case is that intensities in both geometries show singularities at the gap edge $\omega = 2\sqrt{W^2 + E_0^2}$. The intensity at the gap edge in $aa$ geometry is additionally multiplied by a factor $W^2/E_0^2$. Thus, for the case $E_0 \ll W$ the intensity in the $aa$ geometry is expected to dominate. However, for strongly semiconducting case $E_0 \gg W$, the singularity in the $aa$ geometry is expected to be greatly suppressed by $W^2/E_0^2$, at odds to the experimental observation in Fig. 2c of the main text. While the shapes of the singularities here are related to the 1D form of the dispersion taken, we expect the qualitative arguments on the intensity dependencies on the order parameter value to hold even when the effects of non-1D dispersion are taken into account, as those are expected mostly to smear the singularity at the band edge.

Overall, the absence of a discernible singularity in Fig. 2c in $ac$ geometry strongly favors the semimetallic state.

**Effects of a nonlocal order parameter**

The non-locality of the order in real space results in the order parameter in momentum space being momentum-dependent, i.e. $W(p)$. Away from $\Gamma$ point, time reversal and inversion symmetry combined require only that $W(p) = W^*(-p)$, and thus $W(p)$ can be complex, generically written as $W(p) = |W|(p)e^{i\phi(p)}$, where $\phi(p) = -\phi(-p)$. Generalizing 5.11...
with the momentum-dependent order parameter is straightforward and results in the new
eigenvalues and eigenvectors:

\[
\epsilon_{\pm}(p) = E(p) \pm \sqrt{\xi^2(p) + |W|^2(p)};
\]

\[
\Psi_{\pm}(p) = [u_{\pm}(p), v_{\pm}(p)]^T,
\]

\[
u_{\pm}(p) = \pm \sqrt{\frac{1}{2} \left( 1 \mp \frac{\xi}{\sqrt{\xi^2 + |W|^2(p)}} \right)};
\]

\[
v_{\pm}(p) = e^{-i\phi(p)} \sqrt{\frac{1}{2} \left( 1 \mp \frac{\xi}{\sqrt{\xi^2 + |W|^2(p)}} \right)}.
\]

(5.15)

For the semiconducting case, assuming the \( p \) dependence of \( |W|(p) \) does not shift the gap
minimum from the \( \Gamma \) point \( \phi(0) = 0 \) and the results for the Raman intensities are the
same as described above. For the semimetallic case, however, the result changes due to the
presence of a nonzero phase. Assuming the gap to open at \( p_F \) and a quasi-one dimensional
band structure (consistent with ARPES experiments \([309–311]\)), we get close to the gap
edge

\[
I_{Rac} \sim 4\pi g_{ac}^2 \nu_0 \left( \cos^2(\phi(p_F)) \frac{\sqrt{\omega^2/4 - |W|^2(p_F)}}{\omega} + \frac{1}{2} \sin^2(\phi(p_F)) \frac{\omega}{\sqrt{\omega^2/4 - |W|^2(p_F)}} \right) \theta(\omega - 2W);
\]

\[
I_{Raa} \sim \frac{\pi(g_c - g_v)^2 \nu_0 |W|^2(p_F)}{\omega \sqrt{\omega^2/4 - |W|^2(p_F)}} \theta(\omega - 2|W|(p_F)).
\]

(5.16)

One observed that while \( I_{Raa} \) has not changed, \( I_{Rac} \) now contains a contribution, that
diverges at the gap edge with its amplitude proportional to \( \sin^2(\phi(p_F)) \). This result is not
expected to affect the results qualitatively as \( p_F \) in \( Ta_2NiSe_5 \) is quite small and \( \sin^2(\phi(p_F)) \sim k_F^2 a_0^2 \), \( a_0 \) being the lattice constant: for \( k_F \sim 0.1 \text{ Å}^{-1} \) \([309]\) and \( a_0 = 3.49 \text{ Å}[308] \), one gets
the estimate \( k_F^2 a_0^2 \) of the order \( 0.12 \ll 1 \). This estimate holds for, e.g. the recently proposed
\([293]\) case of \( W(k) = W_0 e^{ikx} \). Additionally, this effect of non-locality can contribute to the
apparent “leakage” of the \( aa \) intensity discussed.
Corrections to the Raman vertex in the ordered state

Strictly speaking, at $T < T_c$ the irreps $A_g$ and $B_{2g}$ mix into a single $A_g$ representation and thus the generic form of the Raman vertex operators may mix the ones at $T > T_c$. However, this mixing is apparently rather small in the system, as the ratio of intensities in cross polarization vs. the one in parallel polarizations is below $1/10$. A possible explanation for that is that in the effective mass approximation the appearance of the order parameter does not directly affect the mass.

Effects of disorder

Additionally, a remnant low-energy electronic continuum contribution is observed at low temperatures in Fig. 3g of the main text. Here we show that it can be attributed to the effect of disorder. In particular, we model disorder by a varying chemical potential $V(r)\tau_0$. If considered in Thomas-Fermi approximation to (5.10), is is seen that local $V > W$ creates a metallic “puddle”; due to the absence of translational invariance metals are expected to result in a Drude form of the Raman susceptibility at $q = 0$ due to particle-hole excitations [11], as is observed in the experiment.
5.2 Lattice dynamics of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$

In a narrow-gap semiconductor or semimetal, if the exciton binding energy exceeds the band gap, the Coulomb attraction between electrons and holes favors spontaneous formation of a macroscopic number of excitons. These bosonic quasiparticles then form a coherent state, opening an interaction-induced gap and leading to a insulating phase, named excitonic insulator \[272–274\]. If the electron and hole states belong to bands of different symmetry, the resulting excitonic insulator state is expected to break the crystal lattice symmetry.

Consider the case of a semimetal. If the band gap is indirect, i.e. the valence band maximum and the conduction band minimum are located at different places in the \(k\)-space, condensation of excitons leads to a charge-density-wave (CDW) state and accompanying crystal distortion which breaks translational symmetry \[274\]. The CDW wavevector is then given by the spanning vector that connects the valence band maximum to the conduction band minimum. One such example is semimetal 1T-TiSe$_2$, which has been proposed to hold an excitonic insulating state below 190 K \[279, 322–324\]. In contrast, if the band gap is direct, excitonic condensation only results in lattice distortion which breaks point-group symmetry. In this situation, the size of the unit cell does not change but its shape changes. Ta$_2$NiSe$_5$ is a candidate for excitonic insulator of this kind.

Ta$_2$NiSe$_5$ shows a second-order structural phase transition at \(T_c = 326\) K \[285, 288\]. In the high temperature phase, this material has a orthorhombic structure (point group \(D_{2h}\)); in the low-temperature phase, the structural is monoclinic (point group \(C_{2h}\)) with the angle \(\beta\) between \(a\) and \(c\) directions deviating from 90°, Fig. 5.9. Below \(T_c\), the valence-band top flattens as discovered by angle-resolved photoemission spectroscopy (ARPES) studies \[294, 295, 298\]. Band flatness at low temperature is viewed as a characteristic feature of the excitonic insulator ground state. Moreover, studies of nonequilibrium dynamics have demonstrated photoinduced enhancement of excitonic order \[325, 326\], photoinduced multistage phase transitions \[327\], ultrafast reversal of excitonic order \[328\], and coherent
order-parameter oscillations [329].

The lattice degrees of freedom play an important role in the physics of Ta$_2$NiSe$_5$. In particular, the orthorhombic-to-monoclinic structural change can be induced via electron-phonon coupling [292] even if the origin of the transition is excitonic [293]. Moreover, a recent study combining ultrafast experiments with calculations proposes that the phase transition in Ta$_2$NiSe$_5$ is structural in its nature [300]. Thus, understanding the underlying physics of excitonic insulator candidates requires the lattice dynamics to be examined in a detailed way. Interestingly, substitution of Se with S results in a whole family of compounds Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$, where the orthorhombic-to-monoclinic transition has been suggested to be suppressed with $x$ [285]. While it is known, that S substitution leads to an enhanced direct band gap [330], which is detrimental to the EI state, its effects on the lattice modes has not been systematically studied.

Because the inversion symmetry of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ is preserved across $T_c$, the soft mode of this zero-wavevector structural transition, if any, is Raman active. Polarization resolved low frequency Raman spectroscopy, therefore, is particularly suitable for studying the physics of the phase transition, and for evaluating the contribution of the lattice vibrations to the transition. This experimental method offers both the high energy resolution and the ability to selectively probe bosonic excitations in different symmetry channels [9].
In this section, we present a systematic study of the lattice dynamics for the family of $\text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)_{5}$ ($x = 0, 0.25, 0.67, \text{ and } 1$) pristine crystals and alloys to quantitatively explore the spectral parameters of the phonons. We find the change of selection rules, indicating an orthorhombic-to-monoclinic structural transition at $T_c(x)$, which is finite for all $x$. The transition temperature $T_c(x)$ and the magnitude of lattice distortion both decrease with sulfur concentration $x$.

For $\text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)_{5}$ with $x \leq 0.67$, the two lowest-energy symmetry-breaking $B_{2g}$ phonon modes exhibit strong asymmetric lineshape above the transition temperature, resulting from the coupling between these modes and an excitonic continuum of the same symmetry. We develop an extended model to analyze the physics of this Fano-type interference effect. Using this model, we disentangle the excitonic and phononic contributions to the Raman response, and illustrate the effect of the coupling between them: apart from renormalizing the bare phononic and excitonic responses, this effect also results in an additional interference term in the total Raman response. We find that the $B_{2g}$ phonon modes exhibit no intrinsic softening on cooling towards the transition temperature. In contrast, the excitonic response shows clear soft-mode behavior [6, 8]. Additionally, many modes exhibit an anomalous increase in linewidth above $T_c$, suggesting the closing of the EI gap. For $\text{Ta}_2\text{NiSe}_5$ below $T_c$, we also observe signatures of the acoustic excitations with finite momenta, enabled by the formation of a quasi-periodic structure of domain walls.

For $\text{Ta}_2\text{NiS}_5$, on the contrary, the phonon modes in the symmetry-breaking channel maintain symmetric lineshape, but their frequency anomalously decreases upon cooling. Because the structural change for $\text{Ta}_2\text{NiS}_5$ is very weak, no anomaly of phonon frequency or width is detected around its structural transition temperature.

For all compositions, we find that most phonons exhibit strong dependence of their intensity on temperature, and present arguments in favor of this being a result of a coupling to electronic excitations.
Additionally, we perform density functional theory (DFT) calculations of the lattice dynamics for Ta$_2$NiSe$_5$ and Ta$_2$NiS$_5$. The phonon frequencies agree well with the experiment, and the obtained displacement patterns of the optical modes allow to explain the differences of the couplings of the three non-symmetric phonons to the excitonic continuum.

Finally, we demonstrate that our results are consistent with the modes observed in time-resolved experiments. We show however, that the signatures of the Fano-shaped phonons and the excitonic continuum above $T_c$ may be hard to observe in that type of experiments.

### 5.2.1 Experimental

Single crystals of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family were grown by chemical vapor transport method. Elemental powders of tantalum, nickel, selenium and sulfur were mixed with stoichiometric ratio and then sealed in an evacuated quartz ampule with a small amount of iodine as the transport agent. The mixture was placed in the hot end of the ampule (∼950°C) under a temperature gradient of about 10°C/cm. After about a week mm-sized needle-like single crystals were found at the cold end of the ampule. The crystals are shiny and cleave easily. We used x-ray diffraction and electron dispersive X-ray spectroscopy to verify the exact composition of the crystals and their uniformity. The samples for resistance and Raman measurements are from the same batch.

The resistance is measured along a axis in a four-probe configuration using a Quantum Design PPMS system.

The TEM images of domain structures are taken on a FEI Titan Themis G2 system using a Gatan double-tilt cryostage.

For Raman measurements, the samples were cleaved in ambient conditions to expose the $ac$ plane; the cleaved surfaces were then examined under a Nomarski microscope to find a strain-free area. Raman-scattering measurements were performed in a quasi-back-scattering geometry from the samples mounted in a continuous helium-gas-flow cryostat.

For acquisition of the low frequency Raman response required for this study, we used a
Table 5.1: The Raman selection rules in the high-temperature orthorhombic (point group \(D_{2h}\)) and low-temperature monoclinic (point group \(C_{2h}\)) phases. Upon the reduction of symmetry from \(D_{2h}\) to \(C_{2h}\), the \(A_g\) and \(B_{2g}\) irreducible representations of \(D_{2h}\) group merge into the \(A_g\) irreducible representation of \(C_{2h}\) group.

<table>
<thead>
<tr>
<th>Scattering Geometry</th>
<th>Symmetry Channel ((D_{2h} \text{ group}))</th>
<th>Symmetry Channel ((C_{2h} \text{ group}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>aa</td>
<td>(A_g)</td>
<td>(A_g)</td>
</tr>
<tr>
<td>ac</td>
<td>(B_{2g})</td>
<td>(A_g)</td>
</tr>
</tbody>
</table>

custom fast f/4 high resolution 500/500/660 mm focal lengths triple-grating spectrometer with 1800 \(\text{mm}^{-1}\) master holographic gratings comprised of (i) aberration corrected subtractive stage providing a reliable 12 orders-of-magnitude stray light rejection at as low frequency as 4 \(\text{cm}^{-1}\) from the elastic line, (ii) a third stage monochromator, and (iii) a liquid-nitrogen-cooled charge-coupled device (CCD) detector (Princeton Instruments). All the acquired data were corrected for the spectral response of the spectrometer. Three slit configurations were used: 100 \(\mu\text{m}\) slit width providing 0.19 \(\text{meV}\) spectral resolution; 50 \(\mu\text{m}\) slit width rendering 0.10 \(\text{meV}\) spectral resolution; and, for high resolution data, 25 \(\mu\text{m}\) slit width rendering 0.06 \(\text{meV}\) spectral resolution.

For polarization optics, a Glan-Taylor polarizing prism (Melles Griot) with a better than \(10^{-5}\) extinction ratio to clean the laser excitation beam and a broad-band 50 mm polarizing cube (Karl Lambrecht Corporation) with an extinction ratio better than 1:500 for the analyzer was used. Two polarization configurations were employed to probe excitations in different symmetry channels. The relationship between the scattering geometries and the symmetry channels [9] is given in Table 5.1.

The 647 nm line from a Kr\(^+\) ion laser was used for excitation. Incident light was focused to an elongated along the slit direction 50×100 \(\mu\text{m}^2\) spot. For data taken below 310 K, laser power of 8 mW was used. To reach temperature above 310 K, we kept the environmental temperature at 295 K and increased laser power to reach higher sample temperature in the excitation spot. All reported data were corrected for laser heating in two mutually consistent ways: (i) by Stokes/anti-Stokes intensity ratio analysis, based on the principle of detailed
balance, (ii) by checking laser power that is inducing the phase transition. In addition to that, we performed a thermoconductivity model calculation that suggests a linear scaling of the heating rate with the beam spot size.

The first-principle calculations were performed using DFT within Projector Augmented-Wave (PAW) formalism \[331\] and Perdew-Burke-Ernzerhof (PBE) parametrized exchange-correlation energy functional \[332\]. For Ta$_2$NiSe$_5$, we used the implementation of the Quantum ESPRESSO package \[333\], using the pseudopotentials generated by Dal Corso \[334\] and with grimme-d3 Van-der-Waals correction \[335\] included. For Ta$_2$NiS$_5$, the implementation of the Vienna Ab initio Simulation Package (VASP) code \[229, 336\] was used. The phonon frequencies for both cases were calculated by finite displacement method as implemented in PHONOPY \[337\]. The initial structures subject to relaxation for Ta$_2$NiSe$_5$ and Ta$_2$NiS$_5$ have been taken from experiments on the high-temperature orthorhombic phase, Ref.\[338\] and Ref.\[339\], respectively.

5.2.2 Overview

In this section we show an overview of the phonon spectra of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family, and compare the measured phonon frequencies at low temperatures with the calculated values.

The phonon spectra of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family ($x=0$, 0.25, 0.67, and 1) are summarized in Fig. 5.10. For stoichiometric compositions at high temperature, we observe 8 modes in $aa$ geometry and 3 modes in $ac$ geometry, in agreement with the $8 \, A_g$ and $3 \, B_{2g}$ Raman-active phonon modes expected in the high-temperature orthorhombic phase (space group $Cmcm$): the $A_g$ modes appear in $aa$ scattering geometry and the $B_{2g}$ modes in $ac$ scattering geometry [Table. 5.1]. Except for the Ta$_2$NiS$_5$ sample, the two lowest-energy $B_{2g}$ modes, $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$, exhibit strongly broadened and asymmetric lineshapes at high temperature. This anomalous broadening is almost absent for Ta$_2$NiS$_5$ (note the logarithmic intensity scale in Fig. 5.10).

