

Spin-orbital Fluctuations and Unconventional Quantum
Phases in Lacunar Spinel: Insights from Neutron and X-ray
Scatterings

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Spin-orbital Fluctuations and Unconventional Quantum Phases in Lacunar Spinels: Insights from Neutron and X-ray Scatterings

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Abstract: Spin, orbit, and lattice dynamics are coupled in strong spin-orbit coupling systems. The Lacunar spinel, GaTa_4Se_8 , is a unique Mott insulator that hosts molecular spin-orbit $J_{eff}=3/2$ states as correlation units. However, little is known about the spin-orbital ground state and dynamics in this system. In this thesis, I discuss a series of comprehensive x-ray and neutron total scattering and inelastic neutron scattering measurements that uncover a fluctuating spin-orbital dimer phase in this cluster Mott insulator.

GaTa_4Se_8 has concurrent structural and magnetic transitions at 50 K, forming a spin-orbital singlet valence bond solid ground state. As a result of strong spin-orbit coupling and orbital degeneracy, the magnetic ground state couples with lattice distortion. Our total scattering measurements show that the lattice is locally distorted up to 300 K, indicating that the spin-orbital singlet transition is an order-disorder type. Our inelastic neutron measurements directly reveal the lattice fluctuations preceding the transition and provide direct evidence of spin-orbital fluctuation.

To investigate the interplay between spin-orbit coupling, the Jahn-Teller effect, and exchange coupling. We carried out a series of inelastic neutron scattering measurements on lacunar spinels GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$). Our results reveal the phonon anomaly

in stronger spin-orbit coupling compounds (M=Nb, Ta), while this feature is missing in the vanadates with dominating Jahn-Teller effect. Combining our pair distribution function, synchrotron crystallography, and density functional theory, we demonstrate the spin-orbital ordering and fluctuations in lacunar spinels.

Under high pressure, GaTa₄Se₈ undergoes insulator-metal and metal-superconducting phase transitions at 5 GPa and 10 GPa, respectively. The persistence of the $J_{eff}=3/2$ ground state in both phases suggests that the superconducting phase could be unconventional and topological. To gain a better understanding of the phase transitions, we performed high-pressure x-ray diffraction to identify the structural phase transition that takes place in the superconducting phase.

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Chapter 1

Introduction

This chapter provides the essential background knowledge relevant to the works present in this thesis. The goal of this chapter is to provide a self-contained discussion on the most critical aspects but does not aim to provide exhaustive descriptions, as there are many notable textbooks and review articles available on the subject (such as [1–7]). The chapter is structured as follows: first, a brief introduction to important energy scales and interactions in insulating transition metal materials are discussed. The second part discusses interactions between degrees of freedoms. Finally, an overview of the fundamental properties of the lacunar spinel family and the motivation of this thesis are provided.

1.1 Energy scales and interactions

In strongly correlated systems, electrons interact strongly through Coulomb interaction. The interactions between electrons dominate the collective magnetic, electronic, and dynamic behaviors in such materials. So this is distinct from most materials that the electronic structure can be described reasonably well by treating electrons independently due to the electronic screening effect and broad electronic bands. To discuss the collective behaviors of electrons in strongly correlated materials, we must understand the important energy

scales that influence the properties of transition metal systems. This section starts with a discussion of how the local environment influences the behavior of transition metal ions. Then, the interactions between multiple sites and corresponding magnetic, electronic, and dynamic behaviors are discussed.

1.1.1 Hubbard model and Mott insulator

In a Mott insulator, the electrons are localized due to the on-site Coulomb repulsion, which requires energy costs to put two electrons on the same lattice site. This insulating mechanism contrasts with a typical band insulator, where the energy gap between the occupied and unoccupied energy levels is due to the configuration of the electron filling. For example, Fig. 1.1 shows the schematic illustration for a d^1 transition metal materials. Materials that have a partially occupied band are predicted to be conducting in traditional band theory [Fig. 1.1 (a)]. However, this is not true in systems with strong electron correlations. Therefore, the band theory described by the periodic Bloch function can not provide correct electronic structures in such systems, a semi-empirical parameter U describing the Coulomb repulsion is required [Fig. 1.1 (b)]. Let's start with the simplest model to describe the system with strong correlations which provides the most important physics in Mott insulators. The simplest model that describes a Mott insulator is the Hubbard Hamiltonian which John Hubbard first introduced in 1963 as a simplified model (only considering the nearest-neighbor interaction between electrons) for studying the electronic properties of transition metals:

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow} \quad (1.1)$$

where $c_{i,\sigma}^\dagger$ ($c_{i,\sigma}$) is the creation (annihilation) operator for an electron with spin σ on-site i , $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ is the number operator for an electron with spin σ on site i , t is the hopping amplitude between neighboring sites, and U is the on-site Coulomb repulsion. The first term in Eq. 1.1 describes the electron hops from one site to the other nearest neighbor site,

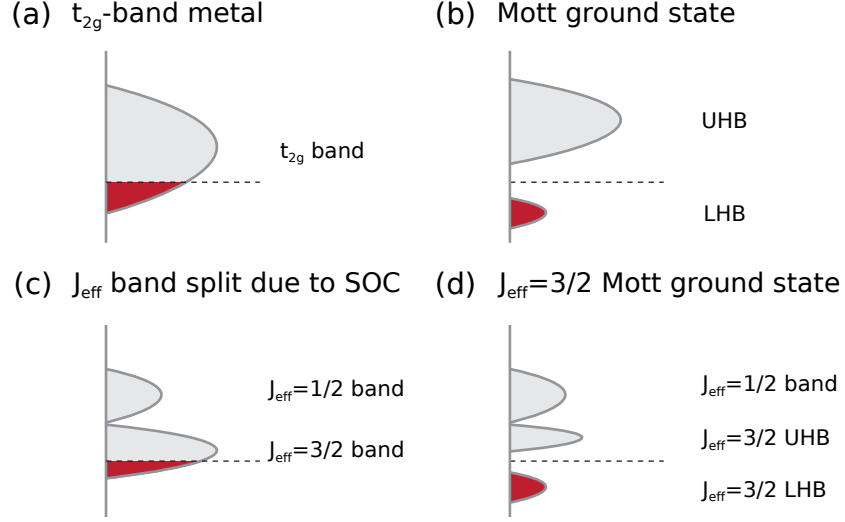


Figure 1.1: Hubbard bands with spin-orbit coupling for d^1 configuration. (a) A partially filled electronic band is conducting from band theory. (b) A system with strong electronic correlation opens a gap and the electronic t_{2g} band splits into a filled lower Hubbard band (LHB) and empty upper Hubbard band (UHB). (c) The the electronic t_{2g} band splits into relativistic $j_{eff}=1/2$ and $j_{eff}=3/2$ bands due to strong spin-orbit coupling. (d) A strong electronic correlation splits the $j_{eff}=3/2$ band into $j_{eff}=3/2$ UHB and LHB. Figure is modified from source [8] for d^1 configuration and $j_{eff} = 3/2$ ground state.

and the spin σ is preserved through the hopping process. The on-site Coulomb repulsion U in the second term prevents two electrons from occupying the same site as it costs the energy proportional to the parameter U .

The electronic conductivity of materials is related to the electronic bandwidth W , which is proportional to t . In general, the electronic correlation (U) in a 3d transition metal system is usually stronger and has a larger band gap because of the narrower bandwidth (W) of the d-electron band. In contrast, the materials with 4d or 5d ion sites usually have smaller band gaps because of the spread of electronic orbitals (larger W), resulting in a smaller energy cost for an electron to hop from one site to another. Therefore, when U is smaller than the electronic bandwidth W , metallic behavior is realized and vice versa. It is worth noting that in some materials the relative strength of U and W can be tuned by changing the interatomic distances, which can be realized by applying the hydrostatic ambient pressure using a diamond anvil cell. This allows us to study the mechanisms in

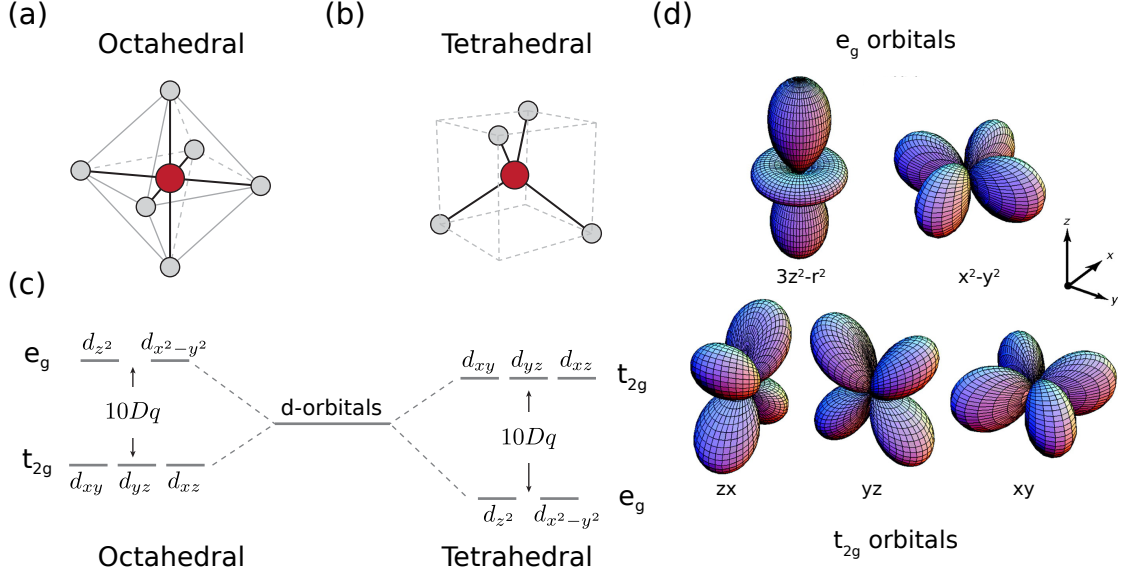


Figure 1.2: Crystal field splitting of (a) Octahedral and (b) Tetrahedral coordination. (c) The hierarchy of the energies of lifted d-orbitals in octahedral and tetrahedral coordination. $10Dq$ is the energy separation of e_g and t_{2g} levels. (d) Schematic illustration of d-orbitals, this figure is adopted from [6].

insulator-metal phase transitions, which will be discussed in chapter 8.

The most important property in the Mott insulator is that the electronic degrees of freedom, spin and orbital, still survive. This property allows numerous possibilities for localized degrees of freedom to interact with each other and create interesting and complex interactions in novel quantum phases. This is also the main problem tackled in this thesis.

1.1.2 Crystal field splitting

In this section, we explore the influences of the local environment on a transition metal ion in more detail. A crucial concept to consider is crystal field splitting, which refers to the splitting of the energy levels of an electronic orbital caused by the non-homogeneous electric field gradient created by a group of ligand atoms in a crystal lattice. For example, the distortion of ligand atoms in octahedral and tetrahedral coordination [Fig. 1.2 (a) and (b)]. The non-uniform electric field surrounding the ion breaks the degeneracy of d-orbitals [Fig. 1.2 (c)], and causes the ordering of the energy levels of split d-orbitals ($10Dq$)

depending on the relative arrangement of the ion and the surrounding ligand atoms. For example, in octahedral coordination, the d-orbitals with lobes along x, y, and z axes [Fig. 1.2 (a) and (d)] have higher energy due to the Coulomb repulsion with p-orbitals of the ligand atoms. Conversely, in tetrahedral coordination [Fig. 1.2 (b) and (d)], the d-orbitals with lobes along diagonal axes have higher energy.

Additionally, the ground state of the electron is determined by the electron filling of the system, following Hund's rule, in which the electrons occupy the states to have the maximum possible total spin. For example, in octahedral coordination [Fig. 1.2 (a)], if we want to fill four electrons (d^4) to the d-levels, each d-orbital in t_{2g} has one electron with parallel spin. The remaining electron will occupy one of the d-orbital in the e_g level [Fig. 1.2 (c)]. This is often written in the form

$$\mathcal{H}_H \sim -J_H \sum_{\alpha \neq \beta} \left(\frac{1}{2} + 2\vec{S}_{i\alpha} \cdot \vec{S}_{i\beta} \right) + \text{const.} \quad (1.2)$$

where J_H is Hund's exchange constant, and $\vec{S}_{i\alpha}$ is the spin of an electron at site i with orbital quantum number $\alpha = l^z$. In both the d^4 and d^1 cases described, there is a degeneracy for orbital filling. In d^1 case electron can occupy either one of three t_{2g} orbitals, while in d^4 case the electron can occupy one of two e_g orbitals. This degeneracy of orbitals is not stable and always introduces small distortions to lift the orbital degeneracy to minimize the total energy of the system.

1.1.3 The Jahn-Teller effect

The Jahn-Teller effect is a spontaneous geometric structure distortion that leads to a lower symmetry structure and reaches a lower total energy of the system resulting in the lifted e_g or t_{2g} level in d-electron transition metal systems. Classically, the simplest way to describe the effect is assuming the distortion of the system can be quantified by a parameter Q of an appropriate normal mode coordinate amplitude [Fig. 1.3 (a)]. Therefore, the elastic potential of a single orbital due to the lattice distortion can be written as

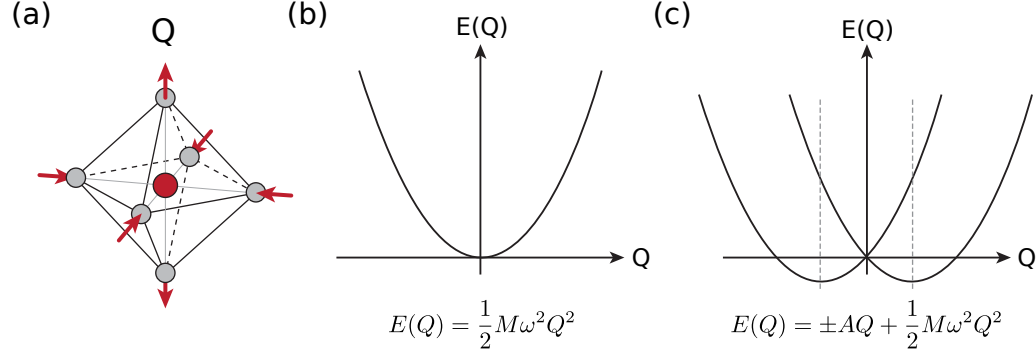


Figure 1.3: The elastic potential of Jahn-Teller distortion. (a) An example of a normal mode describes the distortion, parameterized by the mode amplitude Q . (b) The elastic potential of distortion. (c) The elastic potential of distortion under inhomogeneous electric field gradient. The higher-order terms are ignored due to the assumption of a small displacement Q . Figures are modified from the source [3].