At low temperature, a transition into a monoclinic phase (space group $C2/c$) occurs.
Figure 5.10: Raman response $\chi''$ in the $aa$ and $ac$ scattering geometries for $\text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)_5$ family, plotted in semi-log scale. The phonon modes are classified by the $A_g$ and $B_{2g}$ irreducible representations of $D_{2h}$ point group. The $A_g$ and $B_{2g}$ modes of $\text{Ta}_2\text{NiSe}_5$ are labeled by red and green colors, respectively; the $A_g$ and $B_{2g}$ modes of $\text{Ta}_2\text{NiS}_5$ are labeled by purple and blue colors, respectively. For the samples with $x = 0.25$ and $0.67$, the modes are labeled by the color scheme of $\text{Ta}_2\text{NiSe}_5$ if its energy is close to that of $\text{Ta}_2\text{NiSe}_5$ modes, or the color scheme of $\text{Ta}_2\text{NiS}_5$ if its energy is close to that of $\text{Ta}_2\text{NiS}_5$ modes. The spectral resolution is $0.19\text{ meV}$ for the $ac$ spectra at high temperature, and $0.06\text{ meV}$ for the $ac$ spectra at $35 \text{ K}$ and all $aa$ spectra.
Table 5.2: Comparison of the experimentally measured phonon energies at 35 K and the calculated values for Ta$_2$NiSe$_5$ and Ta$_2$NiS$_5$. Unit is meV; modes are identified by their irreducible representations in the orthorhombic phase, where 8 $A_g$ modes and 3 $B_{2g}$ modes are expected.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Ta$_2$NiSe$_5$ Exp.</th>
<th>Ta$_2$NiSe$_5$ Calc.</th>
<th>Ta$_2$NiS$_5$ Exp.</th>
<th>Ta$_2$NiS$_5$ Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$ (1)</td>
<td>4.22</td>
<td>4.22</td>
<td>5.01</td>
<td>4.82</td>
</tr>
<tr>
<td>$B_{2g}$ (1)</td>
<td>8.66</td>
<td>7.61</td>
<td>6.50</td>
<td>7.66</td>
</tr>
<tr>
<td>$A_g$ (2)</td>
<td>12.28</td>
<td>11.87</td>
<td>16.13</td>
<td>15.18</td>
</tr>
<tr>
<td>$B_{2g}$ (2)</td>
<td>15.25</td>
<td>10.14</td>
<td>16.41</td>
<td>16.20</td>
</tr>
<tr>
<td>$A_g$ (3)</td>
<td>16.76</td>
<td>15.53</td>
<td>19.13</td>
<td>18.27</td>
</tr>
<tr>
<td>$B_{2g}$ (3)</td>
<td>18.38</td>
<td>19.39</td>
<td>32.96</td>
<td>33.23</td>
</tr>
<tr>
<td>$A_g$ (4)</td>
<td>22.17</td>
<td>21.91</td>
<td>33.82</td>
<td>33.82</td>
</tr>
<tr>
<td>$B_{2g}$ (4)</td>
<td>24.14</td>
<td>24.09</td>
<td>36.50</td>
<td>36.36</td>
</tr>
<tr>
<td>$A_g$ (5)</td>
<td>27.02</td>
<td>26.34</td>
<td>40.07</td>
<td>40.13</td>
</tr>
<tr>
<td>$B_{2g}$ (5)</td>
<td>29.39</td>
<td>29.01</td>
<td>43.10</td>
<td>43.07</td>
</tr>
<tr>
<td>$A_g$ (6)</td>
<td>36.32</td>
<td>37.47</td>
<td>49.49</td>
<td>49.62</td>
</tr>
<tr>
<td>$A_g$ (7)</td>
<td>36.32</td>
<td>37.47</td>
<td>49.49</td>
<td>49.62</td>
</tr>
</tbody>
</table>

In the low-temperature phase, because of the mirror symmetry breaking, all Raman-active phonon modes appear in both $aa$ and $ac$ scattering geometries [Table. 5.1]. All of the expected Raman-active modes were observed: they are identified by dashed lines in Fig. 5.10; the additional weak spectral features result from the second-order scattering. For example, the weak feature at 34.1 meV in $aa$ scattering geometry for Ta$_2$NiSe$_5$ corresponds to a second-order scattering feature of the 16.8 meV $B_{2g}$ mode.

The measured phonon frequencies for Ta$_2$NiSe$_5$ and Ta$_2$NiS$_5$ at 35 K generally match well with the calculated values [Table. 5.2]. As the calculations were carried out in the orthorhombic phase, this suggests that monoclinicity by itself does not strongly affect the phonon frequencies. Larger than 10% discrepancies between the measured and calculated values appear only for the $B_{2g}$ (1) and $B_{2g}$ (2) modes of Ta$_2$NiSe$_5$ and the $B_{2g}$ (1) mode of Ta$_2$NiS$_5$. These modes exhibit an anomalous behavior that can be attributed to their strong coupling to the excitons.

For the alloy compositions ($x = 0.25$ and 0.67), the phonon modes show larger linewidth compared with that for the stoichiometric compositions. Moreover, the $B_{2g}$ (3) and $A_g$ (3)-$A_g$ (8)
modes exhibit two distinct frequencies: one close to the frequency of that mode in Ta$_2$NiSe$_5$, and the other close to the frequency in Ta$_2$NiS$_5$. Such behavior is commonly observed for alloys in which the frequencies of the same phonon mode in the two end-point materials differ substantially [340–342]. The doping dependence of the phonon frequencies measured at 35 K is presented in Fig. 5.11. The frequencies of the phonon modes for Ta$_2$NiSe$_5$ are consistent with the recent experimental studies [304, 343–346] and the calculated values [299].

5.2.3 Phase transition

In this section we deduce the phase transition temperatures from the observed change in selection rules in Raman response and compare the results with the resistance measurements.

Below $T_c$, the 11 phonon modes are allowed by symmetry to appear in both scattering
Figure 5.12: Temperature dependence of the integrated intensity of $A_g^{(1)}$ and $B_g^{(1)}$ modes in the “forbidden” scattering geometry ($ac$ and $aa$, respectively) for (a) $\text{Ta}_2\text{NiSe}_5$, (b) $\text{Ta}_2\text{NiS}_5$, (c) $\text{Ta}_2\text{Ni(Se}_{0.75}\text{S}_{0.25})_5$, and (d) $\text{Ta}_2\text{Ni(Se}_{0.33}\text{S}_{0.67})_5$.

Geometries [Table 5.1]; thus, 8 additional modes appear in $ac$ geometry and 3 in $aa$. We call the appearance of phonon modes below $T_c$ in the orthogonal to allowed above $T_c$ scattering geometry as phonon-mode “leakage”. As shown in Fig. 5.10, all four samples exhibit phonon-mode “leakage” at low temperature, indicating presence of a point group symmetry breaking structural phase transition.

In Fig. 5.12 we show the temperature dependence of the “leakage” of $A_g^{(1)}$ and $B_g^{(1)}$ modes for $\text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)_5$ family. The “leakage” of other modes is given in Sec. 5.2.5. For each sample, the “leakage” of different modes appear below the same temperature.

We assign the temperature of the “leakage” onset as the structural phase transition temperature $T_c$. The phase transition temperatures for $\text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)_5$ family are given in Table 5.3. The transition temperatures $T_c(x)$ decrease with sulfur doping $x$. Moreover, for larger sulfur content $x$ the phonon intensities in the “forbidden” scattering geometry also decrease. This quantity is proportional to the square of the order parameter (OP), which can be represented by, e.g., the deviation of the angle $\beta$ between $a$ and $c$ axes [Fig. 5.9 (b)] from 90°. While the general monotonic growth of the leakage intensity on cooling is consistent with these expectations, the details of temperature dependence can vary for different modes [Fig. 5.12(a)]. The decreasing trend of the phonon intensity in the “forbidden” scattering
Table 5.3: The structural phase transition temperature of \( \text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)_{5} \) family determined by observing phonon-mode “leakage” in Raman spectra.

<table>
<thead>
<tr>
<th>Sulfur Content ( x )</th>
<th>Transition Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>328±5</td>
</tr>
<tr>
<td>0.25</td>
<td>260±10</td>
</tr>
<tr>
<td>0.67</td>
<td>170±10</td>
</tr>
<tr>
<td>1</td>
<td>120±10</td>
</tr>
</tbody>
</table>

geometry with sulfur content \( x \) therefore indicates that the structural distortion becomes weaker with higher sulfur concentration.

A complementary way to determine the phase transition temperature was demonstrated in [285], where anomalies in the temperature dependence of resistance have been detected at \( T_c(x) \). In Fig. 5.13 we show the resistance data analysis for the samples from the same batch as used for the Raman measurements. For \( \text{Ta}_2\text{NiSe}_5 \) and \( \text{Ta}_2\text{Ni(Se}_{0.75}\text{S}_{0.25})_5 \), the temperature at which the temperature derivative of resistance displays a kink and that of transport activation gap shows a peak, coincides with the Raman-determined transition temperature. For \( \text{Ta}_2\text{Ni(Se}_{0.33}\text{S}_{0.67})_5 \) and \( \text{Ta}_2\text{NiS}_5 \), though, the features in resistance data are less pronounced. The latter can be anticipated from their much more insulating character, potentially masking a small change of resistance due to transition on top of a large background resistance.

5.2.4 Fano Interference in the \( B_{2g} \) symmetry channel

In this section we analyze the asymmetric lineshape of the \( B_{2g} \)-symmetry phonon modes observed for \( x < 0.7 \) in the high temperature phase. We describe the asymmetric lineshape and its temperature dependence in SubSubSec. 5.2.4. To fit the spectra, we develop a generalized Fano model, discussed in SubSubSec. 5.2.4, in which the asymmetric broadening results from the coupling of the phonon modes to an excitonic continuum. Besides the optical phonon modes, the excitonic continuum also couples to the acoustic phonon mode. We discuss how such coupling enhances the transition temperature \( T_c(x) \), and leads to softening of the \( B_{2g} \)-symmetry acoustic mode in SubSubSec. 5.2.4. The appearance of
Figure 5.13: Temperature dependence of the resistance along a axis for Ta$_2$Ni$_5$(Se$_{1-x}$S$_x$)$_5$ family. (a) The resistance, plotted in semi-log scale. (b) The temperature derivative of resistance, plotted in semi-log scale. (c) The temperature derivative of the transport activation gap $E_g = k_B T \log_{10} \left[ R(T)/R(360K) \right]$. The transition temperatures determined from Raman measurements are marked by dashed lines for comparison.
a quasi-periodic domain wall structure below $T_c$ introduces additional complexity, and in SubSubSec. 5.2.4, we discuss how the fitting model must be modified to account for low-energy spectral features which are absent above $T_c$. The fitting results for Ta$_2$NiSe$_5$, relevant to the excitonic continuum, are presented and interpreted in SubSubSec. 5.2.4 (those related to the intrinsic phonon properties are shown later in SubSec. 5.2.5). It is demonstrated that the strengths of the interactions between individual phonons and excitonic continuum are consistent with the displacement patterns deduced from ab initio calculations. For comparison, the fitting results for the alloy compositions are given in SubSubSec. 5.2.4.

Temperature dependence of asymmetric Fano lineshapes

The temperature dependence of the spectra measured in ac scattering geometry for Ta$_2$NiSe$_5$ is shown in Fig. 5.14. Above $T_c$, the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes have noticeably asymmetric lineshapes, while the lineshape of the $B_{2g}^{(3)}$ mode remains quite symmetric. Upon approaching $T_c$ on cooling, the spectral weight of low-frequency continuum displays an enhancement, and the apparent linewidths of the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes increase. Below $T_c$, the modes recover the conventional Lorentzian lineshapes.

An asymmetric lineshape arises due to Fano interference when a sharp phonon interacts with a broad continuum. In this case, the continuum is due to the overdamped exciton fluctuations [6, 8], and the exciton-phonon interaction is caused by modulation of electronic bands near the Fermi surface by the $B_{2g}$-symmetry lattice vibrations.

The generalized Fano model for data above $T_c$

We describe the Fano model that includes the coupling between the $B_{2g}^{(1-3)}$ phonon modes and the continuum; more details can be found in Appendix 5.2.9.

We first discuss the Raman response of the phonons. The Raman scattering intensity is related to the fluctuation spectrum of the phonon coordinate $\langle Q_\omega Q_{-\omega} \rangle$ [347], which is given by the imaginary part of the phonon coordinate susceptibility $\chi_p''(\omega)$ times the Bose
Figure 5.14: Temperature dependence of Raman response $\chi''$ in the $ac$ scattering geometry for Ta$_2$NiSe$_5$. The data is shown by black dots, along with the Fano fits [Eq. (5.51)] shown as red curves. The spectral resolution is 0.19 meV for panels (a-e), 0.10 meV for panels (f-g), and 0.06 meV for panel (h). The Fano model describes the coupled dynamics of the $B_{2g}^{(1)}$-$B_{2g}^{(3)}$ phonon modes and the overdamped excitonic continuum. The bare phonon modes [Eq. (5.17)] are shown by green curves, and the bare excitonic continuum [Eq. (5.18)] is shown by blue curves. Below $T_c$, especially at 300 K, additional spectral weight is observed at low energies, resulting from the emergence of finite-energy acoustic modes due to scattering off structural domain walls (see Fig. 5.17). The purple curves show the coupled response of the acoustic modes and the excitonic continuum. As the excitonic continuum is suppressed on cooling below $T_c$, the lineshapes of the phonons become essentially symmetric.
factor. The phononic Raman response function consequently has the form:

$$\chi_p''(0)(\omega) = \frac{4t_p^2\omega\omega_p\gamma_p}{(\omega^2 - \omega_p^2)^2 + 2\gamma_p^2(\omega^2 + \omega_p^2) + \gamma_p^4},$$

(5.17)

where $t_p$ is the light-scattering vertex for the phonon, $\omega_p$ is the mode’s bare frequency, and $\gamma_p$ is the half width at half maximum (HWHM) which is related to the oscillator lifetime.

An exciton in a gapped system (a semiconductor or insulator) is expected to have a sharply peaked response at the exciton energy described by a bosonic response function similar to the Eq. (5.17). The most important difference for a semimetal is the presence of a gapless continuum of interband particle-hole excitations enabling the decay of the $q=0$ exciton into unbound particle-hole pairs (Landau damping). To describe the continuum in data, we find it sufficient to assume a purely relaxational dynamics (corresponding to strong overdamping) for the excitonic response. This leads to the form

$$\chi_e''(0)(\omega) = \frac{t_e^2\omega}{(\omega_e^2/\gamma_e)^2 + \omega^2},$$

(5.18)

where $t_e$ controls the overall intensity determined by the light-scattering vertex and the excitonic density of states, $\omega_e$ is the frequency of the over-damped excitation, and $\gamma_e$ is the relaxation rate, typically much larger than $\omega_e$. For the purpose of the fitting description below $\Omega_e(T) = \omega_e^2/\gamma_e$ is a single parameter denoting the temperature-dependent peak frequency in the broad response function $\chi_e''(\omega)$. For a purely excitonic transition this peak represents the soft mode: $\Omega_e(T_{el}) = 0$ is the condition for bare excitonic transition temperature at $T_{el}^{cd}$, where the static excitonic susceptibility $\chi_e(0)$ diverges (see Eq. (5.70)).

In the absence of the exciton-phonon interaction between the modes the respective phononic and excitonic responses [Eqs.(5.17) and (5.18)] simply sum up. The exciton-phonon interaction, however, couples these dynamical responses: in particular, a bilinear coupling of the exciton and the $B_{2g}$ phonon coordinates is expected [292] (the bare phonons are diagonal normal modes and thus no bilinear interaction between them is present). The resulting response can be obtained by solving the coupled equations of motion. Each of the responses $\chi_p''(\omega)$ and $\chi_e''(\omega)$ get renormalized by the interaction, and in addition, the
response of the phonon coordinate to the exciton one, $\chi''(\omega)$, becomes finite. The latter leads to an essential interference term in the total Raman response function [348–350].

To appreciate the effect of renormalization, we first consider a simplified case in which the excitonic continuum couples to a single sharp phonon mode ($\gamma_p \ll \omega_p$). Then, solving the coupled dynamical equations, one obtains the full Raman response function

$$\chi''(\omega) = \frac{\omega[2t_p v \omega_p - t_e (\omega^2 - \omega_p^2)]^2}{(\Omega_e^2 + \omega^2)(\omega^2 - \omega_p^2)^2 + 4\Omega_e v^2 \omega_p (\omega^2 - \omega_p^2) + 4v^4 \omega_p^2}$$

(5.19)

could be broken down into a sum of three contributions:

$$\chi''(\omega) = \chi''(\omega) + \chi''(\omega) + \chi''(\omega),$$

(5.20)

where the first two terms correspond to the phonon response proportional to square of light coupling vertex $t_p^2$ and the excitonic continuum proportional to $t_e^2$, respectively, while the third one, that is proportional to the $t_p t_e$ combination, is the interference term appearing due to the exciton-phonon coupling with strength $v$ [350].

We first discuss the phonon response in the presence of the coupling with the excitonic continuum. As we will show now, the coupling to the continuum of overdamped excitonic excitations renormalizes the bare linewidth to

$$\gamma_p^\nu = \frac{v^2 \omega_p}{\omega_p^2 + \Omega_e^2},$$

(5.21)

thus, the bare $\gamma_p$ can be neglected altogether $^1$ The renormalized phonon response is given by

$$\chi''(\omega) = \frac{4t_p^2 v \omega_p \gamma_p^\nu}{[\omega^2 - (\omega_p^2 - 2\Omega_e \gamma_p^\nu)]^2 + 4\omega_p^2 \gamma_p^\nu^2 + (\omega^2 - \omega_p^2)^2},$$

(5.22)

Comparing Eq. (5.22) to Eq. (5.17) for the bare phonon, the phonon frequency renormalization is $\omega_p^2 \rightarrow \omega_p^2 - 2\Omega_e \gamma_p^\nu$. On increasing coupling strength $v$, the phononic response maximum shifts to $\omega_{p,\text{max}} = \omega_p - \frac{v^2(2\Omega_e \omega - v^2)}{2(\omega_p^2 + \omega_p^2 + \omega_p^2)}$.

$^1$The interaction-induced linewidth $\gamma_p^\nu$ is often significantly larger than the bare width $\gamma_p$, which is the case for presented data above $T_c$. Consequently, an analysis of the phonon lineshape that does not explicitly include the interaction with the continuum (e.g., by simply adding the intensities of Fano-shaped phonons and the continuum) would lead to an erroneous large intrinsic phonon linewidth.

$^2$The cubic term in the denominator can be neglected as long as the frequency is not far from $\omega_p$. 
For the excitonic response $\chi''_e(\omega)$ the renormalization effects are most significant. Those are best illustrated by the low-frequency slope of the excitonic response function $\frac{\partial \chi''_e(\omega)}{\partial \omega} \bigg|_{\omega \to 0}$.

In the absence of exciton-phonon interaction the low frequency slope for the bare response is equal to $t_e^2/\Omega_e^2$ (see Eq. (5.18)), while the interaction $v$ is rapidly enhancing the slope as

$$
\frac{\partial \chi''_e(\omega)}{\partial \omega} \bigg|_{\omega \to 0} = \frac{t_e^2}{\left[\Omega_e(T) - \frac{2v^2}{\omega_p}\right]^2},
$$

(5.23)

leading to a critical value at $v_{cr} = \sqrt{\Omega_e\omega_p}/2$, when the excitonic spectral weight is pushed to the lowest frequencies and thus causing the divergence in the static susceptibility

$$
\chi(\omega \to 0, T) = \frac{t_e^2 - 4t_e t_p v \omega_p}{\Omega_e(T) - \frac{2v^2}{\omega_p}},
$$

(5.24)

signifying the enhancement of the excitonic phase transition temperature, caused by coupling to the optical phonon.

Finally, the mutual response of the exciton and phonon coordinates appearing due to the coupling $v$ between them, leads to the sign-changing interference term

$$
\chi''_{int}(\omega) = \frac{4t_e t_p v \omega_p^2}{\left[\omega^2 - (\omega_p^2 - 2\Omega_e v^2)\right]^2 + 4\omega_p^2 v^2 + \frac{(\omega^2 - \omega_p^2)^2}{\omega_p^2 + \Omega_e^2}}.
$$

(5.25)

The sign of this term depends on phase difference between the exciton and phonon oscillators. Because the phase of driven by light phononic oscillator is flipping to the opposite one at the resonant frequency, the sign of this term changes close to the bare phonon frequency $\omega_p$. Thus, this term is chiefly responsible for a skewed, asymmetric shape of the resulting Fano feature. Depending on the sign of $v$ the peak is skewed to the left or to the right of the original phonon frequency. Even for weak coupling $v \ll \omega_p$ this term can have an appreciable magnitude close to the phonon energy.

To analyze the actual measured low-frequency data shown in Fig. 5.14, we use the model with three $B_{2g}$ optical phonon modes, all interacting with the excitonic continuum. As above, the total Raman response $\chi''(\omega)$ can be similarly decomposed into three contributions, Eq. (5.20): the first two describing the renormalized phononic and excitonic responses,
Figure 5.15: The effect of coupling on Raman spectrum, relevant to the data measured for Ta₂NiSe₅ at 380 K. The Raman response functions are shown for bare (dashed lines) and renormalized by interaction (solid lines), $\chi''_{e,p}(0)$ and $\chi''_{e,p}(\omega)$ correspondingly. The interference term $\chi''_{int}(\omega)$ is shown by solid orange line. The solid red line corresponds to the total sum of the solid blue, solid green, and solid orange lines, Eq. (5.20). The black dots represent the experimentally measured spectrum.

respectively, with the third one arising due to the interference effects. In Fig. 5.15, an example of such decomposition is shown for the data taken at 380 K, along with the deduced bare responses (without the effect of coupling), $\chi''_{p}(0)$ and $\chi''_{e}(0)$. The renormalized phonon features become broader due to the interaction with the continuum and their frequencies shift. Most importantly, the coupling noticeably increases the excitonic response at low frequencies. The sign-changing interference term enhances the asymmetric lineshape of the combined response.

To fit the $ac$ spectra, first, we determine the $t_e$ parameter of the excitonic continuum (Eq. (5.18)) by fitting the phonon free region of spectra between 25 and 40 meV. As expected, this quantity remains temperature-independent [Fig. 5.18(b)]. Second, we perform a global fitting of the spectral region below 22 meV for all measured temperatures. We assume (consistently with the expectation due to anharmonic effects, see Eq. (5.32-5.33) below) the linewidth of the three $B_{2g}$-symmetry phonon modes to be a linear function of temperature above $T_c$. For spectra below $T_c$, we fit the “leaked” phonon modes with the Lorentzian
lineshapes, and account for their contribution in the global fitting.

The coupling between excitonic continuum and acoustic modes

Besides the optical phonon modes, the excitonic continuum also couples to the acoustic phonon modes. The acoustic branch has a linear dispersion \( \omega_s(q) = c_s q \) (\( c_s \) is sound velocity) at small wavevectors \( q \); its coupling to light and to the excitonic continuum both vanish in the long-wavelength limit \[171\]:

\[
t_s = \tau_s \sqrt{q} \quad \text{and} \quad v_s = \beta_s \sqrt{q} \quad (\tau_s \text{ and } \beta_s \text{ are constants}).
\]

However, the acoustic mode has important contribution to the enhancement of the phase-transition temperature \[307\]. The the diverging condition for static Raman susceptibility \( \chi(\omega \to 0, T) \) is defined by coupling to all modes, optical and acoustic:

\[
\tilde{\Omega}_e(T_c) - \frac{2 \beta_s^2}{c_s} = 0, \quad (5.26)
\]

in which

\[
\tilde{\Omega}_e(T) = \Omega_e(T) - \sum_{i=1}^{3} \frac{2 v_i^2}{\omega_{pi}}.
\]

This equation determines the symmetry-breaking phase transition temperature \( T_c \).

Because the spectroscopic Fano feature associated with the coupling between the long-wavelength longitudinal acoustic mode and the excitonic continuum lies at frequencies far below accessibility of Raman experiment, the constant \( \beta_s \) cannot be derived directly from an interference feature of a typical Raman spectra. Nevertheless, the coupling constant \( \beta_s \) has observable consequences already above \( T_c \). In particular, the acoustic mode has been shown to soft on cooling towards \( T_c \) \[308\]. This softening does not result from intrinsic instability of the acoustic modes; rather, it is caused by the coupling of the acoustic mode to the softening excitonic excitations [Eq. (5.18)].

To demonstrate this point, we solve for the lowest-energy pole of the Green’s function for the interacting phononic and excitonic excitations assuming an infinitesimal \( q \). The energy of the pole gives the renormalized (experimentally-measured) sound velocity \( \tilde{c}_s \) above
\[ \tilde{c}_s^2 = c_s^2 - \frac{2\beta_s^2 c_s}{\Omega_e(T)}, \]  
\[ (5.28) \]

in which \( c_s \) is the bare sound velocity in the absence of coupling to the excitons. Eq. (5.26) enables us to rewrite Eq. (5.28) as

\[ \tilde{c}_s(T) = c_s \sqrt{1 - \frac{\Omega_e(T_c)}{\Omega_e(T)}}, \]  
\[ (5.29) \]

From Eq. (5.29), it is clear that the sound velocity softens to zero at \( T_c \) in the absence of any intrinsic ferroelastic instability. The renormalization of the sound velocity above \( T_c \) can be estimated by using Eq. (5.29). Using the low-temperature value of the sound velocity \( c_s \) [308], we can then calculate \( \tilde{c}_s(T) \) with the parameters obtained from the Fano fits, i.e. without free parameters. The result yields \( \tilde{c}_s(T = 400K)/c_s \approx 0.65 \), which is in remarkable agreement with the experimental ratio \( \tilde{c}_{s,exp}(T = 400K)/c_{s,exp} \approx 0.65 \). The agreement between the estimated and experimentally-determined values suggests that in \( Ta_2NiSe_5 \), the softening of the acoustic mode results solely from the coupling to the softening excitonic excitations.

**The generalized Fano model for data below \( T_c \)**

Below \( T_c \), especially around 300 K, this model appears to be insufficient to account for an additional low-frequency spectral weight, see Fig. 5.14(e) and Fig. 5.16. To understand the origin of this spectral feature below a few meV, we recall that below \( T_c \) formation of quasi-periodic structural domains have been observed by transmission electron microscopy (TEM) [288, 327]. Such quasi-periodic structure can take a recoil of quasi-momenta, enabling Raman coupling to acoustic mode at finite momentum \( q_d = \frac{2\pi}{d} \), where \( d \) is the periodicity of the domain pattern, causing the appearance of the additional spectral feature at frequency \( \omega_d \approx c_s q_d \). Therefore, fitting this ultra-low-frequency spectral feature provides an independent approach to determine the coupling constant \( v_d = \beta_s \sqrt{q_d} \) between the acoustic lattice excitations and the excitonic continuum, and hence define the constant \( \beta_s \).
Figure 5.16: The contribution from the acoustic modes to low-frequency Raman spectrum in ac polarization, relevant to the data measured for Ta$_2$NiSe$_5$ at 300 K. The data is shown by black dots; the total Fano fit is shown as red curve; the bare excitonic and phononic components are presented in blue and green, respectively; the coupled response of the acoustic and excitonic components is shown in purple.

that controls the enhancement of the transition temperature to $T_c$ due to coupling between excitons and longitudinal strain fields of the same symmetry. This low-energy feature due to recoil on the quasi-periodic structure of domain walls is best seen about 30 K below $T_c$, when the excitonic continuum is sufficiently suppressed but still adequate to provide a Fano-interference feature.

In Fig. 5.17 we compare two TEM images from ac plane of Ta$_2$NiSe$_5$ measured above and below $T_c$. The domains have stripe shape, aligned parallel to the a-axis. The average spacing $\bar{d}$ between these stripes along c-axis direction is on the order of 200 Å. For the purpose of spectral analysis, we will assume that the spacing between stripes $i$ in units of the crystal unit cell constant $c$ follows the Poisson distribution

$$P(i; \mu = \frac{\bar{d}}{c}) = \frac{\mu^i e^{-\mu}}{i!}, \quad (5.30)$$

where $\mu$ is average inter-domain distance in the number of c-direction unit cells.

We deduce the unrenormalized speed of sound from the dispersion of the acoustic mode measured by inelastic x-ray scattering at temperatures far away from $T_c$: $c_s \approx 30$ meV Å, see Ref. [308]. We also note that at high temperatures the acoustic excitations away from
long-wavelength limit are significantly broadened [308].

Recognizing that the low-frequency feature is inhomogeneously broadened by random
distribution of the stripe distances, for the fitting procedure to the measured response
function we perform summation over the distribution function:

\[
\chi''(\omega) = \sum_{i=1}^{\infty} P(i; \mu) \chi''_i(\omega),
\]

in which each \( \chi''_i(\omega) \) is the full response function containing coupling to acoustic mode for
domain walls \( i \) lattice constants apart, see Eq. (5.67) in Appendix. As a reminder, for each
individual component, the frequency and HWHM are proportional to \( q_i \); the light-scattering
vertex and coupling are proportional to \( \sqrt{q_i} \).

**The fitting results for Ta\textsubscript{2}NiSe\textsubscript{5}**

The fits to the data, as well as the phononic and excitonic components, are shown in
Fig. 5.14. For the 300 K and 265 K spectra below \( T_c \) we also include the acoustic contribution
due to coupling via quasi-periodic structure of domain walls. In Fig. 5.16 we show the
acoustic contribution at 300 K. The coupling of the excitonic continuum to the acoustic
components enhances the low-energy response. The parameter \( \beta = 7.7 \text{ meV } \AA^{-1} \) is consistent
with Eq. (5.26) for \( T_c \).
The spectral parameters: frequency, FWHM and integrated intensity, of the three \( B_{2g} \) phonon modes are shown in SubSubSection 5.2.5. The rest of the fitting parameters are given in Fig. 5.18.

The temperature dependence of the coupling strength between the individual phonon modes and the excitonic continuum are detailed in Fig. 5.18(a). The ratios of the coupling strength to the phonon frequency for the \( B_{2g}^{(1)} \) and \( B_{2g}^{(2)} \) modes above \( T_c \) are 0.32 and -0.34, respectively. These ratios are an order of magnitude larger than the typical values for stable systems with similar phonon frequency [350–352]. On the contrary, the exciton-phonon interaction with the \( B_{2g}^{(3)} \) mode is weak. The signs of the coupling for the \( B_{2g}^{(1)} \) and \( B_{2g}^{(2)} \) modes are opposite. For these two modes, the magnitude of coupling is temperature independent above \( T_c \), but decreases and saturates on cooling below \( T_c \). The temperature dependence of the coupling strength is influenced mainly by two factors: the screening effect of free carriers, reduced below \( T_c \) due to the emergence of a pronounced spectral gap [6, 291], and the change of the crystal structure below \( T_c \).

The difference in magnitude of the exciton-phonon coupling for \( B_{2g}^{(1,2)} \) and \( B_{2g}^{(3)} \) modes can be readily understood from the corresponding displacement patterns obtained from the DFT calculations for \( Ta_2NiSe_5 \) and shown in Fig. 5.19. The calculated patterns are consistent with those reported in other studies [300, 308]. While both the \( B_{2g}^{(1,2)} \) modes involve displacements of Ta and Se, the \( B_{2g}^{(3)} \) mode involve a displacement of Se almost exclusively (the Ni atoms are at the inversion centers and thus do not contribute to the Raman-active phonon modes). As the electronic bands in \( Ta_2NiSe_5 \) close to the Fermi level are believed to be predominantly formed by Ta and Ni electrons [292, 293, 298], with much smaller contribution of Se, it appears natural that the \( B_{2g}^{(3)} \) mode does not couple to the low-energy electronic degrees of freedom. Furthermore, the vibration of the Ta atoms for \( B_{2g}^{(1)} \) and \( B_{2g}^{(2)} \) displacements are in anti-phase, which can explain the opposite signs of the exciton-phonon coupling for these modes.

The temperature dependence of the light-scattering vertex \( t_e \) and the frequency \( \Omega_e \) at
Figure 5.18: Temperature dependence of the Fano fitting parameters for the ac Raman spectra of Ta$_2$NiSe$_5$. (a) The coupling strength $v_i$ (i=1,2,3) in Eq. (5.54). (b) The light-scattering vertex $t_e$, and the frequency at which the excitonic continuum has maximum intensity $\Omega_e(T) = \omega^2_e/\gamma_e$, Eq. (5.18). The blue line is a linear fit to the $\Omega_e(T)$ data above $T_c$. The dashed lines indicate transition temperature $T_c$ and bare excitonic transition temperature $T^{ex}_c$.

Figure 5.19: The calculated vibrational patterns corresponding to the three B$_{2g}$-symmetry phonon modes of Ta$_2$NiSe$_5$. 
which the continuum has maximum intensity are shown in Fig. 5.18(b). Above $T_c$, the quantity $\Omega_e$ linearly decreases on cooling; below $T_c$, it rapidly increases and saturates at low temperature.

The fitting results for $\text{Ta}_2\text{Ni}(\text{Se}_{1-x}\text{S}_x)_5$ with $x = 0.25$ and 0.67

To compare with the results for $\text{Ta}_2\text{NiSe}_5$, we also fit the ac polarization spectra for the alloy compositions ($x = 0.25$ and 0.67) above their transition temperature. We are not able to perform a Fano analysis below $T_c$ for two reasons: (a) we have no knowledge of the domain structure and the sound velocity; and (b) we cannot properly subtract the leakage of the $A_g$ modes. In Fig. 5.20 we show one characteristic Fano fit for $\text{Ta}_2\text{Ni}(\text{Se}_{0.75}\text{S}_{0.25})_5$ and $\text{Ta}_2\text{Ni}(\text{Se}_{0.33}\text{S}_{0.67})_5$, respectively. The fitting parameters are given in Fig. 5.21.

The results are similar to the case of $\text{Ta}_2\text{NiSe}_5$: for the coupling strength, we find positive $v_1$, negative $v_2$, and negligible $v_3$; the light-scattering vertex $t_e$ has no temperature dependence above the transition temperature; the energy at which the excitonic continuum has maximum intensity, $\Omega_e = \omega_e^2/\gamma_e$, decreases linearly on cooling above the transition temperature. Extrapolating to zero value of $\Omega_e$, we obtain $55 \pm 18$ K for $\text{Ta}_2\text{Ni}(\text{Se}_{0.75}\text{S}_{0.25})_5$ and $-400 \pm 70$ K for $\text{Ta}_2\text{Ni}(\text{Se}_{0.33}\text{S}_{0.67})_5$.