$$E(Q) = \frac{1}{2}M\omega^2Q^2 \quad (1.3)$$

where M is the mass of the centered ion, and ω is the frequency corresponding to the normal mode described by the amplitude Q . It is clear that $E(Q)$ has a minimum at $Q = 0$ [Fig. 1.3 (b)]. In practical cases, electronic energy can be complicated for degenerate d-orbitals. We can always expand it using Taylor expansion when Q is small. Therefore, we can keep the first-order term and rewrite the electric energy as

$$E(Q) = \pm AQ + \frac{1}{2}M\omega^2Q^2 \quad (1.4)$$

where A is a positive constant and represent forces that distort the system along coordinates of normal modes and lift the degeneracy. The distortion $Q_0 = \frac{A}{M\omega^2}$ has minimal energy $E_{min} = -\frac{A^2}{2M\omega^2}$, and $E_{min} < 0$. Therefore the distorted structure is energetically preferred.

Because of the spatial distribution of t_{2g} wavefunctions, orbitals are sensitive to all trigonal, tetragonal, and orthorhombic distortions. On the other hand, e_g -orbitals are only sensitive to tetragonal and orthorhombic distortions [Fig. 1.2 (d)].

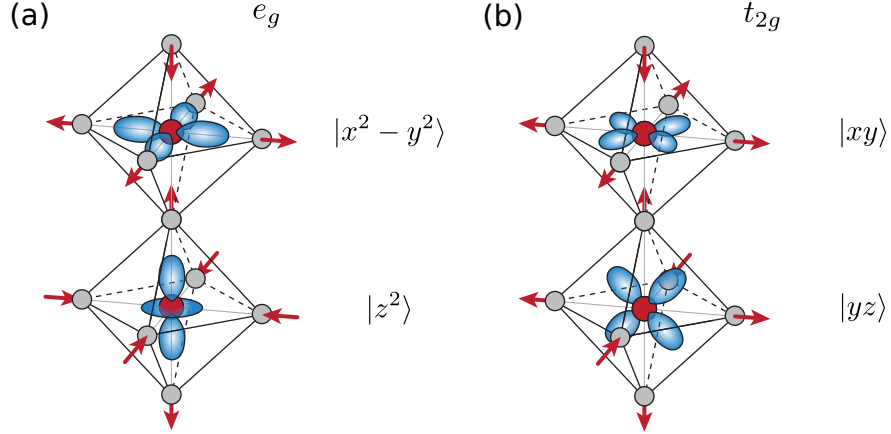


Figure 1.4: Examples of orbital order and lattice distortion. (a) For e_g ground state. (b) For t_{2g} ground state.

1.1.4 Cooperative Jahn-Teller effect and orbital ordering

In a cooperative Jahn-Teller effect, the distortion is not limited to a single ion site but involves a group of ions that interact with each other. This interaction can result in a cooperative distortion that lowers the energy of the entire system and always happens with orbital ordering which refers to a certain arrangement of electronic orbitals in materials [Fig. 1.4]. For example, if an ion has a degenerate e_g ground state, the degeneracy of this e_g -level can be broken by a tetragonal distortion [Fig. 1.4 (a)]. Since the degenerate level is unstable and prefers a small distortion to lower the total energy, the crystal contains multiple ions that prefer to collectively form an alternating $|z^2\rangle$ and $|x^2 - y^2\rangle$ orbitals to minimize the total energy of the system [Fig. 1.4 (a)]. Similar situation can happen in systems have t_{2g} ground state for $|xy\rangle$ and $|yz\rangle$ [Fig. 1.4 (b)]. This collective behavior can be static or dynamic. The static Jahn-Teller effect has a stable, long-lived deformation presenting the ground state. On the other hand, the dynamic Jahn-Teller effect shows a fluctuating, short-lived deformation, described by the linear combination of degenerate ground states.

1.1.5 Magnetic and orbital interactions

In the previous sections, we discussed the interaction between lattice and orbitals and treated the spin degrees of freedom separately. In some materials, it is true that the orbital ordering strongly influences the exchange interaction and results in altered magnetic properties. In this situation, orbital ordering occurs independently of spin ordering, and semi-empirical Goodenough-Kanamori-Anderson (GKA) rules predict the order of magnetic moments [9]. However, orbital ordering can be introduced by a pure electronic mechanism, which Kugel and Khomskii discussed in 1982 [10]. Taking e_g -electrons as an example, the Hubbard model for the doubly degenerate case is

$$\mathcal{H} = - \sum_{\langle ij \rangle, \alpha\beta, \sigma} t_{ij}^{\alpha\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + \sum_{i, \alpha\sigma \neq \beta\sigma'} U_{\alpha\beta} n_{i\alpha\sigma} n_{i\beta\sigma'} - J_H \sum_i (2\hat{S}_{i1} \cdot \hat{S}_{i2} + \frac{1}{2}) \quad (1.5)$$

where $\alpha, \beta = 1, 2$ are the orbital indices ($1 \longleftrightarrow |z^2\rangle, 2 \longleftrightarrow |x^2 - y^2\rangle$). $t_{ij}^{\alpha\beta}$ is the hopping integrals that depend on the involving orbitals and the direction between i and j sites. $c^\dagger$ and c are creation and annihilation operators. The Coulomb matrix elements $U_{\alpha\beta}$ depend on the orbitals. For example, the Coulomb repulsion on the same orbital is larger than on different ones, which makes $U_{11} = U_{22} > U_{12}$. However, this difference is usually ignored at the discussion on the first approximation level. $n_{i\alpha\sigma}$ is the occupation number of i -site electron with α orbital and σ spin configuration. The third term is related to Hund's coupling, and J_H represents Hund's energy. Fig. 1.5 shows four possible situations for the doubly degenerate ground state when $U \gg t$. The coupling between neighboring sites is provided by the virtual hopping of electrons to neighboring sites and back. Similar to the consequence of superexchange, if the hopping is allowed, the energy would decrease.

For $n = 1$ and $t/U \ll 1$, the effective model would have the schematic form (see Chapter 6 of [3] for more detail)

$$\mathcal{H}_{eff} = J_1 \sum_{\langle ij \rangle} \hat{S}_i \cdot \hat{S}_j + J_2 \sum_{\langle ij \rangle} \tau_i \tau_j + 4J_3 \sum_{\langle ij \rangle} (\hat{S}_i \cdot \hat{S}_j)(\tau_i \tau_j) \quad (1.6)$$

where $\hat{S}$ and τ are spin and orbital states. The coefficients J_1, J_2 , and J_3 contain terms