In Table. 5.4 we present the doping dependence of the relevant physical quantities above the transition temperature for $\text{Ta}_2\text{Ni}(\text{Se}_{1-x}\text{S}_x)_5$ family. Because the coupling strength increases with sulfur doping, determining the intrinsic phonon parameters, especially the linewidth, becomes more difficult for $\text{Ta}_2\text{Ni}(\text{Se}_{0.75}\text{S}_{0.25})_5$ and $\text{Ta}_2\text{Ni}(\text{Se}_{0.33}\text{S}_{0.67})_5$.

5.2.5 Temperature dependence of the intrinsic phonon parameters

In this subsection we present the temperature dependence of intrinsic phonon-mode parameters: energies, intensities and linewidths. The results for $B_{2g}$-symmetry modes are given in SubSubSec. 5.2.5, and those for $A_g$-symmetry modes are given in SubSubSec. 5.2.5.
Figure 5.20: Raman response $\chi''$, represented by black dots, in the ac scattering geometry for $Ta_2Ni(Se_{0.75}S_{0.25})_5$ and $Ta_2Ni(Se_{0.33}S_{0.67})_5$ with the Fano fits [Eq. (5.52)] shown as red curves. The spectral resolution is 0.19 meV. The phonon modes [Eq. (5.17)] and excitonic continuum [Eq. (5.18)] are represented by green and blue curves, respectively.

Table 5.4: The doping dependence of the scattering vertex and the coupling above the transition temperature for the interaction between the excitonic continuum and phonon modes in the $B_{2g}$ scattering geometry of $Ta_2Ni(Se_{1-x}S_x)_5$ family. The quantities $t_e$ is the vertex of light scattering process for the excitonic continuum. The quantities $v_i$ (i=1,2) are the coupling between the excitonic continuum and the $B_{2g}^{(i)}$ phonon mode.

<table>
<thead>
<tr>
<th>x</th>
<th>$t_e$ (arb. units)</th>
<th>$v_1$ (meV)</th>
<th>$v_2$ (meV)</th>
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<td>0</td>
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<td>-4.03</td>
</tr>
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<td>0.25</td>
<td>7.36</td>
<td>2.61</td>
<td>-4.61</td>
</tr>
<tr>
<td>0.67</td>
<td>7.48</td>
<td>3.61</td>
<td>-5.87</td>
</tr>
</tbody>
</table>
Figure 5.21: Temperature dependence of the Fano fitting parameters for the ac Raman spectra of Ta$_2$Ni(Se$_{0.75}$S$_{0.25}$)$_5$ (a-b) and Ta$_2$Ni(Se$_{0.33}$S$_{0.67}$)$_5$ (c-d). (a,c) The coupling strength $v_i$ (i=1,2,3) in Eq. (5.54). (b,d) the light-scattering vertex $t_e$, and the energy at which the excitonic continuum has maximum intensity $\Omega_e = \omega_2^2/\gamma_e$ of the overdamped electronic mode, Eq. (5.56). The blue line is a linear fit to the $\Omega_e$ data.

**B$_{2g}$-symmetry Phonon Modes**

(a) Ta$_2$NiSe$_5$

In Fig. 5.22 we show the temperature dependence of the spectral parameters for B$_{2g}$-symmetry phonon modes in Ta$_2$NiSe$_5$: the bare phonon frequency, FWHM, and integrated intensity.

Below $T_c$, the temperature dependence of both frequency $\omega_p(T)$ and FWHM $\Gamma_p(T) = 2\gamma_p(T)$ of the phonon modes can be accounted for by standard model assuming anharmonic decay into two phonons with identical frequencies and opposite momenta [166]:

$$\omega_p(T) = \omega_0 - \omega_2 [1 + \frac{2}{e^{\hbar\omega_0/2k_B T} - 1}],$$  \hspace{1cm} (5.32)

and

$$\Gamma_p(T) = \Gamma_0 + \Gamma_2 [1 + \frac{2}{e^{\hbar\omega_0/2k_B T} - 1}].$$  \hspace{1cm} (5.33)

We note that a low value of $\Gamma_0$ indicated high quality of the crystals.

Above $T_c$, however, the slope of the FWHM increases for the three phonon modes, and the FWHM becomes larger than the value predicted by the anharmonic decay model.
Figure 5.22: Temperature dependence of the spectral parameters: the bare frequency, FWHM, and the integrated intensity, for the $B_{2g}$-symmetry phonon modes of Ta$_2$NiSe$_5$. For each mode, the left panel presents the frequency and FWHM; and the right panel presents the integrated intensity in the allowed and “forbidden” scattering geometries. The solid lines represent the fits to the anharmonic decay model [Eqs. (5.32-5.33)].
The appearance of additional decay channels above $T_c$ is related to the presence of gapless particle-hole pairs. Indeed, above $T_c$ Ta$_2$NiSe$_5$ is gapless spectroscopically[6], while below $T_c$ a gap rapidly develops at low energies, suppressing the damping due to particle-hole pairs. Because the Fano model used for fitting takes into account the damping due to exciton-phonon interaction, existence of additional damping above $T_c$ suggests the importance of the interactions beyond that model, i.e. nonlinear ones.

More noticeable is that the frequencies of the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes exhibit a large increase on cooling from around 350K to $T_c$. The frequency of the $B_{2g}^{(3)}$ mode, however, does not show such anomaly. Only $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes exhibit this anomaly; interestingly (1) they are allowed to couple to interband scattering by symmetry selection rules and (2) their corresponding vibration involve motion of Ni atoms and hence they couple to the electronic bands near Fermi level. Although $B_{2g}^{(3)}$ mode can also couple to the interband scattering, its vibrational pattern almost does not contain motion of Ni atoms.

As for the integrated intensity, $B_{2g}^{(1)}$ and $B_{2g}^{(3)}$ modes have around 2-fold increase of intensity on cooling below $T_c$, while $B_{2g}^{(2)}$ mode shows temperature-independent intensity. Two factors could influence the intensity. First, the interaction-induced gap opening up below $T_c$ should play a major role. The system gradually changes from a semimetal at high temperature to an insulator at low temperature. The screening effect, which reduces the light-scattering vertex, and in turn, the intensity for phonon modes, is suppressed on cooling. This factor therefore favors increase of intensity on cooling. Second, the structural change below $T_c$ could play also a role. The ion positions are shifted within the unit cell below $T_c$, and the vibrational patterns of the three $B_{2g}$ modes are modified. Therefore, the polarizability induced by lattice vibrations, which is proportional to the phonon intensity, also change with temperature. The fact that $B_{2g}^{(2)}$ mode shows temperature-independent intensity might be related to its unique vibrational pattern.

(b) The alloy compositions ($x=0.25, 0.67$)

In Fig.5.23 and 5.24 we show the temperature dependence of the $B_{2g}$-mode spectral
Figure 5.23: Temperature dependence of the spectral parameters: frequency, FWHM, and integrated intensity, for the B$_{2g}$-symmetry phonon modes of Ta$_2$Ni(Se$_{0.75}$S$_{0.25}$)$_5$. For each mode, the left panel presents the energy and FWHM; the right panel presents the integrated intensity in the allowed and “forbidden” scattering geometries.

parameters for Ta$_2$Ni(Se$_{0.75}$S$_{0.25}$)$_5$ and Ta$_2$Ni(Se$_{0.33}$S$_{0.67}$)$_5$, respectively. Although we do not perform Fano analysis for the data below $T_c$, we use Lorentzian lineshape to fit the B$_{2g}^{(1)}$ mode at low-enough temperatures, at which the lineshape is essentially symmetric. For the B$_{2g}^{(2)}$ and B$_{2g}^{(3)}$ modes, because they are not well separated from the leakage of A$_g$ modes, it is difficult to reliably obtain their spectral parameters.

For the alloy compositions, the increase of the FWHM slope above $T_c$ is not as strong as in the case of Ta$_2$NiSe$_5$. Moreover, although for Ta$_2$NiSe$_5$ the large frequency increase of the B$_{2g}^{(1)}$ mode on cooling happens in a 20 K energy range, the frequency increase for the alloy compositions happens in a much larger energy range.

(c) Ta$_2$NiS$_5$

Ta$_2$NiS$_5$ is a semiconductor that, in contrast to Ta$_2$NiSe$_5$, does not show signatures of an excitonic insulator like the flattening of valence band dispersion [330, 353]. Consistent with its semiconductor nature, we observe no excitonic continuum and in turn no asymmetric lineshape for the phonon modes, Fig. 5.10(c-d). In Fig. 5.25 we zoom in on the temperature
dependence of the phonons in ac scattering geometry. The three $B_{2g}$-symmetry phonon modes exhibit conventional Lorentzian lineshapes, and the linewidth has almost 4-fold decrease on cooling from 315 K to 35 K. Moreover, the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes show softening behavior on cooling.

In Fig. 5.26 we show the temperature dependence of the spectral parameters for the $B_{2g}$-symmetry phonon modes for Ta$_2$NiS$_5$: the frequency, FWHM, and the integrated intensity. These spectral parameters are obtained by fitting the measured spectral features with Lorentzian lineshapes.

The behavior of the $B_{2g}$-symmetry modes is not consistent with the anharmonic decay model: for $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes, the frequency anomalously decreases on cooling; for $B_{2g}^{(3)}$ mode, the decrease of FWHM on cooling is too steep to be accounted by the anharmonic decay model. Hence, we suggest that there is a change in the phonon self energy, which must affect the apparent mode frequency. For the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes, whose frequency is below 30 meV, the energy decreases on cooling; for the $B_{2g}^{(3)}$ mode, whose frequency is
Figure 5.25: Temperature dependence of B$_{2g}$ phonons in the $ac$ scattering geometry for Ta$_2$NiS$_5$. The spectral resolution is 0.19 meV for the 315 K data, and 0.06 meV for the other data.
Figure 5.26: Temperature dependence of the spectral parameters: frequency, FWHM, and integrated intensity, for the $B_{2g}$-symmetry phonon modes of Ta$_2$NiS$_5$. For each mode, the left panel presents the energy and FWHM; the right panel presents the integrated intensity in the allowed and “forbidden” scattering geometries.
above 30 meV, the energy increases on cooling.

The integrated intensity of $B^{(2)}_{2g}$ mode is temperature-independent, while that of the other modes increases on cooling. However, different from the case of Ta$_2$NiSe$_5$, in which the increase of the intensity happens below $T_c$, the intensity increase of the Ta$_2$NiS$_5$ modes is through the whole measured temperature range.

**A$_g$-symmetry Phonon Modes**

In this subsection we discuss the properties of the full-symmetric phonon modes; the relevant results are shown in Fig. 5.27 with respect to the overall spectral weight distribution in the A$_g$ channel, and in Figs. 5.28 and 5.29 regarding the spectral parameters of the individual A$_g$ modes. In Fig. 5.29 we compare the temperature dependence of the spectral parameters (frequency, FWHM, and integrated intensity) of the A$_g$-symmetry phonon modes for Ta$_2$NiSe$_5$ and Ta$_2$NiS$_5$ crystals. The temperature dependence of both frequency and FWHM above $T_c$ for these modes can be accounted by the anharmonic decay model [Eq. (5.32-5.33)].

The FWHM of the A$_g$-symmetry modes (except for A$_g^{(3)}$ and A$_g^{(8)}$) for Ta$_2$NiSe$_5$ exhibit an anomalous increase above the transition temperature, which we attribute to enhanced electron-phonon scattering rate in its semimetal phase. However, the modes of Ta$_2$NiS$_5$ show no anomaly of FWHM, because it is a semiconductor with a direct gap observed throughout the measured temperature range.

The intensity of most modes has more than 2-fold increase on cooling, with a few exceptions: for Ta$_2$NiSe$_5$, the intensity of the A$_g^{(1)}$ mode is independent of temperature, while the intensity of the A$_g^{(2)}$ phonon mode decreases on cooling; for Ta$_2$NiS$_5$, the intensities of the A$_g^{(1)}$ and A$_g^{(2)}$ modes are temperature independent.

The enhancement of intensity on cooling in the semimetallic samples could in principle be related to the change of electronic structure (less screening effect) below $T_c$. However, an interesting insight can be further obtained by computing the integral $I_{aa}(\omega) = \int_0^{\omega} \frac{\chi''_{aa}(\omega')}{\omega'} d\omega'$. 
The integral \( I_{aa}(\omega) = \int_0^\omega \frac{\chi''_{aa}(\omega')}{\omega'} d\omega' \) as a function of the Raman shift \( \omega \) for Ta\(_2\)NiSe\(_5\) in \( aa \) scattering geometry.

(Fig. 5.27). In the limit \( \omega \to \infty \) this integral is proportional to the static susceptibility in the \( aa \) scattering geometry, which is expected to be approximately constant as a function of temperature since there is no instability in A\(_g\) channel. On cooling, the phonon intensity is enhanced [Fig. 5.29], while the electronic continuum is suppressed [Fig. 5.10(a)]. However, the integral \( I_{aa} \) is essentially temperature independent at 70 meV. This conservation implies that the enhancement of the phonon intensity is balanced by the reduction of the electronic intensity. These effects occur at temperatures below \( T_c \), where the continuum in B\(_{2g}\) symmetry is strongly suppressed, indicating the opening of a gap. On the other hand, strong correlation effects have been shown to lead to a non-zero intensity within the gap [6]. Thus, the peculiar balance between the electronic and phononic contributions at low energies implies an unconventional coupling of the electronic modes to the A\(_g\) phonons in the correlated excitonic insulator state.

For comparison, in Fig. 5.28 we show the temperature dependence of the spectral parameters for the A\(_g^{(1)}\) mode for Ta\(_2\)Ni(Se\(_{1-x}\)S\(_x\))\(_5\) with \( x = 0.25 \) and 0.67. Because of the difficulty caused by broad lineshape and two-frequency behavior of the phonon modes for alloy compositions, only the lowest-frequency A\(_g^{(1)}\) mode, which are well separated from other modes in frequency, renders reliable fitting results. For Ta\(_2\)Ni(Se\(_{0.75}\)S\(_{0.25}\))\(_5\), some linewidth broadening is observed above \( T_c \), which is weaker than for Ta\(_2\)NiSe\(_5\). However,
Figure 5.28: Temperature dependence of the spectral parameters: frequency, FWHM, and integrated intensity, – for the $A^{(1)}_g$ phonon mode of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ with $x = 0.25$ (a-b) and 0.67 (c-d). For each sample, the left panel presents the energy and FWHM; the right panel presents the integrated intensity. The solid lines represent the fits to the anharmonic decay model [Eqs. (5.32-5.33)].

for Ta$_2$Ni(Se$_{0.33}$S$_{0.67}$)$_5$ almost no broadening is observed.

5.2.6 Relation to time-resolved experiments

In this section we convert Raman response from frequency domain to time domain, and discuss relevant time-resolved studies on Ta$_2$NiSe$_5$.

We first discuss the appearance of $B^{(1)}_{2g}$-symmetry excitations in the time domain, obtained by inverse Fourier transform of the Raman response, see Fig. 5.30. Above the transition temperature, the phonon-exciton interaction significantly broadens the spectral features [Fig. 5.30(a)]; as a result the deduced time-resolved response decays fast and essentially dies out before 5 ps [Fig. 5.30(b)]. For the bare phononic response, the time-domain signal beyond 4 ps is dominated by the oscillation of 2 THz mode [Fig. 5.30(c)], corresponding to the $B^{(1)}_{2g}$ phonon. The signal of the bare excitonic response shows a pure relaxational behavior [Fig. 5.30(d)]. Comparing Fig. 5.30(b) and (c), we note that it is difficult to identify the Fano interference feature from time-domain signal, because such interference exhibits no distinct characters in the time domain, except for that the oscillations are strongly damped. Indeed, in ultrafast studies, the interference nature is not revealed even after Fourier transform of
Figure 5.29: Temperature dependence of the spectral parameters: frequency, FWHM, and integrated intensity, – for the $A_g$-symmetry phonon modes for Ta$_2$NiSe$_5$ and Ta$_2$NiS$_5$. For each mode, the left panel presents the energy and FWHM; the right panel presents the integrated intensity. The solid lines represent the fits to the anharmonic decay model [Eqs. (5.32-5.33)].
Figure 5.30: Time-domain signal for the B$_{2g}$-symmetry excitations of Ta$_2$NiSe$_5$. (a) The Raman response for Ta$_2$NiSe$_5$ measured in ac geometry at 380 K. The Fano fit [Eq. (5.51)] is shown as the red curve; the bare phonon modes [Eq. (5.17)] are shown by the green curve; the bare excitonic continuum [Eq. (5.18)] is shown by the blue curve. The time-domain signal corresponding to the Fano fit, bare phonon modes, and bare excitonic continuum, obtained by inverse Fourier transform, are shown in (b), (c), and (d), respectively. (e) The Raman response for Ta$_2$NiSe$_5$ measured in ac geometry at 35 K. The corresponding time-domain signals are shown in (f), (g), and (h), respectively.

the time-domain data to the frequency domain [300, 328, 329]. The likely reason for that is the high pump fluence used, causing the exciton and phonon responses decouple already on the very early time scales.

Below the transition temperature, the energy at which the continuum has maximum response moves to higher energy, and the phonon-exciton coupling strength is reduced. Consequently, the interference effect is suppressed and the combined response is essentially the same as the bare phononic response [Fig. 5.30(f-g)]. The bare excitonic response still has a pure relaxational time dependence, with very short lifetime [Fig. 5.30(d) and (h)].
Figure 5.31: Time-domain signal for the $A_g$-symmetry excitations of Ta$_2$NiSe$_5$. (a) The Raman response for Ta$_2$NiSe$_5$ measured in aa geometry at 380 K. The time-domain signal, obtained by inverse Fourier transform of the data, is shown in (b). (c) The Raman response for Ta$_2$NiSe$_5$ measured in aa geometry at 35 K. The corresponding time-domain signal is shown in (d).

For comparison, in Fig. 5.31 we present the time-domain signal for the $A_g$-symmetry excitations. Above the transition temperature, although multiple oscillations are simultaneously present at short time scale, beyond 10 ps the time-domain signal is dominated by the oscillation of 1 THz [Fig. 5.31(b)], corresponding to the $A_g^{(1)}$ phonon mode whose spectral width is much smaller than others [Fig. 5.31(a)]. At low temperature, the difference between the spectral widths of various modes is reduced [Fig. 5.31(c)]; hence, these modes have comparable lifetime and multiple oscillations survive beyond 10 ps [Fig. 5.31(d)].

In relation to the ultra-fast studies of Ta$_2$NiSe$_5$ [327, 329, 354, 355], the Raman results are consistent with the ultra-fast data under low fluence. One ultra-fast work [329] provides evidence for coupling between the $A_g^{(1)}$ mode and the amplitude mode of the condensate under high-fluence pumping. In our studies we can unambiguously identify the amplitude mode with the excitonic continuum we observe. Above the transition temperature, the overdamped excitonic mode softens on cooling towards $T_c$; just below the transition temperature, its energy increases on further cooling. Such temperature dependence of mode energy is characteristic of an amplitude mode while the optical $B_{2g}$ phonons only harden.
Figure 5.32: Time-domain signal for the excitonic continuum of Ta$_2$NiSe$_5$ above and below the transition temperature, plotted in semi-log scale. The data above $T_c$ are dashed for clarity. The relaxation time starts to decrease just below $T_c$. Inset: temperature dependence of the energy at which the excitonic continuum has maximum intensity, $\Omega_e(T)$.

on cooling. In Fig. 5.32 we present the time-domain signal corresponding to the excitonic mode around the transition temperature.

Additionally, a mode associated with the phase of the excitonic order parameter may exist. The electron-phonon coupling and exchange interactions modify the otherwise Mexican-hat-shape free-energy landscape, reducing the continuous U(1) symmetry to a discrete $Z_2$ symmetry, leading to a finite energy of the phase mode. A recent pump-probe microscopy study suggests that the phase-mode energy is smaller than the $A_g^{(1)}$-mode energy (around 4 meV) [354]. However, we do not observe any mode down to 0.4 meV at low temperature [Fig. 5.30(e)]. Furthermore, the phase oscillations of the order parameter should harden above $T_c$, which would have manifested itself in the low-energy range of the spectra. Such signatures are not observed, either [Fig. 5.14]. Therefore, existence of the phase mode below 4 meV is not supported by the Raman data.

5.2.7 Conclusion

We have employed polarization resolved Raman spectroscopy to conduct a systematic spectroscopic study of the lattice dynamics in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ ($x = 0, ..., 1$) family of the excitonic insulators.
We identify and classify by symmetry all the Raman active phonon modes of $A_g$ and $B_{2g}$ symmetries. A change in selection rules is detected at temperature $T_c(x)$, indicating the orthorhombic-to-monoclinic structural phase transition related to the excitonic insulator state [6, 8]. We find that the symmetry breaking transition persists for entire $\text{Ta}_2\text{Ni(Se}_{1-x}\text{S}_x)\text{S}_5$ family with $T_c(x)$ monotonically decreasing from 328 K for $x = 0$ to 120 K for $x = 1$. Its signatures in the resistivity data, however, become weak or undetectable for large sulfur concentration $x$ that we attribute to the weakness of the symmetry breaking at large $x$, demonstrated by the decrease of phonon intensity in the “forbidden” scattering geometry.

For $x < 0.7$, the two lowest-frequency $ac$-quadrupole-symmetry $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ phonon modes show strongly asymmetric lineshapes at high temperatures, which is indicative of coupling between the phonons and an excitonic continuum of the same symmetry [6, 8]. Within the framework of extended Fano model, we develop a quantitative description of the observed lineshapes, enabling us to disentangle the excitonic and phononic contributions to the spectra, to derive the intrinsic phonon parameters and determine the exciton-phonon interaction strength, that affects the transition temperature $T_c(x)$ [8]. The displacement patterns obtained from ab-initio calculations explain the trends in the deduced exciton-phonon coupling values. At $T < T_c$ the remnant excitonic continuum demonstrates signatures of coupling to the finite-momentum $B_{2g}$-symmetry acoustic phonons, allowed due to scattering on a quasi-periodic structural of domain walls. We have also shown that the coupling to the excitonic continuum explains the acoustic mode softening observed in [8, 308].

The intrinsic parameters of the optical phonons for $\text{Ta}_2\text{NiSe}_5$ and $\text{Ta}_2\text{NiS}_5$ at low temperatures are mostly in good agreement with anharmonic decay model and DFT calculations. For alloy compositions a two-mode behavior is found for most modes, where signatures appear at two frequencies, corresponding to the ones in $\text{Ta}_2\text{NiSe}_5$ and $\text{Ta}_2\text{NiS}_5$. However, several types of anomalous behavior have been observed in the temperature dependencies.
For $x < 0.7$, the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes anomalously harden close to $T_c$ (e.g., Fig. 5.22), indicating an interaction with continuum beyond Fano model description [6]. For $\text{Ta}_2\text{NiS}_5$ (Fig. 5.26) the $B_{2g}^{(1)}$ and $B_{2g}^{(2)}$ modes do not show Fano shapes, but the frequencies of these modes anomalously soften on cooling, although never going critical. Finally, the intensity of the most modes is strongly temperature dependent. Interestingly, for $\text{Ta}_2\text{NiSe}_5$ we observe that the sum of electronic and phononic contributions to the $aa$ static susceptibility is conserved (Fig. 5.27), pointing to an unexpected electron-phonon coupling mechanism within the excitonic insulator state.

In addition, by performing Fourier transform we convert the measured Raman response to time domain, and discuss the signatures expected from the modes we have observed, see Figs. 5.30, 5.31 and 5.32. Overall, this work provides a comprehensive study lattice dynamics in $\text{Ta}_2\text{Ni}(\text{Se}_{1-x}\text{S}_x)_5$; more generally, the unconventional behaviors we observed point to the importance of the effects of electron-phonon coupling in correlated semimetals.

### 5.2.8 Estimation of heating in excitation laser spot

We use three methods to estimate the heating rate, a measure of the temperature increase per unit laser power in the focused laser spot (K/mW): (i) Stokes/anti-Stokes Raman scattering intensity ratio analysis; (ii) monitoring laser power that is inducing the phase transition; and (iii) a thermoconductivity model calculation. We use data for $\text{Ta}_2\text{NiSe}_5$ as an example to illustrate these methods.

For the first method, we note that the Stokes scattering cross section $I_S$ and Anti-Stokes cross section $I_{AS}$ are related by the detailed balance principle [9]

$$nI_S(\omega) = (n + 1)I_{AS}(\omega),$$

(5.34)

in which $n$ stands for the Bose factor

$$n(\omega, T) = \frac{1}{\exp(\hbar\omega/k_BT) - 1},$$

(5.35)
where $\hbar$ is the reduced Planck’s constant, $\omega$ is frequency, $k_B$ is the Boltzmann’s constant, and $T$ is the temperature in the laser spot.

Using Eq. (5.34-5.35), the temperature can be derived as

$$T = \frac{\hbar \omega}{k_B \ln(I_S/I_{AS})},$$

(5.36)

or, numerically,

$$T[K] = \frac{11.605 \omega}{\ln(I_S/I_{AS})}[meV].$$

(5.37)

We studied the Stokes and Anti-Stokes cross section relation for the $ac$ scattering geometry at 295 K environmental temperature with various laser power. In Fig. 5.33 we show the results measured with 8 mW laser power as an example. The Raman responses calculated from Stokes and Anti-Stokes cross sections match well with the temperature at the laser spot being 307 K. We use Eq. (5.37) with the phonon intensity integrated from 7.5 to 8.5 meV to calculate the temperature at the laser spot. By a linear fit to the power dependence of the laser-spot temperature, we find the heating rate to be $1.29 \pm 0.17$ K/mW.

For the second method, we gradually increase laser power at 295 K environmental temperature. We find that when the laser power is in the range of $26 \pm 4$ mW, the domain stripes, which are visible across the sample surface under laser illumination, disappear inside the laser spot. Moreover, the temperature dependence of phonon width and intensity has a sudden change. We assume that at this laser power, the temperature at the laser spot reaches the transition temperature 328 K [285, 288], yielding the heating rate of $1.25 \pm 0.20$ K/mW. For Ta$_2$NiS$_5$, we do not observe domain stripes below its transition temperature 120 K; its transition temperature is identified by the sudden change of phonon intensity, see Fig. 5.26(b) for example.

For the third method, we consider a heated region shown in Fig. 5.34 of a rectangular shape, with the dimensions given by the beam spot size and the penetration depth. The
Figure 5.33: Stokes-Anti-Stokes analysis of the ac spectra for Ta₂NiSe₅. (a) The Stokes and Anti-Stokes cross sections measured at environmental temperature \( T_E = 295 \text{K} \) with laser power \( P = 8 \text{mW} \). (b) The Raman response calculated from the measured spectra in (a). The laser-spot temperature, which appears in the Bose factor \( n \), is 307 K. The spectral resolution is 0.19 meV for panels (a-b). (c) The laser-power dependence of the laser-spot temperature. The straight line represents a linear fit.
Figure 5.34: The geometry of the heated volume. The lengths $l_a$ and $l_c$ are determined by the spot size, while $l_b$ is approximated by the skin depth; the $S_b$ is in the cleave plane facing the vacuum, while the other faces are in the bulk. Within the region marked by dashed lines, the heat flow is mostly along $b$ axis, while outside the region heat flows in all directions comparably, such that the temperature increase above the base temperature $\Delta T$ decays as $1/r$, $r$ being the distance from the heated region.

The static heat equation takes the form:

$$
-\kappa_x \frac{\partial^2 T}{\partial x^2} - \kappa_y \frac{\partial^2 T}{\partial y^2} - \kappa_z \frac{\partial^2 T}{\partial z^2} = \mathcal{P}(r),
$$

$$
\left. \frac{\partial T(r)}{\partial z} \right|_{y=0} = 0;
$$

$$
\partial T(x \to \pm \infty, y \to -\infty, z \to \pm \infty) = T_0.
$$

where $\mathcal{P}(r)$ is the power density. We ignore the cooling provided by the helium gas flow above the sample surface, so that there is no heat flow at the $y = 0$ boundary, while deep inside the bulk the temperature should reach the base temperature $T_0$. Eq. (5.38) can be solved using Green’s function of the Laplace equation and image method to satisfy the first boundary condition. In the latter, we extend the equation formally to $y > 0$ half-space and add an “image” power density

$$
\mathcal{P}(x, y, z)\theta(-y) \to \mathcal{P}(x, y, z)\theta(-y) + \mathcal{P}(x, -y, z)\theta(y).
$$

The solution is then given by:

$$
T(r) - T_0 = \int \frac{d\tilde{x}' d\tilde{y}' d\tilde{z}'}{4\pi} \frac{\mathcal{P}(\sqrt{\kappa_x \tilde{x}'}, \ldots)\theta(-\tilde{y}')}{|\tilde{r} - \tilde{r}'|} + \tilde{y}' \to -\tilde{y}',
$$
where \( \hat{r} = (x/\sqrt{\kappa_x}, y/\sqrt{\kappa_y}, z/\sqrt{\kappa_z}) \). The solution decays as \( 1/r \) at large distances and thus satisfies the second boundary condition of Eq. (5.38).

An analytical result can be obtained for

\[
P(x, y, z) = \frac{tP}{l_al_bl_c} \theta(l_a/2 - |x|)\theta(l_b - |y|)\theta(l_c/2 - |z|)
\]

at \( r = 0 \) in the limit \( l_b^2/\kappa_b \ll l_{a,c}^2/\kappa_{a,c} \), where \( P \) is the laser power and \( t \) is the transmission coefficient of the sample. Performing the integral one obtains

\[
T(0) - T_0 \approx \frac{tP}{\sqrt{\kappa_b\pi l_al_c}} \left( \frac{l_b}{\sqrt{\kappa_a}} \ln \frac{l_c + \sqrt{l_b^2 + l_c^2}}{l_c/\sqrt{\kappa_a}} + a \leftrightarrow c \right).
\]

Qualitatively, the result can be understood as follows. Due to the anisotropic shape of the heated region, right below it most heat is transferred along the \( b \) axis. However, the one-dimensional heat equation would result in a linear solution \( T(y) \), depending on the cutoff scale \( l_{c,eff} \). It can be estimated from the condition of the heat flow to the lateral direction being equal to the heat flow along \( b \). Approximating the temperature gradient along \( a, b, c \) as \( \Delta T/l_{a,b,c} \) one gets the condition

\[
2l_{c,eff} l_c \Delta T/l_c + 2l_{a,eff} l_a \kappa_a \Delta T/l_a = l_a l_c \kappa_b \Delta T/l_{b,eff}.
\]

that results in the estimate

\[
l_{b,eff} = \sqrt{\frac{l_a^2 l_c^2 \kappa_b}{2l_a^2 \kappa_c + 2l_c^2 \kappa_a}}.
\]

Equating the total heat flow outside this region to the input power one obtains the estimate

\[
\Delta T \approx \frac{tP}{\sqrt{8\kappa_b(l_a^2 \kappa_c + l_c^2 \kappa_a)}}.
\]

Overall, one notices that the temperature increase scales with the linear size of the spot. The laser heating power \( R \) is then determined as \( \Delta T/P \); for the actual estimate we thus need to find the transmission coefficient \( t \) first.

The transmission coefficient can be calculated from the complex index of refraction \( n \) by the relationship \( t = 1 - |(n-1)/(n+1)|^2 \):

\[
t = \frac{4n_1}{(n_1+1)^2 + n_2^2}.
\]
Table 5.5: The various parameters used in calculating the laser heating rate at 295 K. The transmission coefficient is 0.64.

<table>
<thead>
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<th>Quantity (unit)</th>
<th>a-axis</th>
<th>c-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$ (mWK$^{-1}$cm$^{-1}$)</td>
<td>208</td>
<td>57.4</td>
</tr>
<tr>
<td>$l$ (10$^{-3}$cm)</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

in which $n_1$ and $n_2$ are the real and imaginary part of $n$. The complex index of refraction can be obtained from the complex dielectric constant $\epsilon$ by the relationship $\epsilon = n^2$:

$$n_1 = \sqrt{\frac{\epsilon_1^2 + \epsilon_2^2 + \epsilon_1}{2}}, n_2 = \sqrt{\frac{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1}{2}},$$ (5.47)

where $\epsilon_1$ and $\epsilon_2$ are the real and imaginary part of $\epsilon$. The imaginary part $\epsilon_2$ can be calculated from the real part of the optical conductivity $\sigma_1$:

$$\epsilon_2 = \frac{60}{\omega} \sigma_1,$$ (5.48)

in which the unit of $\omega$ is cm$^{-1}$ and that of $\sigma_1$ is $\Omega^{-1}$cm$^{-1}$. The polarization of the incoming light is along a-axis of the sample. Because the quantities $\epsilon_1$ and $\sigma_1$ are 8.13 and 2.47 $\Omega^{-1}$cm$^{-1}$ respectively at the laser wavelength [291], we find $t=0.64$.

The experimentally measured thermal conductivity [356] at 295 K is $\kappa_a = 208$ mWK$^{-1}$cm$^{-1}$ and $\kappa_c = 57.4$ mWK$^{-1}$cm$^{-1}$.

The length scales $l_a = 5 \times 10^{-3}$ cm and $l_c = 1 \times 10^{-2}$ cm is determined by the 50 x 100 $\mu$m$^2$ laser spot. The length $l_b$ is the skin depth, which is calculated from the imaginary part of the index of refraction $n_2$:

$$l_b = \frac{1}{2\pi\omega n_2},$$ (5.49)

in which the unit of $\omega$ is cm$^{-1}$ and that of $l_b$ is cm. At the laser wavelength, $n_2=1.5$, and we find $l_b = 7 \times 10^{-6}$ cm (70 nm).

The known values for the variables in Eq. (5.42) are summarized in Table 5.5. Because $\kappa_b$ is unknown, we cannot use Eq. (5.42) to calculate the laser heating rate. However, if the heating rate is 1.29 K/mW at 295 K, as determined from the Stokes/anti-Stokes analysis, the value for $\kappa_b$ should be 1.38 mWK$^{-1}$cm$^{-1}$. 
Figure 5.35: Temperature dependence of the laser heating rate \( R \), calculated by Eq. (5.42) with the thermal conductivity data taken from Ref. [356].