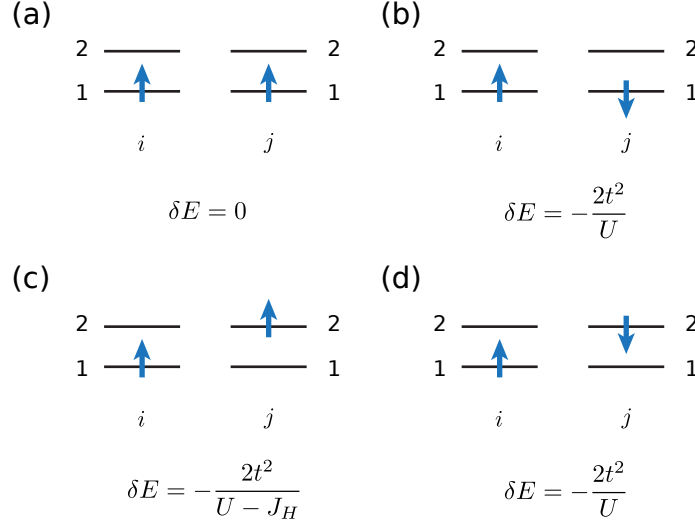


Figure 1.5: Schematics of the interplay between magnetic and orbital degrees of freedom in doubly degenerate ground states. The energy change in the second-order perturbation theory is based on the assumption: $t^{11} = t^{22} = t$, $t^{12} = 0$. The result shows (c) is preferable for the Kugel-Khomskii interaction. This figure is modified from the source [3, 11].

t^2/U and $(t^2/U)(J_H/U)$. This spin and orbital model is called Kugel-Khomskii model. For the simple symmetric cases in Fig. 1.5, and assume the hopping matrix indices $t^{11} = t^{22} = t$, $t^{12} = 0$. The effective Hamiltonian can be simplified as

$$\mathcal{H}_{eff} = \sum_{\langle ij \rangle} \left[J_1 \hat{S}_i \cdot \hat{S}_j + J_2 \hat{\tau}_i \cdot \hat{\tau}_j + 4J_3 (\hat{S}_i \cdot \hat{S}_j)(\hat{\tau}_i \cdot \hat{\tau}_j) \right] \quad (1.7)$$

where

$$J_1 = \frac{2t^2}{U} \left(1 - \frac{J_H}{U} \right) \quad (1.8)$$

$$J_2 = J_3 = \frac{2t^2}{U} \left(1 + \frac{J_H}{U} \right) \quad (1.9)$$

In this case, the orbital operator $\hat{\tau}_i$ acts similarly to spins and also have a Heisenberg interaction. In particular, Eq. 1.7 shows a $SU(2) \times SU(2)$ symmetry. For $J_H = 0$, the Hamiltonian shows even higher $SU(4)$ symmetry. In recent studies, the emergent $SU(4)$ Heisenberg model would potentially have a quantum spin-orbital liquid ground state due to the frustration in materials [12, 13], making the topic even more attractive for researchers.

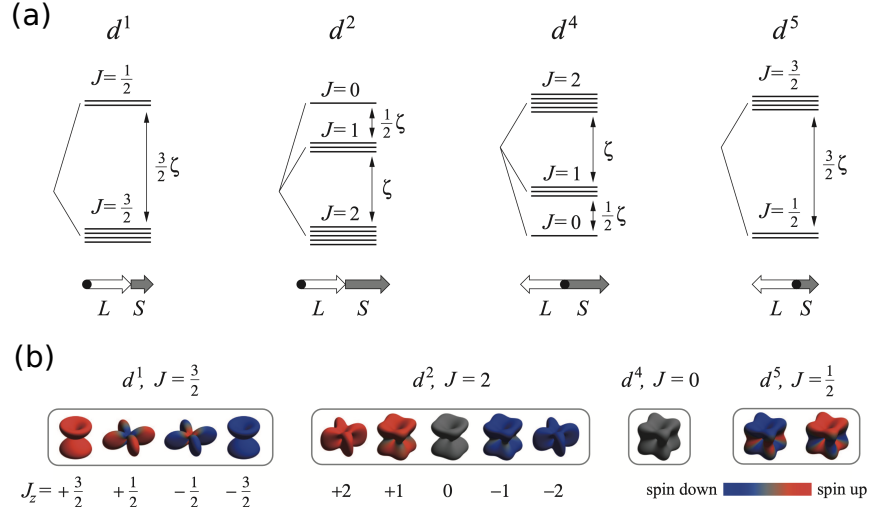


Figure 1.6: Electron filling and energy levels of t_{2g} ground state. (a) (b) . Figure is adopted from the source [4].

1.2 The importance of spin-orbit coupling

Spin-orbit coupling (SOC) is a relativistic effect of a particle's spin interacting with its orbital part. SOC is crucial because it connects the spin and orbital sectors. The energy of spin-orbit coupling is proportional to the inner product of the spin and orbital angular momentum.

$$\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S} \quad (1.10)$$

where $\mathbf{S} = \sum \mathbf{S}_i$ is the total spin, and $\mathbf{L} = \sum \mathbf{l}_i$ is the total orbital angular momentum. $\lambda > 0$ for less than half-filled shells because spin and angular momentum tend to align to each other, see the d^1 and d^2 cases in Fig. 1.6 (a). On the other hand, $\lambda < 0$ for more than half-filled shells, see the d^4 and d^5 cases in Fig. 1.6 (a). In general, SOC becomes important in 4d, and 5d transition metal systems due to the strength of SOC is related to $Z^2 \sim Z^4$ [3], where Z is the atomic number. The wavefunctions for e_g and t_{2g} states are shown in Eq. 1.11.

$$\begin{aligned}
e_g : \begin{cases} |z^2\rangle = |3z^2 - r^2\rangle = |l^z = 0\rangle \\ |x^2 - y^2\rangle = \frac{1}{\sqrt{2}}(|l^z = 2\rangle + |l^z = -2\rangle) \end{cases} & \quad t_{2g} : \begin{cases} |xy\rangle = -\frac{i}{\sqrt{2}}(|l^z = 2\rangle - |l^z = -2\rangle) \\ |xz\rangle = -\frac{1}{\sqrt{2}}(|l^z = 1\rangle - |l^z = -1\rangle) \\ |yz\rangle = \frac{i}{\sqrt{2}}(|l^z = 1\rangle + |l^z = -1\rangle) \end{cases} \\
& \hspace{15em} (1.11)
\end{aligned}$$

The influence of SOC is prominent in t_{2g} than e_g ground state. This is because the e_g levels are composed of $|l^z = -2\rangle$, $|l^z = 0\rangle$, and $|l^z = 2\rangle$ [see Eq. 1.11]. Therefore the expectation value of the angular momentum $\langle e_g | l | e_g \rangle = 0$, which quenches the orbital sector at the first order and minimizes the influence of $\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S}$. Further, t_{2g} has smaller crystal field splitting in the octahedral coordination due to the lobes of t_{2g} -orbitals pointing to the midpoint of the edge in the octahedral cage, making spin-orbit coupling and crystal field splitting comparable.

Here, we concentrate on the systems with t_{2g} ground state, which have a stronger SOC than e_g states. Fig. 1.6 shows the energy levels and wavefunctions for d^1 , d^2 , d^4 , and d^5 in t_{2g} configurations. In general, d^1 and d^2 ion with $J > \frac{1}{2}$ can host higher order unconventional states. The d^4 configuration has nonmagnetic $J = 0$ ions. The d^5 with $J = \frac{1}{2}$ Kramer doublet is similar to spin one-half quantum magnets.

In a strong SOC system, the phase is determined by stabilizing the complex wavefunctions [Fig. 1.6 (b)], and the magnetic order is coupled to the orbitals. In d^1 and d^2 systems, the magnetic quadrupolar order breaks the point group of crystal and rotational symmetry in the magnetic space. Therefore, spin-orbit coupling provides another possibility for Jahn-Teller effect to influence the magnetic ground state.

So far, we have discussed the energy scales and interactions that govern the properties of transition metal compounds. From the strength of the crystal field splitting to the influence of spin-orbit coupling, each energy scale plays a crucial role in determining the electronic and magnetic properties of the system. Additionally, the interplay between these energy scales can give rise to a variety of fascinating phenomena, such as quantum spin

liquid, or spin-orbital fluctuations. By comparing these energy scales and their influence on the system, we can gain a deeper understanding of d-electron systems and explain novel quantum phases in materials.

1.3 Mexican hat potential and tunneling effect

1.3.1 Vibronic state of d-electron system

In the previous section, we had a semi-classical picture of the Jahn-Teller distortions [Fig. 1.3]. The positive and negative sign of Q stabilize $|z^2\rangle$ and $|x^2 - y^2\rangle$ orbitals, with the same total energy. Quantum mechanically, the states with the same energy can tunnel from one state to another, and the crystal ground state is the superposition of these wavefunctions

$$|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\Psi_1\rangle \pm |\Psi_2\rangle) \quad (1.12)$$

where $|\Psi_1\rangle$ ($|\Psi_2\rangle$) is the wavefunction of the state which stabilizes $|z^2\rangle$ ($|x^2 - y^2\rangle$) orbital. If we treat the orbital and lattice part with adiabatic approximation, then we have $|\Psi_i\rangle_{ad} = |\psi_i\rangle|\phi_i\rangle$, where $|\psi_i\rangle$ and $|\phi_i\rangle$ are the electronic occupation and lattice distortion, respectively. The basis state is so called *vibronic state* which describes the electronic and vibrational state of the crystal

$$\begin{aligned} |\Psi_1\rangle &= |\psi_1\rangle|\phi_1\rangle \\ |\Psi_2\rangle &= |\psi_2\rangle|\phi_2\rangle \end{aligned} \quad (1.13)$$

while the average distortion $\langle \mathbf{u} \rangle = \langle \Psi_+ | \mathbf{u} | \Psi_+ \rangle = \langle \Psi_- | \mathbf{u} | \Psi_- \rangle = 0$. Although the average distortion is zero, the fact is that different electronic states $|\psi_i\rangle$ now always go each with their own lattice configurations $|\phi_i\rangle$. This strongly influences many physical properties of such systems.

In the case of e_g -electrons, electrons interact with two degenerate E_g vibration modes,

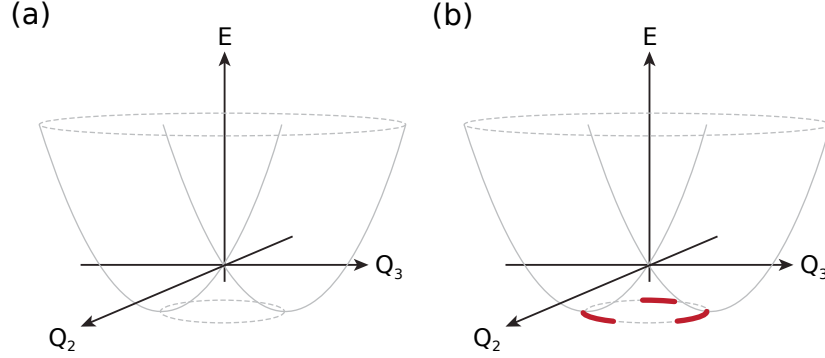


Figure 1.7: Effective potential for e_g -electrons as the function of two vibration modes Q_2 and Q_3 . (a) Mexican hat potential has an azimuth-independent continuous minimum. (b) With higher order electron-lattice coupling term, the potential is azimuth-dependent. The minima are indicated by the red marks.

Q_2 and Q_3 . The Hamiltonian describes the interaction can be written as

$$\mathcal{H}_{JT}^{(e_g)} = -\frac{1}{2}g\{(c_1^\dagger c_1 - c_2^\dagger c_2)Q_3 + (c_1^\dagger c_2 Q_2 + h.c.)\} \quad (1.14)$$

where c_1 and c_2 are electronic operators at ion site for $|z^2\rangle$ and $|x^2 - y^2\rangle$ orbitals in e_g -configuration [3]. In this case, there are two normal modes, Q_2 and Q_3 , that can lift the degeneracy of e_g -orbitals. Therefore, instead of a one-dimensional potential [Fig. 1.3 (c)], now we have a ground state that only depends on $Q_2^2 + Q_3^2$ which has a Mexican hat potential form and can facilitate various quantum phenomena [Fig. 1.7 (a)]. However, in reality, the higher order electron-lattice interactions can perturb the azimuth-independent Mexican hat potential and produce a finite number of minima in the "trough" of the potential. For example, the high order term of energy has the form $E_2 \sim \gamma \cos 3\theta$ for e_g -electrons (more detailed discussion can be found in [3]). Therefore, the modified Mexican hat potential has three minima at $\theta = 0, \pm \frac{2\pi}{3}$ as indicated in Fig. 1.7 (b). These minima correspond to the stabilized $|z^2\rangle$, $|y^2\rangle$, and $|x^2\rangle$ of octahedral elongation along z , y , and x axis.

1.3.2 Mexican hat potential and spin-orbit coupling

The Hamiltonian includes spin-orbit coupling, Jahn-Teller effect, and electron correlation can be written as the following [14]

$$\mathcal{H} = \mathcal{H}_{SOC} + \mathcal{H}_{JT} + \mathcal{H}_U \quad (1.15)$$

where the $\mathcal{H}_{SOC}$ has the same form as Eq. 1.10, while $\mathbf{L}$ and $\mathbf{S}$ are the total orbital and spin moment of the system.

$$\mathcal{H}_{SOC} = -\lambda \hat{L} \cdot \hat{S} \quad (1.16)$$

where $\hat{L} = \sum_{\alpha} \hat{l}_{\alpha}$, $\hat{S} = \sum_{\alpha} \hat{s}_{\alpha}$, where $\hat{l}_{\alpha}$ and $\hat{s}_{\alpha}$ are orbital and spin moment of α -th electron. $\lambda = \zeta/2S$ for SOC weaker than Hund's coupling. The second term ($\mathcal{H}_{JT}$) contains the elastic energy described by the angular moments with two normal coordinates (Q_2 and Q_3 [Fig. 1.4 (b)]) of lattice distortions.

$$\mathcal{H}_{JT} = -\frac{g}{\sqrt{3}} \sum_{\alpha} [(\hat{l}_{\alpha}^x)^2 - (\hat{l}_{\alpha}^y)^2] Q_2 - g \sum_{\alpha} [(\hat{l}_{\alpha}^z)^2 - \frac{2}{3}] Q_3 + \frac{B}{2} (Q_2^2 + Q_3^2) \quad (1.17)$$