An estimate for the electronic contribution to thermal conductivity \( \kappa^{(e)} \) could be calculated from the electric resistivity \( \rho \) by virtue of Wiedemann-Franz law:

\[
\kappa^{(e)} = \frac{LT}{\rho},
\]

in which \( L = 2.44 \times 10^{-5} \text{ mW} \Omega \text{K}^{-2} \) is the Lorenz number. The resistivity along b axis at 295 K is \( \rho_b = 2.34 \times 10^{-1} \Omega \text{cm} \) [357], and we find \( \kappa_b^{(e)} = 0.0308 \text{ mWK}^{-1} \text{cm}^{-1} \). The ratio of \( \kappa_b^{(e)} \) to \( \kappa_b \) is consistent with the ratios obtained along a and c axes [356]. Moreover, that \( \kappa_b \ll \kappa_{a,c} \) is consistent with the quasi-2D structure of the system [358].

To illustrate that the laser heating rate is strongly temperature dependent, we use Eq. (5.42) to calculate the heating rate as a function of temperature. The temperature dependence of \( \kappa_a \) and \( \kappa_c \) are taken from Ref. [356]. We assume that the ratio of \( \kappa_b \) to \( \kappa_c \) is temperature independent, and fix this ratio to be \( 1.38/57.4 = 2.40\% \). In Fig. 5.35 we show the calculated heating rate. Because of such assumption, the laser heating rate at 295 K is the same as that determined from the Stokes/anti-Stokes analysis.

5.2.9 Theoretical details

The fitting model for the Fano interference

Above \( T_c \), the \( B_{2g}^{(1)} \) and \( B_{2g}^{(2)} \) phonon modes of Ta\(_2\)NiSe\(_5\) exhibit strongly asymmetric Fano lineshapes. To analyze the physics of this Fano interference features, we propose a model
describing three phonon modes individually coupled to broad excitonic continuum. The total Raman response is described in the following way:

\[ \chi'' \sim \text{Im} T^T G T, \]

where \( T^T = (T^T_{ph} \ t_e) \) denotes the vertices for light scattering process (the subscript “T” denotes “Transpose”), in which \( T^T_{ph} = (t_{p1} \ t_{p2} \ t_{p3}) \). \( G \) comprises the Green’s functions for the interacting phononic and excitonic excitations that can be obtained by solving the Dyson equation:

\[ G = (G^{-1}_0 - V)^{-1}. \] (5.52)

In Eq. (5.52)

\[ G_0 = \begin{pmatrix} G^0_{ph} & 0 \\ 0 & G^0_e \end{pmatrix} \] (5.53)

is the bare Green’s function and

\[ V = \begin{pmatrix} 0 & V_{e-ph} \\ V^T_{e-ph} & 0 \end{pmatrix} \] (5.54)

is the exciton-phonon interaction. Here the bare phononic Green’s function

\[ G^0_{ph} = \text{diag}[G^0_{pi}] = \text{diag}[-\left(\frac{1}{\omega - \omega_{pi} + i\gamma_{pi}} - \frac{1}{\omega + \omega_{pi} + i\gamma_{pi}}\right)], \] (5.55)

correspond to the \( B_{2g}^{(i)} \)-symmetry phonon modes \((i=1,2,3)\),

\[ G^0_e = \frac{1}{\omega_e^2/\gamma_e - i\omega} \] (5.56)

represents the excitonic continuum, and \( V^T_{e-ph} = (v_1 \ v_2 \ v_3) \) denotes exciton interaction strength with the corresponding phonons. For phononic equation, the parameters \( \omega_{pi} \) and \( \gamma_{pi} \) have the meaning of the mode frequency and the half width at half maximum (HWHM), respectively. For the excitonic equation, \( \omega_e \) is the energy of the overdamped excitations and \( \gamma_e \) represents the relaxation rate. The quantity \( \Omega_e = \omega_e^2/\gamma_e \) denotes the energy at which the excitonic continuum has maximum intensity.
The bare phononic and excitonic responses are
\[
\chi^{''\prime}_{p(0)} = \text{Im} T_{ph}^{T} G_{ph}^{0} T_{ph} = \sum_{i=1}^{3} t_{pi}^{2} \text{Im} G_{pi}^{0}
\] (5.57)

and
\[
\chi^{''\prime}_{e(0)} = t_{e}^{2} \text{Im} G_{e}^{0}.
\] (5.58)

These two expressions are related to Eqs. (5.17-5.18) in the main text.

The renormalized phononic and excitonic responses, \(\chi^{''}_{p}\) and \(\chi^{''}_{e}\), as well as the interference term \(\chi^{''}_{int}\) are calculated from the renormalized Green’s function \(G\):
\[
G = \begin{pmatrix} G_{ph} & G_{e-ph} \\ G_{e-ph}^{T} & G_{e} \end{pmatrix},
\] (5.59)

where \(G_{e-ph}^{T} = ( G_{1e} \quad G_{2e} \quad G_{3e} \) represents the interference between the phononic modes and the continuum.

The phononic term is calculated from the 3x3 phononic block:
\[
\chi^{''}_{p} = \text{Im} T_{ph}^{T} G_{ph} T_{ph} ;
\] (5.60)

the excitonic term results from the 1x1 excitonic block:
\[
\chi^{''}_{e} = t_{e}^{2} \text{Im} G_{e} ;
\] (5.61)

and the interference term is given by the off-diagonal block
\[
\chi^{''}_{int} = t_{e} \sum_{i=1}^{3} t_{pi} \text{Im} G_{ie} .
\] (5.62)

These three terms, as defined, satisfy Eq. (5.20):
\[
\chi^{''} = \chi^{''}_{p} + \chi^{''}_{e} + \chi^{''}_{int}.
\] (5.63)

For the \(ac\) spectra below \(T_{c}\), especially at about 300 K, this model cannot properly account for the low frequency Raman response. This additional spectral feature is related to Raman coupling to the longitudinal acoustic excitations at finite momenta in the presence
of quasi-periodic domain walls, detailed in the main text. The Green’s function of each individual acoustic mode has form similar to the phononic Green’s function:

\[ G_s(\omega, q) = -\frac{1}{\omega - c_s q + i r_s q} - \frac{1}{\omega + c_s q + i r_s q}. \]  
(5.64)

Its light-scattering vertex \( t_s(q) \) and coupling to the excitonic continuum \( v_s(q) \) are both proportional to the square root of wavevector: \( t_s = \tau_s \sqrt{q} \) and \( v_s = \beta_s \sqrt{q} \). The frequency \( \omega_s \) and the HWHM \( \gamma_s \) are both proportional to the wavevector: \( \omega_s = c_s q \) and \( \gamma_s = r_s q \).

After introducing this mode, Eqs. (5.53-5.54) extend to

\[ G'_0 = \begin{pmatrix} G_{ph}^0 & 0 & 0 \\ 0 & G_s & 0 \\ 0 & 0 & G_e \end{pmatrix}, \]  
(5.65)

\[ V' = \begin{pmatrix} 0 & 0 & V_{e-ph} \\ 0 & 0 & \beta_s \sqrt{q} \\ V_{e-ph}^T & \beta_s \sqrt{q} & 0 \end{pmatrix}, \]  
(5.66)

and the vertex for light-scattering process becomes \( T'T'' = (T_{ph}^T \tau_s \sqrt{q} t_e) \).

Then the total response function containing coupling to acoustic mode for domain walls \( i \) lattice constants apart is given by

\[ \chi''_i \sim \text{Im} T'T G'T'. \]  
(5.67)

Due to the requirement of causality, the real part of susceptibility should be an even function while the imaginary part should be an odd function. Therefore, the static Raman susceptibility is purely real. The total static Raman susceptibility is given by

\[ \chi(\omega = 0) \sim \text{Re} T'T G(\omega = 0)T. \]  
(5.68)

The bare phononic static Raman susceptibility can be obtained from

\[ \chi_p^{(0)}(\omega = 0) \sim \text{Re} T_{ph}^T G_{ph}^0(\omega = 0)T_{ph} = \sum_{i=1}^{3} \frac{2t_{pi}^2 \omega_{pi}}{\omega_{pi}^2 + \gamma_{pi}^2}, \]  
(5.69)
Similarly, the bare excitonic static Raman susceptibility is given by
\[
\chi_e^{(0)}(\omega = 0) \sim t_e^2 \text{Re } G_e^0(\omega = 0) = \frac{t_e^2}{\Omega_e},
\] (5.70)

For temperature-independent \(t_e\), the temperature dependence of \(1/\chi_e\) directly follows that of \(\Omega_e(T) = \omega_e^2/\gamma_e\).

Using the Green’s function \(G'\), which describes the interacting phononic (both optical and acoustic) and excitonic excitations, we can evaluate the renormalization of sound velocity above \(T_c\). Because the relevant frequencies for the acoustic mode are much lower than that of the optical or excitonic modes, we can keep \(\omega\) only in the bare acoustic mode’s Green’s function:
\[
G_s = \begin{pmatrix}
\frac{\omega_{p1}}{2} & 0 & 0 & 0 & -v_1 \\
0 & \frac{\omega_{p2}}{2} & 0 & 0 & -v_2 \\
0 & 0 & \frac{\omega_{p3}}{2} & 0 & -v_3 \\
0 & 0 & 0 & -\frac{\omega^2 - c_s^2 q^2}{2 c_s q} & -\beta_s \sqrt{q} \\
-v_1 & -v_2 & -v_3 & -\beta_s \sqrt{q} & \Omega_e
\end{pmatrix}^{-1},
\] (5.71)
in which finite linewidths of phonon modes are neglected. The pole of this Green’s function is obtained by requiring the determinant of inverse \(G_s\) to be zero:
\[
\frac{\omega^2 - c_s^2 q^2}{2 c_s q} = -\frac{\beta_s^2 q}{\Omega_e - \sum_{i=1}^{3} \frac{2 v_i^2}{\omega_{pi}}},
\] (5.72)
Identifying \(\omega^2\) as \(\tilde{c}_s^2 q^2\), in which \(\tilde{c}_s\) represents the renormalized sound velocity above \(T_c\), we have
\[
\tilde{c}_s^2 = c_s^2 - \frac{2 \beta_s^2 c_s}{\Omega_e - \sum_{i=1}^{3} \frac{2 v_i^2}{\omega_{pi}}},
\] (5.73)

**Illustration of the fitting model for the Fano interference**

To provide more insights into the fitting model described in Appendix 5.2.9, we consider a simplified case in which only one phonon mode couples to an excitonic continuum. When exciton-phonon interaction \(v\) is zero, the total Raman response is reduced to the sum of the
excitonic component and the phononic component:

\[
\chi_0''(\omega) = \frac{t^2_e \omega}{\Omega_e^2 + \omega^2} + \frac{4t^2_p \gamma_p \omega p \omega}{(\omega^2 - \omega_p^2)^2 + 2\gamma^2_p (\omega^2 + \omega_p^2) + \gamma^4_p},
\]

(5.74)
in which \(\Omega_e\) stands for \(\omega_e^2/\gamma_e\).

In Fig. 5.36 we show the excitonic continuum coupling with the \(B_{2g}^{(1)}\) and \(B_{2g}^{(2)}\) phonon modes in an individually way to illustrate the effect of coupling. First we discuss the renormalization effect. The renormalized phonon mode shifts in energy and broadens in lineshape. If we neglect the bare phonon width \(\gamma_p\) for simplicity, the central energy of the renormalized phonon mode, \(\omega_{pv}\), can be expressed as

\[
\omega_{pv} = \omega_p + \frac{v^2 (v^2 - 2 \omega_p \Omega_e)}{2 (v^2 \Omega_e + \omega_p \Omega_e^2 + \omega_p^3)}.
\]

(5.75)

For both the \(B_{2g}^{(1)}\) and \(B_{2g}^{(2)}\) phonon modes, \(v^2\) is smaller than \(2 \omega_p \Omega_e\); therefore \(\omega_{pv}\) is smaller than \(\omega_p\), meaning the renormalized phonon mode shifts to lower energy. Interestingly, at frequency \(\omega_{pv}\) the renormalized excitonic continuum has the same intensity as the un-renormalized continuum; below \(\omega_{pv}\) the excitonic response is enhanced while above \(\omega_{pv}\) the excitonic response is suppressed.

Second we discuss the interference effect. For the interference term, corresponding to the off-diagonal elements of the renormalized Green’s function, there is a frequency \(\omega_{int}\) at which it changes the sign. The frequency \(\omega_{int}\) has the following expression

\[
\omega_{int} = \sqrt{2 \Omega_e \gamma_p + \gamma^2_p + \omega^2_p}.
\]

(5.76)

We note that \(\omega_{int}\) is a bit larger than \(\omega_p\). The shape of the interference term is controlled by sign of \(v\): for positive \(v\), below the zero-intensity point the interference term has positive intensity while the intensity is negative above the zero-intensity point; for negative \(v\), the opposite is true. Far away from the resonance, the interference term decays to zero because the phonon mode has negligible intensity at such high energy.

In Fig. 5.37 we show how the coupling strength \(v\), and the energy at which the excitonic continuum has maximum intensity \(\Omega_e = \omega_e^2/\gamma_e\) influence the combined Raman response.
Figure 5.36: Coupling of the excitonic continuum with (a) the $B_{2g}^{(1)}$ phonon mode and (b) the $B_{2g}^{(2)}$ phonon mode. The parameters used for plotting are obtained from fitting the 380 K spectrum of Ta$_2$NiSe$_5$. The Raman response $\chi''(\omega)$ of the excitonic and phononic excitations for cases without (dashed lines) and with (solid lines) the effect of coupling are compared. The solid red lines correspond to the addition of the solid blue, solid green, and solid orange lines.
Figure 5.37: The influence of the coupling strength $v$, and the frequency at which the excitonic continuum has maximum intensity $\Omega_e = \omega_e^2 / \gamma_e$ on the Raman response $\chi''(\omega)$ of the coupled excitonic and phononic modes. (a) The combined response for varying $v/\omega_p$ with fixed $\Omega_e/\omega_p=1.3$; (b) The combined response for varying $\Omega_e/\omega_p$ with fixed $v/\omega_p=0.3$. For all panels, $t_p=3.8$ arb. units; $t_e=7.2$ arb. units; $\omega_p=7.8$ meV; $\gamma_p=0.38$ meV. The ratios derived from the 380 K spectrum of Ta$_2$NiSe$_5$ are $\Omega_e/\omega_p=1.3$ and $v/\omega_p=0.3$. The horizontal axis is normalized to the phonon frequency $\omega_p$.

The lineshape becomes more asymmetric with increasing $v/\omega_p$ [Fig. 5.37 (a)]. When $\Omega_e$ is varied, we find that the lineshape becomes more asymmetric for smaller $\Omega_e$ [Fig. 5.37 (b)].

Finally we note that when $\omega$ is much larger than $\omega_p$ and $\gamma_e$, the Raman response is approximately $t_e^2 / \omega$. Therefore, $t_e$ can be determined by fitting the data at large $\omega$. 
5.3 Electronic phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$

One of the fascinating manifestations of interactions between electrons in solids is the emergence of electronic orders. The fluctuations close to the respective quantum critical points are also believed to be the drivers of a wealth of yet unexplained behaviors, including strange metallicity and high-T$_c$ superconductivity [359–362]. In many cases (such as, e.g., nematic [363, 364] or density-wave [365, 366] orders) electronic order breaks the symmetries of the crystalline lattice and the corresponding transitions can be, symmetry-wise, identical to structural ones. This raises the question of the role of the interplay between electronic and lattice degrees of freedom in the ordering. Even in cases where the lattice only weakly responds to the transition [367, 368], the critical temperatures [306, 307] and quantum critical properties [369] can be strongly modified. Moreover, in a number of cases the origin of the order is still under debate [279, 370, 371], as the lattice may develop an instability of its own.

The electronic-lattice dichotomy has recently come to the fore in studies of Ta$_2$NiSe$_5$ [285, 288, 294] - one of the few candidate material for the excitonic insulator (EI) phase [276–281]. EI results from a proliferation of excitons driven by Coulomb attraction between electrons and holes in a semiconductor or a semimetal [271–275]. Ta$_2$NiSe$_5$ exhibits a phase transition at $T_c = 328$ K; while the pronounced changes in band structure [294], transport [285] and optical [291] properties are consistent with the ones expected for an EI, they allow an alternative interpretation in terms of a purely structural phase transition [298–300, 372]. Indeed, EI state in Ta$_2$NiSe$_5$ is expected to break mirror symmetries of the lattice due to the distinct symmetries of the electron and hole states forming the exciton [293], similar to a structural transition [299]. Intriguingly, substitution of Se with S has been shown to suppress $T_c$ in transport experiments to zero [285], suggesting a possible quantum phase transition (QPT) at $x = x_c$ in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. Increasing $x$ enhances the band gap in the electronic structure [373], which is known to suppress the EI [273, 275], consistent with an EI QPT. On the other hand, the lattice degrees of freedom also evolve with $x$ making
it imperative to separately assess the roles of electronic and lattice degrees of freedom throughout the phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. A promising technique to address this challenge is to probe the critical dynamics with polarization-resolved Raman scattering that also allows to detect symmetry breaking independently [2, 27].