The correlation term

$$\mathcal{H}_U = (U - 3J_H) \frac{\hat{N}(\hat{N} - 1)}{2} - 2J_H \hat{S}^2 - \frac{J_H}{2} \hat{L}^2 + \frac{5}{2} \hat{N} \quad (1.18)$$

where J_H indicates the Hund's energy and $\hat{N}$ is the occupation operator. For d^1 configuration, the Hund's coupling is silent, and the energy surface as a function of λ is shown in Fig. 1.8 (a)–(c). When $\lambda = 0$ (pure JT effect) [Fig. 1.8 (a)], the system has three minima with energies $E_{JT}^0 = -\frac{4}{9}(g^2/2B)$, which stabilize the crystal with compressed distortion along x , y , or z direction. The amplitude of the JT distortion in each minima is $u_0 = \sqrt{(Q_2^2 + Q_3^2)} = \frac{2}{3}(g/B)$ [14]. As SOC increases, the JT effect is gradually suppressed but remains a finite value even for $\lambda \rightarrow \infty$ [Fig. 1.8 (a)–(c)]. At large SOC limit, the tetragonal compression $c/a < 1$ and $c/a > 1$ are equivalent [Fig. 1.8 (d) and (e)]. The

wavefunctions for $j = \frac{3}{2}$ are two Kramer doublets with $j_{\pm 3/2}^z$ and $j_{\pm 1/2}^z$ as the following

$$\begin{aligned} |j_{3/2}, j_{3/2}^z\rangle &= |l_1^z, \uparrow\rangle = -\frac{1}{\sqrt{2}}(i|xz, \uparrow\rangle + |yz, \uparrow\rangle) \\ |j_{3/2}, j_{-3/2}^z\rangle &= |l_{-1}^z, \downarrow\rangle = -\frac{1}{\sqrt{2}}(i|xz, \downarrow\rangle - |yz, \downarrow\rangle) \end{aligned} \quad (1.19)$$

$$\begin{aligned} |j_{3/2}, j_{1/2}^z\rangle &= \sqrt{\frac{2}{3}}|l_0^z, \uparrow\rangle + \frac{1}{\sqrt{3}}|l_1^z, \downarrow\rangle = \sqrt{\frac{2}{3}}|xy, \uparrow\rangle - \frac{1}{\sqrt{6}}|ixz + yz, \downarrow\rangle \\ |j_{3/2}, j_{-1/2}^z\rangle &= \sqrt{\frac{2}{3}}|l_0^z, \downarrow\rangle + \frac{1}{\sqrt{3}}|l_{-1}^z, \uparrow\rangle = \sqrt{\frac{2}{3}}|xy, \downarrow\rangle - \frac{1}{\sqrt{6}}|ixz - yz, \uparrow\rangle \end{aligned} \quad (1.20)$$

It becomes clear if we calculate the Jahn-Teller energy $E_{JT} = \langle \psi | \mathcal{H}_{JT} | \psi \rangle$, where $|\psi\rangle$ is one of the spin-orbit wavefunctions in Eq. 1.19 and 1.20. In $j_z = \pm 3/2$ cases, only $|xz\rangle$ and $|yz\rangle$ participate the interaction. Using the $\mathcal{H}_{JT}$ in Eq. 1.17, one can obtain the JT distortion is $\frac{1}{3}(g/B)$ and $E_{JT}^{\pm 3/2} = -\frac{1}{9}(g^2/2B) = \frac{1}{4}E_{JT}^0$ [14]. On the other hand, the $j_z = \pm 1/2$ cases contain all t_{2g} -orbitals and $|xy\rangle$ has predominate weight than $|xz\rangle$ and $|yz\rangle$ orbitals. The amplitude of distortion and the energy are indicated by the compressed case in Fig. 1.8 (d) and (e). Thus, the tetragonal elongation and compression are equivalent at strong SOC limit.

1.3.3 Quantum tunneling effect in materials

In previous discussions, we mentioned the Mexican hat potentials for the system with and without spin-orbit interactions. In the vibronic scheme, the continuous minima are altered by the higher order electron-lattice coupling and have three minima [Fig. 1.7 (b)]. Quantum tunneling between three minima is possible. Similar in the case with spin-orbit coupling [Fig. 1.8 (a)–(c)], but the wavefunctions are complex, which influence orbital and spin sectors simultaneously. In this case, the quantum tunneling between minimums is represented by spin, orbital, and lattice. Therefore, the phonon anomaly associated with the lattice fluctuation could be observed by inelastic neutron scattering, which we will discuss in Chapters 5, 6, and 7.

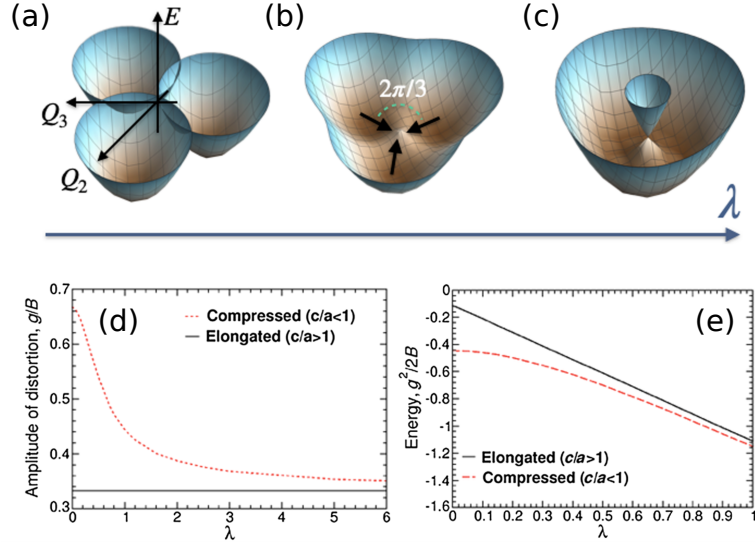


Figure 1.8: Energy surface, distortion, and energy as a function of spin-orbit coupling λ for t_{2g}^1 configuration. (a)–(c) show the evolution of the energy surface versus the strength of the spin-orbit coupling. (d) The amplitude of distortion versus the strength of the spin-orbit coupling. (e) The total energy for elongated and compressed scenarios. The figure is adopted from the source [14].

1.4 Molecular orbitals in transition metals

In the previous discussion, we know that the system with t_{2g} ground states can host novel phases because the spin-orbit coupling effect is strong enough to compete with other energy scales. Especially for d^1 -configuration, the silent Hund's coupling makes the competition between the Jahn-Teller effect and spin-orbit coupling more prominent. In terms of materialization, lacunar spinels provide an unrepresented opportunity to study the interaction between those energy scales. The substitution of the M-site atom is associated with the strength of spin-orbit coupling (SOC), electronic bandwidth (W), and electronic correlations (U) [Fig. 1.9 (a)]. On the other hand, the size of the ligand site atoms alters the distance between transition metals, resulting in the exchange-correlation change [Fig. 1.9 (b)]. Therefore, we must understand the fundamental properties of such a group of d^1 cluster Mott insulators which contains a single unpaired electron at the molecular t_2 -level.

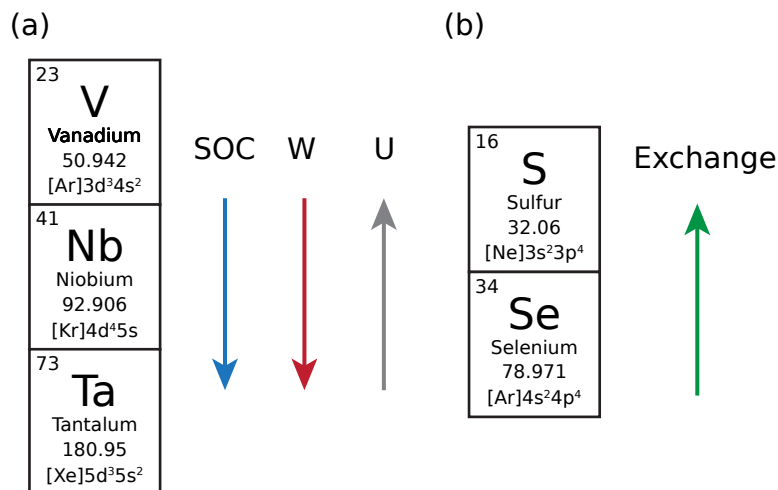


Figure 1.9: Systematic comparison of d^1 lacunar spinels, GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$). (a) Spin-orbit coupling (SOC) increases with atomic number and the bandwidth of the electronic band. On the other hand, the electronic correlation (U) is weaker in heavier atoms. (b) The size of the ligand atom changes the distances between correlation units (M_4X_4 clusters). Therefore, with $\text{X}=\text{S}$, the exchange coupling is stronger than $\text{X}=\text{Se}$ lacunar spinels.

Lacunar spinel refers to a broad range of compounds with the chemical formula AM_4X_8 , where $\text{A}=\text{Ga}$ or Ge , and $\text{M} = \text{V}, \text{Nb}, \text{or Ta}$, while $\text{X} = \text{S}$ or Se . The term "lacunae," which means empty in French, refers to the periodic absence of Ga atoms in a standard spinel with the chemical formula AM_2X_4 . This absence of half of the Ga-site leads to an alternating size of M_4 clusters, forming the tetrahedral M_4 correlation unit in lacunar spinel [Fig. 1.10], giving rise to the name "breathing lattice." The increased inter-cluster distance reduces electron hopping between sites due to stronger electronic correlation. The electronic gap in lacunar spinels is similar to that of small band gap semiconductors, and the strong electronic correlation effect explains the mechanism of insulation. This thesis concentrates on lacunar spinels with $\text{A}=\text{Ga}$, where a single occupied molecular t_2 electron exists on each M_4 -site in the ground state. The interplay of structure, spin, orbit, and lattice dynamics is extensively studied by systematically varying the M-site and X-site atoms.

Lacunar spinels display a cubic ($\text{F}\bar{4}3\text{m}$) structure at room temperature, but their low-

temperature structures differ depending on their metallic M-site, which can be classified into three categories. While the vanadium compounds exhibit an elongation of the unit cell along cubic $\langle 111 \rangle$, the niobium and tantalum compounds undergo a doubling of the unit cell. This behavior suggests a competition between the Jahn-Teller effect and spin-orbital coupling [15, 16]. The magnetic ground state of lacunar spinels is particularly intriguing, with a Néel-type skyrmion magnetic ground state observed in GaV_4S_8 and GaV_4Se_8 with a small external field [17, 18]. Conversely, GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 have a nonmagnetic ground state, which is likely a valence-bond solid or spin-singlet ground state [16, 19].

The molecular orbital correlation unit is widely accepted in interpreting lacunar spinels' electronic and magnetic properties. By counting the number of electrons in a single chemical formula, GaM_4X_8 , one can realize that there are 7 electrons on each M_4 -cluster. Due to the crystal field, the molecular d-orbital splits into e and t_2 manifold. Therefore, a single unpaired electron occupies the lower energy molecular t_2 level and presents a spin-1/2 character. In stronger spin-orbital coupling situations (GaNb_4S_8 , GaNb_4Se_8 and GaTa_4Se_8), the molecular t_2 level splits into $j_{eff} = 1/2$ and $3/2$ levels. The $j_{eff} = 3/2$ ground state is verified by resonant inelastic x-ray scattering (RIXS) and density functional calculations (DFT) [20].

Table 1.1: Structural and magnetic phase transitions of lacunar spinels.

	T_s	T_N	LT structure	Θ_{CW}	Magnetism	Ref.
GaV_4S_8	40	10	R3m		FM, Cyc, SkL, $s=1/2$	[18, 21, 22]
GaV_4Se_8	42	18	R3m	-84.6	FM, Cyc, SkL, $s=1/2$	[23, 24]
GaNb_4S_8	32	32	$\text{P}2_12_12_1$	-300	singlet, $j=3/2$	[19, 25]
GaNb_4Se_8	32, 50	32	$\text{P}2_12_12_1$, $\text{P}2_13$	-139	singlet, $j=3/2$	[26]
GaTa_4Se_8	50	50	$\text{P}42_1\text{m}$	-285	singlet, $j=3/2$	[16, 27]

1.5 Overview of this thesis

In this thesis, we studied crystal structures, local structures, lattice dynamics, and spin-orbital fluctuations of entire d^1 lacunar spinels using multiple neutron and x-ray scattering

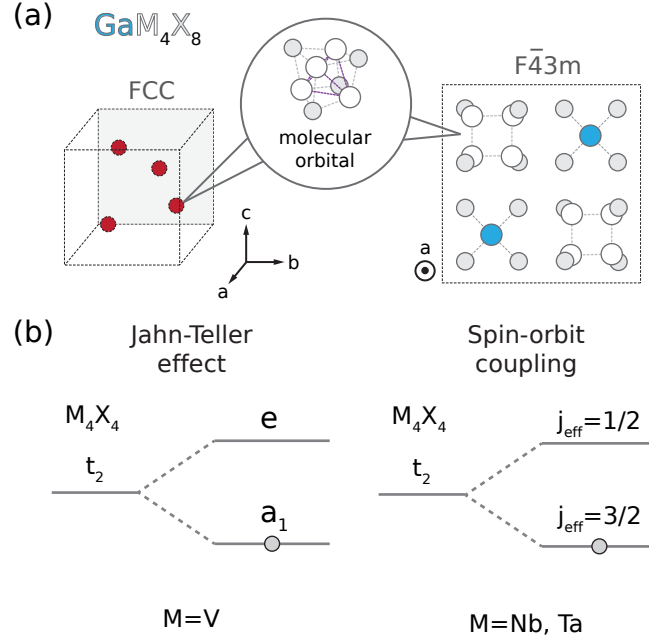


Figure 1.10: Crystal structure and molecular orbital of lacunar spinels GaM_4X_8 ($\text{M}=\text{V}$, Nb , Ta ; $\text{X}=\text{S}$, Se). (a) Crystal structure at room temperature. The structure is a face-center-cubic (FCC) with a non-centrosymmetric $F\bar{4}3m$ space group. The M_4X_4 cubane has a single unpaired electron occupying the molecular t_2 level. (b) Molecular energy level splitting due to the Jahn-Teller effect and spin-orbit coupling.

techniques. The comprehensive structures and lattice dynamics studies were carried out using state-of-art synchrotron experiments at Argonne and Brookhaven national laboratory and Oak Ridge national laboratory.

Chapter 2 provides a broad overview of experimental techniques, including neutron scattering, x-ray scattering, and high-pressure diamond anvil cell (HPDAC). First, the scattering cross-sections of neutron and x-ray scatterings are discussed. The discussion covers the essential theoretical background and focuses on the connection to measurable quantities of neutron and x-ray scatterings. Second, the technical information of crystallography, total scattering method, inelastic neutron scattering, and high-pressure diamond anvil cell are discussed. Chapter 3 shifts the discussion to computational methods, including the density functional theory and first principle phonon calculation. A broad overview of the two methods is provided.

Chapter 4 provides the information for synthesizing lacunar spinels and characterization of samples. First, the methods and parameters for synthesizing crystalline and single crystal samples are provided. Then powder X-ray diffraction measurements and crystallography for single crystals are presented.