Here we use polarization-resolved Raman scattering to study the dynamics of electronic excitations throughout the phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. We reveal the presence of low-energy excitonic modes that soften on cooling towards $T_c(x)$. This softening indicates, that in the absence of lattice effects, a purely excitonic transition would have taken place at $T_{ex}(x)$, which we deduce to be smaller than $T_c(x)$. On increasing sulfur content $x$, $T_{ex}(x)$ is suppressed to negative values and for $x = 1$ low-energy excitons are no longer observed, as expected for an excitonic insulator quantum phase transition. However, the actual $T_c(x)$ remains finite for all $x$, implying the presence of a cooperating lattice instability, obscuring the suppression of the excitonic order. The study thus reveals a “failed” excitonic quantum phase transition in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ masked by a preemptive structural order, that takes over as the electronic instability is suppressed.

5.3.1 Experimental

We performed Raman scattering experiments on four Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ samples with varying Se/S content grown using the chemical vapor transport (CVT) method [7]. The measurements were performed in a quasi-back-scattering geometry on samples cleaved to expose the $ac$ crystallographic plane with the 647 nm line from a Kr$^+$ ion laser excitation, details presented in Ref. [7]. The selection rules in the high-temperature orthorhombic (point group $D_{2h}$) phase imply that $ac$ polarization geometry probes excitations with $B_{2g}$ symmetry (same as that of the order parameter), while $aa$ geometry probes the fully symmetric $A_g$ ones. Below $T_c$, the point group symmetry is reduced to $C_{2h}$ and the two irreducible representations merge, such that excitations from $ac$ geometry above $T_c$ may appear in $aa$ geometry and vice versa. Their appearance allows to determine $T_c$ from the Raman spectra.
5.3.2 Data overview

Summarized temperature dependence of the Raman susceptibility $\chi''(\omega, T)$ is presented in Fig. 5.38. The samples with $x = 0, 0.25, 0.67$ show qualitatively similar spectra. At low energies, phonon peaks are observed on top of a smooth background, which we attribute to electronic excitations. On cooling, a pronounced redistribution of electronic intensity in a wide range of energies is observed, leading to a formation of a gap-like suppression followed by a high-energy peak Fig. 5.38(a)-(c). This peak at 380 meV for Ta$_2$NiSe$_5$ has been attributed to the coherence factors at the gap edge of an EI [6]. In ac geometry, a pronounced enhancement at low energies is evident close to $T_c$, consistent with critical mode softening near a second-order phase transition, Fig. 5.38(i)-(k). In the same temperature region, the lineshapes of the low-energy phonons show strongly asymmetric Fano form (Fig. 5.38(m)-(o)) - a known signature of interaction with an electronic excitation continuum [6, 7, 349]. This indicates the presence of low-energy symmetry-breaking electronic excitations, that soften close to $T_c$. At low temperatures, the asymmetry disappears (Fig. 5.38(e)-(g)), a behavior consistent with a gap opening in an EI. On increasing sulfur content $x$, the temperature where the strongest low-energy enhancement is observed progressively lowers (Fig. 5.38(i)-(k)), and the $A_g$-symmetry peak at about 380 meV becomes less pronounced and moves slightly to lower energy.

The signatures for Ta$_2$NiS$_5$ ($x = 1$) are rather different: in the ac geometry, low-energy electronic excitations are absent at all temperatures, indicating the presence of a direct gap. This implies that between $x = 0.67$ and $x = 1$ the electronic structure undergoes a Lifschitz transition from a semimetallic to an insulating one. The intensity in the aa geometry at low energies is also much smaller than for the other samples and no broad high-energy peak is observed at low temperatures. On the contrary, a sharp feature at about 0.3 eV emerges in ac geometry on cooling below 100 K.
Figure 5.38: Overview of the polarization-resolved Raman response $\chi''(\omega,T)$ in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. (a-d) Response in $aa$ polarization geometry corresponding to fully symmetric ($A_g$) excitations above (red) and below (blue) $T_c$ for $x = 0 - 1$. Shading highlights the bare electronic contribution to the response. (e-f) Same for $ac$ geometry, probing the excitations with the symmetry of the order parameter ($B_{2g}$) for $T > T_c$ (red). Unlike $aa$ geometry, phonons show an extremely anisotropic Fano lineshape (hatching), indicating their strong interaction with the electronic continuum (red shading). For $T < T_c$ (blue) excitations observed in $aa$ geometry above $T_c$ appear (arrow) due to symmetry breaking. (i-l) Temperature dependence of $\chi''_{ac}(\omega,T)$; an enhancement at low energies near $T_c$ (arrow) is observed for $x = 0, 0.25, 0.67$. For $x = 1$ no low-energy response is present. (m-p) Details of $\chi''_{ac}(\omega,T)$ for regions marked by dashed lines in (i-k). (m-o) Fano lineshape of low-energy phonons due to interaction with electronic continuum. (p) High-energy peak due to an uncondensed exciton in Ta$_2$NiS$_5$. 
5.3.3 Symmetry-breaking transition

We address first the presence of a phase transition by studying the appearance of new modes in the broken-symmetry phase, as outlined above. In Fig. 5.39(a) we show the temperature dependence of such a “leakage” phonon intensity marked by arrow in Fig. 5.38(e)-(h). One can see the appearance of the “leaked” intensity below $T_c$ in the pure Se case, as well as the decrease of $T_c$ with S doping. “Leakages” of other modes appear below the same temperature $T_c$ [7]. At low $x$ the obtained values of $T_c$ agree with the ones deduced from transport and specific heat measurements [7, 285], Fig. 5.40. However, in contrast to the transport data reported in Ref. [285], we find that the symmetry-breaking transition persists for all compositions, although the “leakage” intensity is strongly suppressed with higher $x$. The latter suggests that the phase transition signatures in thermodynamic and transport measurements may become too weak to be observed at large $x$, especially since the system becomes more insulating with $x$. The structural signatures, e.g. the deviation of the monoclinic angle $\beta$ from $90^\circ$, should be also strongly suppressed, being already weak at $x = 0$ [288].

The phase transition for $x = 1$, where no low-energy softening is observed (Fig. 5.38(l)), indicates a different transition mechanism. Below we analyze our data to elucidate the origin of the transition as a function of $x$.

5.3.4 Electronic contribution to the phase transition

We investigate first the soft-mode behavior observed for $x \leq 0.67$ (Fig. 5.38(i-k)). In particular, we analyze the asymmetric lineshapes of the low-energy part of $\chi''_{ac}(\omega,T)$ around $T_c$ (Fig. 5.38(m-o)) using an extended Fano model [6, 7]. The model assumes three phononic oscillators (which is the number of $B_{2g}$ modes in the orthorhombic phase) interacting with a continuum of excitonic origin. The latter is expected to arise from the excitonic fluctuations in a semimetal, overdamped due to the allowed decay into particle-hole pairs. Close to the transition, the dynamics of the excitonic mode is governed by the time-dependent Landau
Figure 5.39: The parameters deduced from the Raman response data, Fig. 5.38. (a) Integrated “leakage” intensity into $ac$ scattering geometries of the lowest-energy $A_g$ phonon mode labeled in panels Fig. 5.38(e-h), normalized by the intensity in the dominant $aa$ geometry. The mode’s appearance in the $ac$ scattering geometry below $T_c$ implies the onset of symmetry breaking. (b) Bright points: Excitonic energy $\Omega_e(T)$, Eq. (5.77); Bleak points: the renormalized energy $\Omega_{e,\text{comb}}(T)$ including the exciton-phonon interaction obtained from the Fano fits to the lineshapes in Fig. 5.38. Lines represent linear fits to the points.
equations [374–377]. Together with the standard oscillator dynamics of the phonons the system is described by

\[
\{\partial_t + \Omega_e(T)\} \varphi + \sum_{i=1}^{3} \tilde{v}_i \eta_i = 0, \\
\{\partial_t^2 + 2\gamma_i(T)\partial_t + \omega_{pi}^2(T)\} \eta_i + \tilde{v}_i \varphi = 0,
\]

where \(\eta_{i=1,2,3}\) and \(\varphi\) are the collective coordinates (order parameters) of the optical phonons and excitons, respectively. \(\Omega_e(T)\) is the characteristic energy of the excitonic fluctuations, \(\omega_{pi}(T)\) and \(\gamma_i(T)\) are the phonon frequencies and scattering rates, and a bilinear exciton phonon-coupling \(\tilde{v}_i\) is assumed. The linear response of the system Eq. (5.77) determines the Raman susceptibility. The resulting model is a generalization of the standard Fano model [349] for Raman scattering in metals to the case of three phonons and the continuum response determined from the Landau theory, Eq. (5.77). The purely excitonic part of the response has then the form of a broad continuum \(\chi''_{\text{cont}}(\omega,T) \propto \frac{\omega}{\Omega_e^2(T)+\omega^2}\), in contrast to the Lorentzian phonon peaks. The interaction between the phonons and the excitonic continuum leads to an asymmetric broadening of the peaks [7], allowing to capture the observed lineshapes in great detail [6, 7].

We now discuss the parameters deduced from the Fano model fits. The phonon frequencies \(\omega_{pi}(T)\) do not soften near \(T_c\) [7], ruling out a zone-center phonon instability [299]. On the other hand, \(\Omega_e(T)\) (Fig. 5.39(b), solid lines) consistently softens above \(T_c\) for all semimetallic samples. The linear temperature dependence \(\Omega_e(T) \sim T - T_{ex}\) implies that a purely electronic transition would have taken place at \(T_{ex} < T_c\) for \(x = 0, 0.25\) (Fig. 5.40, blue symbols). The strongly negative \(T_{ex}\) for \(x = 0.67\) indicates that the exciton softening alone would not have lead to a transition at this sulfur concentration.

The suppression of the excitonic instability with \(x\) is even more evident in \(\text{Ta}_2\text{NiS}_5\), Fig. 5.38(d,h,l), where the low-energy electronic response is altogether absent due to a direct band gap [373]. Instead, we observe a sharp \(B_{2g}\)-symmetry mode at 0.3 eV, Fig. 5.38(p), consistent with an in-gap exciton. It is followed by a weaker feature at 0.325 eV and an
intensity “tail” at higher energies up to around 0.4 eV. The natural interpretation of the second peak is the second state of the Rydberg series (i.e. 2S exciton), while the high-energy intensity “tail” can be attributed, in analogy with optical absorption spectroscopy, to the Rydberg states of higher order and interband transitions [378, 379] with possible contributions from phonon-assisted exciton transitions [380, 381]. A “leakage” of the exciton features is also observed in $aa$ geometry due to symmetry breaking, Fig. 5.38(d). On heating, all the features broaden and eventually smear out above 100 K. The increase of the linewidth of the excitonic features can be attributed to the interaction with acoustic and optical phonons [382].

5.3.5 Lattice effects and the phase diagram

The presented observations show that the excitonic instability on its own cannot explain the occurrence of a transition for samples with large $x$, calling for a more careful consideration of the lattice effects. First, the coupling of excitons with the otherwise inert optical phonons can increase the transition temperature. For a coupled excitonic-optical phonon system (Eqs. (5.77)), the transition occurs at $T_{comb}(x)$, where $\Omega_{e}^{comb}(T) = \Omega_{e}(T) - \sum_{i} \frac{v_{i}^{2}}{\omega_{pi}(T)}$ becomes zero. The deduced $\Omega_{e}^{comb}(T)$ shown in Fig. 5.39(b), dashed lines, indeed softens to zero at a temperature $T_{comb}(x)$ higher than $T_{ex}(x)$, green points in Fig. 5.40. $T_{comb}(x = 0.67)$ is however still negative, while the actual $T_c$ is 170 K. For $\text{Ta}_2\text{NiS}_5$, where the soft excitons are absent, the optical phonon modes exhibit around 15% softening on cooling. However, their energies never soften below 6.5 meV, Fig. 5.38(l), ruling them out as the driving force of the transition for $\text{Ta}_2\text{NiS}_5$ [7].

The only remaining option is an instability of the acoustic modes in $\text{Ta}_2\text{NiS}_5$, i.e. ferroelasticity [302], driven by softening of the $B_{2g}$ shear modulus $C_{ac}(T)$. The acoustic modes are not observed in Raman due to their extremely low energies and weak coupling to light [7, 171]. The intrinsic softening of shear modulus also affects the excitonic-driven transition via linear coupling $\lambda$ of $\varphi$ to the strain tensor component $\varepsilon_{ac}$ that further enhances the transition.
Figure 5.40: Phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. Orange points: the symmetry breaking transition temperature $T_c(x)$ obtained from the onset of phonon intensity “leakage”, Fig. 5.39(a). Red points and crosses: $T'_c(x)$ adapted from transport studies Refs. [7, 285]. For low sulfur concentration $x$, the soft excitonic mode, Fig. 5.39(b), would drive the transition at temperature $T_{ex}(x)$ (blue points), that is enhanced to $T_{comb}(x)$ by coupling to inert optical phonons (green points), and is further enhanced to $T_{str}^{comb}(x)$ by coupling to the $B_{2g}$ strain (purple triangles). For large $x$, the excitonic softening is suppressed, while a ferroelastic instability leads to a finite $T_{FE}^{comb}(x)$ (black squares). In the absence of the lattice instability, a lattice-shifted electronic QPT would have occurred at $x_c$ (dashed purple line). Additionally, in the same proximity, the band structure undergoes semimetal-to-semiconductor Lifschitz transition (see text).

Ignoring ferroelastic softening (i.e., taking $C_{ac}^{-1}(T) = C_{ac}^{-1}(0)$, the purple dashed line $T_{str}^{comb}$ in Fig. 5.40) leads to a large deviation from actual $T_c(x)$ already at $x = 0.67$ and a complete suppression of ordering at $x_c \approx 0.8$. This picture bears important consequences for the physics of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. At low $x$, the transition is driven, to a good approximation, only by the excitonic softening. On increasing $x$, the lattice softening becomes more important, and for $x = 1$ the transition is purely ferroelastic. In the absence of ferroelasticity, a lattice-shifted electronic QPT would have occurred at $x_c \approx 0.8$. While the presence of the lattice symmetry breaking at $T_c$
suppresses the signatures of the QPT at low $T$, at temperatures higher than 120 K, the associated critical fluctuations are expected to appear \cite{369}. The presence of quantum critical fluctuations due to a “failed” excitonic QPT lends a natural explanation to the signatures of strong correlations observed in Ta$_2$NiSe$_5$. In particular, a filling-in, rather then closing of the gap in $aa$ Raman spectra has recently been connected to strong electronic correlations \cite{6}; moreover, ARPES studies \cite{295} suggest the presence of “preformed excitons” well above $T_c$ also characteristic of correlated regime. Similar temperature evolution of $aa$ spectra is also observed for the doped samples, Fig. 5.38(b,c). Interestingly, while the intensity of the coherent $aa$ peak is suppressed with doping, as is expected from mean-field theory \cite{3}, the position of the peak changes only weakly. The latter behavior indicates strong correlations which get a natural explanation in terms of the quantum critical fluctuations from the “failed” QPT. Finally, ferroelasticity may be suppressed by strain \cite{383} or pressure \cite{285} raising the possibility to reveal the bare EI QPT at low temperatures. For a semimetallic band structure, the EI QPT has been predicted to lead to non-Fermi liquid behavior \cite{384}, mass enhancement \cite{385} or emergence of superconductivity \cite{386}. Interestingly, superconducting dome near the end point of the monoclinic phase has been recently reported in Ta$_2$NiSe$_5$ under pressure \cite{387}.

### 5.3.6 Conclusions

In this work, we used polarized Raman scattering to reveal a “failed” excitonic insulator quantum phase transition at $x_c \approx 0.8$ in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$, hidden by the onset of symmetry breaking due to a lattice instability. At low sulfur content $x$ we observed a soft excitonic mode driving the transition, while at large $x$ this mode ultimately transforms into a high-energy exciton, unable to drive the transition. We further exclude the instability of optical phonons and demonstrate that a cooperating ferroelastic instability yields an explanation of the observed symmetry breaking transition. While the lattice instability masks

\footnote{In a two-band model of EI $\chi''_{aa}(\omega) \sim \nu_0 \sqrt{2W/(\omega - 2W)}$ \cite{6}, where $\nu$ is the density of states above $T_c$ and $W$ is the interband hybridization, which is the order parameter for pure EI \cite{293}.}
the presence of the excitonic quantum phase transition, the associated critical fluctuations may still explain the correlation effects in Ta$_2$NiSe$_5$ at high temperatures. Furthermore, a controlled suppression of the structural instability by, strain [383] or pressure [285], can turn Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ into a platform to study the excitonic QPT at low temperatures as well as quantum critical ferroelasticity [388].

5.3.7 Experimental details

The exciton mode

In Fig. 5.41(a) we compare the exciton mode of Ta$_2$NiS$_5$ measured by two different excitation wavelengths at 647 and 676 nm. The Raman shift of this mode at about 300 meV is excitation-independent, indicating that the mode is a genuine Raman feature. In Fig. 5.41(b) we show, for comparison, the scattering cross section plotted against absolute photon energy. We interpret the weaker spectral feature at 325 meV as the second state of the Rydberg series, the 2S exciton, which exhibits less intensity than the 1S exciton at 300 meV. The apparent continuum of excitations up to about 400 meV can then be attributed, in analogy with optical absorption spectroscopy, to the interband transitions [378, 379] with possible contributions from phonon-assisted exciton transitions [380, 381] to finite-momentum exciton states as well as Rydberg states of higher order [378, 379].

The structural phase transition

Due to the breaking of two mirror-plane symmetry operations below T$_c$, the A$_g$ and B$_{2g}$ representations of the high-temperature phase, point group D$_{2h}$, merge into A$_g$ representations of the point group C$_{2h}$. Thus, the orthorhombic-to-monoclinic structural phase transition removes the orthogonality between A$_g$ and B$_{2g}$ [D$_{2h}$] representations, making the phonon modes observable in “forbidden” scattering geometry, namely, the A$_g$-symmetry modes start to appear in the ac geometry, and the B$_{2g}$-symmetry modes begin to appear in the aa geometry below the transition temperature. In Fig. 5.42 (a-b) we present the phonon
Figure 5.41: The high-energy spectra of Ta$_2$NiS$_5$ measured in the ac scattering geometry at 35 K. (a) Raman response as a function of Raman shift, the energy difference between the laser-photon energy and the scattered-photon energy. The inset of (a) shows the high-resolution spectrum of the exciton mode at 10 K, corresponding to the energy range enclosed by the dashed box in (a). The full width at half maximum (FWHM) of the exciton mode is 7 meV. (b) Differential cross section as a function of scattering-photon energy.
Figure 5.42: The low-energy phonon spectra of Ta$_2$NiS$_5$. (a) Raman response in the aa geometry at 35 K. (b) Raman response in the ac geometry at 35 K. (c) Raman response in the aa geometry at 140 K. (d) Raman response in the ac geometry at 140 K. The $A_g$ phonon modes are labelled with orange numbers and the $B_{2g}$ modes with purple numbers.

spectra of Ta$_2$NiS$_5$ at 35 K in the two scattering geometries. The $A_g^{(1)}$, $A_g^{(3)}$, and $B_{2g}^{(1)}$ modes appears in the “forbidden” scattering geometry as a distinct spectral peak, while the $A_g^{(2)}$ and $B_{2g}^{(2)}$ modes show a weak shoulder feature in the “forbidden” scattering geometry. On the contrary, there are no such spectral features in the orthogonal scattering geometry at 140 K [Fig. 5.42(c-d)]. Such difference clearly indicates the broken symmetry due to structural phase transition for Ta$_2$NiS$_5$. Moreover, the fact that $aa$ can $ac$ scattering geometries become no longer orthogonal below the phase transition temperature indicates that the two broken mirror-plane symmetry operations specifically are $a \rightarrow -a$ and $c \rightarrow -c$.

Within the Landau theory, the intensity of the modes in the “forbidden” scattering geometry is proportional to the square of the order parameter, which can be represented by, e.g., the deviation of the angle $\beta$ between $a$ and $c$ axes from 90°. It is therefore expected that such intensity remains zero above the transition temperature, and starts to increase monotonically on cooling below the transition temperature. The effect of fluctuations might lead to a finite intensity in the “forbidden” scattering geometry in a narrow temperature range above the transition temperature. In Fig. 5.43 we show the temperature dependence of the intensity in the “forbidden” scattering geometry for the $A_g^{(1)}$, $A_g^{(3)}$, and $B_{2g}^{(1)}$ modes [7].
Figure 5.43: Temperature dependence of the intensity in the “forbidden” scattering geometry for the three phonon modes (labelled in Fig. 5.42), normalized by their respective intensity in the dominant scattering geometry.

As the mode’s appearance in the “forbidden” scattering geometry implies the onset of symmetry breaking, we determine the transition temperature for \( \text{Ta}_2\text{NiS}_5 \) to be 120±10 K.

The symmetry breaking not only allows the phonon modes to appear in the “forbidden” scattering geometry, but also has an influence on the electronic excitations. Hence, the high-energy \( \text{B}_{2g} \)-symmetry [in the high-temperature \( \text{D}_{2h} \) point group] exciton mode should emerge in the \( aa \) scattering geometry at low temperature as well. This is indeed the case, as shown in Fig. 5.44. To quantify this effect as a function of temperature, we show in Fig. 5.45 the Raman response at the exciton peak energy as a function of temperature. For both geometries we have subtracted the value at 315 K. One observes that in the \( ac \) geometry the intensity grows on cooling at all temperatures, although the increase is faster below 120 K.
Figure 5.44: The high-energy spectra of Ta$_2$NiS$_5$. (a) Raman response in the aa geometry at 35 K. (b) Raman response in the ac geometry at 35 K. (c) Raman response in the aa geometry at 140 K. (d) Raman response in the ac geometry at 140 K.

In the aa geometry, on the other hand, the intensity does not evolve at all between 315 K and 120 K, consistent with the energy being below that of the interband transition. Below 120 K, the intensity starts to grow in the “forbidden” for this B$_{2g}$-symmetry exciton aa scattering geometry, consistent with the symmetry-breaking transition temperature deduced from the “leakage” of phonon modes.

We can also study the leakage of the whole exciton-associated feature below $T_c$. As the exciton intensity in the ac scattering geometry is much larger than that in aa geometry, we can neglect the leakage of aa into ac, and consider only the former effect. To demonstrate that the weak spectral peak in the aa scattering geometry results from the symmetry breaking, in Fig. 5.46 we analyze $\chi''_{\text{aa}}(\omega) - p \cdot \chi''_{\text{ac}}(\omega)$, where $0 < p < 1$. We find that for $p = 2.4\%$, the spectrum after subtraction becomes essentially featureless. This suggests all the low-temperature evolution of intensity around 0.3 eV in aa geometry can be attributed to “leakage” from ac geometry.
Figure 5.45: Temperature dependence of the Raman response $\chi''(T)$ at the peak energy of the exciton mode (0.298 eV) for Ta$_2$NiS$_5$, with the value measured at 315 K, $\chi''(315\text{K})$, subtracted.

Figure 5.46: Analysis of the exciton-mode “leakage” at 35 K. Red line is the measured spectrum in the $aa$ scattering geometry; subtracting 2.4% of the $ac$ spectrum (blue line) from the $aa$ spectrum renders an essentially featureless spectrum (purple line), indicating that there is a 2.4% leakage of the exciton mode.
Figure 5.47: The excitation dependence of the secondary-emission intensity $I$ measured in aa geometry at 30 K for Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family. For each doping level $x$, the left panel is plotted against Raman shift, and the right panel against the absolute energy of the secondary-emission photons.

Excitation dependence of secondary-emission intensity

In Fig. 5.47 we present the excitation dependence of the secondary-emission intensity measured in aa geometry at 30 K for Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family. The energy of Raman features are excitation-independent when plotting against Raman shift, while that of photo-luminescence features are excitation-independent when plotting against absolute energy.

For Ta$_2$NiSe$_5$, we identify the intense peak at 0.38 eV [Fig. 5.47(a)], resulting from the coherent superposition of the band states at the gap edge. This Raman feature decreases in intensity with sulfur doping $x$, and becomes absent for $x = 1$. The three photo-luminescence features are observed at 1.5, 1.9, and 2.1 eV, respectively [Fig. 5.47(b)].

For Ta$_2$NiS$_5$, we observe a strong Raman peak at 0.78 eV [Fig. 5.47(g)], corresponding to an interband transition. It is resonant enhanced with green laser excitations (2.3-2.4 eV incoming photon energy). This Raman feature can also be identified for alloyed samples [Fig. 5.47(c) and (e)]. The two photo-luminescence features of Ta$_2$NiS$_5$ are at 1.5 and 1.6 eV, respectively [Fig. 5.47(h)].

In Fig. 5.48 we present the excitation dependence of the secondary-emission intensity measured in ac geometry at 30 K. For Ta$_2$NiSe$_5$, we find two photo-luminescence features
Figure 5.48: The excitation dependence of the secondary-emission intensity $I$ measured in ac geometry at 30 K for Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family. For each doping level $x$, the left panel is plotted against Raman shift, and the right panel against the absolute energy of the secondary-emission photons.

at 1.5 and 1.8 eV as spectral peaks and one photo-luminescence feature at 2.1 eV as spectral shoulder. The energy of these three features is consistent with that measured in aa geometry, because the photo-luminescence signal in most cases has no definite symmetry.

For Ta$_2$NiS$_5$, the Raman feature of the exciton mode at 0.3 eV is resonant enhanced with red laser excitations (1.8-1.9 eV incoming photon energy). As for the photo-luminescence features, besides those at 1.5 and 1.6 eV observed in aa geometry, there is one more at 2.4 eV [Fig. 5.48(h)].

5.3.8 Theoretical details

Phase diagram

The purely excitonic transition temperature is defined by the excitonic mode having zero energy $\Omega_e(T_{ex}) = 0$. One observes, however, that it precisely coincides with the condition for the static ($\omega = 0$) electronic susceptibility to diverge:

$$\chi_{cont}(\omega = 0, T) = \frac{t^2}{\Omega_e(T)}; \quad \chi_{cont}(\omega = 0, T_{ex}) \to \infty,$$

(5.78)
corresponding to a thermodynamic phase transition in a purely excitonic system (i.e. ignoring phonons).
In the presence of optical phonons, the static response of the system is given by

$$\chi(\omega = 0, T) = \sum_{ij} T_i G_{ij}(\omega = 0, T) T_j,$$

the thermodynamic transition $$\chi(\omega = 0, T) \to \infty$$ occurs at $$T_{\text{comb}}$$. It can be shown that (see also \[6, 7\]) this occurs when the determinant of $$G_{ij}^{-1}(\omega = 0, T)$$ vanishes, i.e.

$$\Omega_e(T_{\text{comb}}) - \sum_i \frac{2\nu_i^2}{\omega_p(T_{\text{comb}})} \equiv \Omega_e^{\text{comb}}(T_{\text{comb}}) = 0.$$  \hspace{1cm} (5.80)

The influence of the acoustic modes can be taken into account within the same formalism as above, by introducing an additional phonon mode into Eq. (5.54) with energy $$\omega_s = c_s q$$, linewidth $$\gamma_s = r_s q$$ and coupling to excitons $$v_s = \beta_q \sqrt{q}$$, where $$q$$ is the wavevector that is infinitesimally small for Raman scattering (see \[6, 7\] for details). Nonetheless, even in the $$q \to 0$$ limit, the susceptibility of the system including interaction of excitons with both acoustic and optical modes diverges only when:

$$\Omega_e^{\text{comb}}(T_{\text{comb}}) - \sum_i \frac{2\nu_i^2}{\omega_p(T_{\text{comb}})} = \Omega_e^{\text{comb}}(T_{\text{comb}}) = 0,$$

where \(\frac{2\beta_s^2}{c_s} \equiv \lambda^2/(2C_{ac})\). This can be generalized to the case of the presence of a ferroelastic instability by using a temperature-dependent $$C_{ac}(T)$$:

$$C_{ac}^{-1}(T) = C_{ac(0)}^{-1} + \frac{a}{T - T_{FE}},$$

in which $$T_{FE} = 120$$ K corresponds to the phase transition temperature of Ta$_2$NiS$_5$. Because $$T_{\text{comb}}^F$$ satisfies

$$\Omega_e^{\text{comb}}(T_{\text{comb}}^F) - \frac{\lambda^2}{2C_{ac}(T_{\text{comb}}^F)} = \Omega_e^{\text{comb}}(T_{\text{comb}}^F) - \frac{\lambda^2}{2C_{ac(0)}^{T_{\text{comb}}^F}} = 0,$$

we obtain the values of $$\lambda^2 C_{ac(0)}^{-1}$$ and $$\lambda^2 a$$ by fitting the phase transition temperatures of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family with Eq. (5.83), and then use Eq. (5.83) to obtain $$T_{\text{comb}}^F$$ (Fig. 4, black line).
In this thesis study, the quadrupolar fluctuations and crystal-field (CF) excitations of 4f-electron systems, and the nature of unconventional insulating phases of 5d-electron systems are investigated by inelastic light scattering. In particular, the unique advantages of light-scattering techniques in studying these correlated electron systems are demonstrated.

The zero-wavevector quadrupolar fluctuations of ferroquadrupolar systems can be directly probed by inelastic light scattering with high energy resolution. By calculating the corresponding static Raman susceptibility from the measured Raman response, the electronic Weiss temperature can be obtained. For YbRu$_2$Ge$_2$, the electronic static Raman susceptibilities in quadrupolar symmetry channels exhibit nearly Curie law behavior, and the electron-lattice coupling is essential for the FQ transition. The finite-wavevector quadrupolar fluctuations of antiferroquadrupolar systems cannot be directly probed by inelastic light scattering. However, the tendency towards antiferroquadrupolar ordering could induce ferromagnetic correlations which manifest as long-wavelength magnetic fluctuations. For CeB$_6$, the static Raman susceptibility corresponding to these fluctuations shows the same temperature dependence as the magnetic susceptibility.

Physical properties including the symmetry, energy, and lifetime of CF states can be obtained by inelastic light scattering. The symmetry of CF levels can be resolved by performing measurements using different scattering geometries; the central position and width of measured spectral peaks are related to the energy and lifetime of CF levels. For CeB$_6$, the spectral linewidth of the CF excitations is broadened by Kondo effect. The evolution of the CF eigenstates and eigenenergies as a function of CF potential and SOC strength is
derived from a model Hamiltonian calculation. For YbRu$_2$Ge$_2$, the ground state is a quasi-quartet composed of one $\Gamma_6$ and one $\Gamma_7$ doublets, and this quasi-degeneracy is essential for the ferroquadrupolar phase. For TbInO$_3$: strain field, the determined CF level scheme can well account for the low-temperature specific-heat data.

Moreover, spectral features indicating coupling between CF transitions and phonon modes of the same symmetry are observed in all three systems. For CeB$_6$, there is a sum mode in the full symmetric channel whose energy equals to one CF mode plus one phonon mode of the same symmetry. For YbRu$_2$Ge$_2$, the increase of the integrated intensity of two phonon modes on cooling is related to the coupling between these two modes with CF excitations. For TbInO$_3$, the increase of the apparent linewidth of two phonon modes on cooling can be attributed to the coupling between these two modes with CF excitations. Theoretical models, based on Green’s function formalism, are developed to provide quantitative description of these effects.

For insulating iridates composed of face-sharing IrO$_6$ octahedra, the $j_{\text{eff}} = 1/2$ local moment picture, commonly adopted for discussing electronic and magnetic properties of iridate compounds with IrO$_6$ octahedra, may not be applicable. The shorter Ir-Ir distance in the face-sharing geometry, compared to corner- or edge-sharing structures, leads to strong covalency between neighboring Ir. Then this strong covalency results in the formation of molecular orbitals at each Ir trimers as the low-energy electronic degree of freedom. For Ba$_5$CuIr$_3$O$_{12}$, the theoretically predicted three-peak structure in the joint density of states is a distinct indication of deviation from the $j_{\text{eff}} = 1/2$ picture. This prediction is verified by observing the three-peak structure in the electronic excitation spectrum of inelastic light scattering.

Absence of magnetic order and a high Weiss temperature inferred from magnetic-susceptibility data are usually considered as a evidence for spin-liquid phases. However, these results could result from a random singlet state. It is crucial to measure magnetization in high field at low temperature to distinguish spin-liquid and random-singlet phases.
For Ba$_5$CuIr$_3$O$_{12}$, the temperature dependence of magnetic susceptibility and heat capacity shows only weak antiferromagnetic correlations, but the magnetization does not saturate up to a field of 59 T. These behaviors can be well explained by a random singlet state which processes a distribution of exchange energy due to structural imperfections.

Excitonic insulator is a coherent phase resulting from the formation of a macroscopic number of bound electron-hole pairs when the corresponding binding energy is smaller than the band gap. Because of the coupling between the electronic and phononic degrees of freedom, there will be a accompanying structural change below the phase transition temperature. Particularly, if the band gap is direct, the volume of the unit cell remains the same but the shape of the unit cell changes as a result of the symmetry breaking, and the structural change therefore has zero wavevector. In this case the excitonic soft mode and the phonon modes which couples to it are all Raman active and makes inelastic light scattering a suitable experimental choice. For Ta$_2$NiSe$_5$, the excitonic mode, which has quadrupolar symmetry, softens close to the phase transition; its coupling to non-critical lattice modes enhances the transition temperature.

Interband transitions can be captured by inelastic light scattering as well. From the symmetry analysis of the transitions, the hybridization of valance and conducting bands can be revealed. For Ta$_2$NiSe$_5$, coherent superpositions of band states at the correlated insulator gap edge gradually emerges on cooling, with noticeable departures from mean-field predictions.

Spectroscopically, it is further found that the critical excitonic fluctuations of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family diminish with sulfur doping, and ultimately shift to high energies. A structural phase transition at finite temperatures is detected at all doping level, exposing a ferroelastic instability for large doping levels.

Looking forward, we expect that more insights into the correlated phenomena of solid-state materials will be provided by inelastic light scattering. With the improving of experimental techniques, more relevant parameters can be adjusted, for instance magnetic field,
strain field, and pressure. Among them, magnetic field can alter the antiferromagnetic ground state of CeB$_6$, and the proposed spin-liquid ground state of TbInO$_3$; strain field can tune the transition temperature of the Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ family. Applying these fields in light-scattering experiments enables us to reveal new physical phenomena, which in turn promotes deeper physical understanding.
Bibliography


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