Chapter 5 presents the results of the bond ordering and spin-orbital fluctuations in GaTa_4Se_8 . Starting from the structure solution from synchrotron crystallography experiments, we provide a reliable low-temperature structure below the single magnetic and structural phase transition. Our result indicates the unit cell doubles and forms cluster dimers at low temperatures. Then the complete temperature-dependent neutron and x-ray pair distribution function measurements uncover the disorder-order phase transition and imply the dynamic distortion in GaTa_4Se_8 . To obtain more insights into the dynamic properties of the phase transition, we carried out inelastic phonon scattering experiments to measure the phonon density of states. Comparing the experimental results with our first principle calculations, we confirm the symmetry of the system is already broken above the phase transition. This study demonstrates the importance of the competing Jahn-Teller effect and spin-orbit coupling, which realize the quantum tunneling effect in the altered Mexican hat potential in condensed matter.

Chapter 6 studies the phase transitions in GaNb_4Se_8 , which has an additional structural phase transition compared to other d^1 lacunar spinels. First, we provide high-fidelity structure solutions in three phases. The results show that the first structural phase transition at 50 K is a cubic-to-cubic and second-order phase transition. The transition can be explained by the gradual increase of the Jahn-Teller active X_5 distortion mode. The structure below the concurrent structural and magnetic phase transition is a unit cell doubled orthorhombic cell and Nb_4 clusters ordered in dimer patterns. Our crystallography result indicates the dimerized clusters in a unit cell doubled orthorhombic unit cell. The group theory analysis shows different mechanisms drive two phase transitions, the Jahn-Teller effect and spin-orbit coupling. Therefore, the studies of GaNb_4Se_8 in Chapter 6 provides more insights into the phase transitions in strong spin-orbit coupling lacunar

spinel.

Chapter 7 discusses the local structures and dynamic properties for entire d^1 lacunar spinels with the chemical formula GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$). We performed the pair distribution function measurements for all studied compounds to gain more information about the local structure. Our results show the local structures of GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 constantly obtain better fits with the low-temperature structure, distinct to GaV_4S_8 and GaV_4Se_8 , in which the local structures always have better agreement with the global symmetry. The dynamic properties are studied by inelastic neutron scattering. We find that the anomalous phonon mode appears in GaNb_4S_8 , GNSe , and GaTa_4Se_8 , which have strong spin-orbit coupling. Compared to our first principle phonon calculations, we verify the spin-orbital fluctuations in lacunar spinels with strong spin-orbit coupling.

Chapter 8 shows the preliminary results for high-pressure diamond anvil cell experiments on GaTa_4Se_8 . GaTa_4Se_8 has a insulator-metal phase transition at 5 GPa, and a metal-superconductor phase transition at 10 GPa. Therefore, it is crucial to investigate the structure at the metallic and superconduction phases. At 7 GPa, we observe the rearrangement of Bragg's peak intensities, but the extinction rule keeps the same as ambient pressure. Implying the amplitudes of the distortion modes change across the insulator-metal phase transition. Above 10 GPa, in the superconducting phase, the change of x-ray distinction rules indicates the low-temperature structure is a doubled I-centered tetragonal unit cell.

Chapter 9 demonstrates the inelastic neutron scattering measurements on co-aligned GaTa_4Se_8 single crystal arrays. The design of the sample mount, co-aligned single crystal samples, and preliminary results are presented.

Chapter 2

Scattering Techniques

This chapter provides an overview of neutron and x-ray scatterings and related techniques, with a focus on how they can be used to connect physical properties of materials to measurable values. The chapter is structured as follows: the first half of the chapter explores the cross-sections of neutron and x-ray scatterings, which are crucial measurable quantities that relate to the structure, magnetic property, and lattice dynamics of materials. The second half of the chapter contains experimental techniques, including crystallography, total scattering measurements, time-of-flight neutron scattering, and high-pressure diamond anvil cell experiments. These techniques have been utilized in this thesis and will be discussed in more detail.

2.1 Introduction

In recent decades, scattering techniques have gained widespread use in scientific research areas such as biology, geology, and materials science due to their versatile applications. The development of synchrotron facilities and the invention of time-of-flight neutron scattering have dramatically accelerated scientific research. Throughout my Ph.D. studies, I have benefited from the powerful capabilities of these instruments.

Neutron and x-ray scattering are complementary techniques. Neutrons carry no net

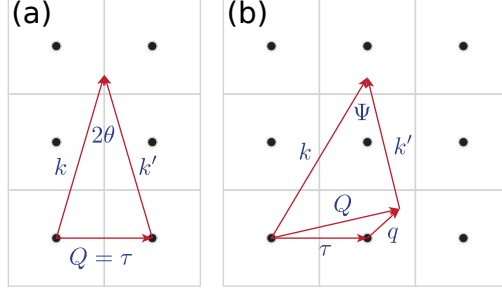


Figure 2.1: Momentum and energy transfer for (a) Elastic scattering. There is no energy transfer after scattered $\hbar\omega = 0$. The momentum transfer is $\vec{Q} = \vec{k} - \vec{k}' = \vec{\tau}$ (b) Inelastic scattering. The energy transfer $\hbar\omega \neq 0$. The momentum transfer is $\vec{Q} = \vec{\tau} + \vec{q}$

charge and possess a spin ($S=1/2$), allowing them to interact directly with the magnetic moments of materials without being disturbed by electrons. X-rays, on the other hand, interact with electrons and are more sensitive to heavier elements. The tendency of scattering power of atoms are significantly different in neutron and x-ray scatterings. For instance, hydrogen is a very strong scattering element for neutron scattering but is difficult to detect using x-rays. This disparity underscores the importance of using both techniques in studying the properties of materials.

Momentum transfer

$$\hbar\vec{Q} = \hbar(\vec{k} - \vec{k}') \quad (2.1)$$

Energy transfer

$$\hbar\omega = \frac{\hbar^2}{2m}(k^2 - k'^2) \quad (2.2)$$

2.2 The Cross-Section

In order to interpret the experimental data, we have to understand the relation between the scattered beam and the charge, structure, magnetic moments, and other excitations in materials. It becomes clear if we start with the differential cross-sections. The general definition of the partial differential cross-section of a generic scattering experiment is

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{I_{sc}}{\Phi_0 d\Omega dE'} \quad (2.3)$$

where the s_c is the number of neutrons/photons scattered into $d\Omega$ with the energy between E' and $E' + dE'$. The strength of the incident beam is Φ_0 , which has the unit of the number of scattering neutrons/photons per unit area per second. $\Delta\Omega$ is the corresponding solid angle of the area of the detector at a specific position [Fig. ??].

If we do not have energy resolution of the scattered beam, and simply count the number of events scattered into the solid angle $d\Omega$ in the direction θ and ϕ . The cross-section corresponding to this measurement is known as a differential cross-section. The definition is

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \left(\frac{d^2\sigma}{dE' d\Omega} \right) dE' \quad (2.4)$$

$$\sigma_{tot} = \int_{all} \left(\frac{d\sigma}{d\Omega} \right) d\Omega \quad (2.5)$$

2.2.1 Neutron Scattering

Neutron scattering is the most precise experimental technique which is able to measure the dispersion relation $\hbar\omega(\vec{q})$ at any predetermined point in reciprocal space. Starting from the general form of the differential cross-section [Eq. 2.3], we can construct the cross-section for neutron scattering based on the physical quantities we are interested.

Fermi's Golden rule

Theoretical expressions for the cross-section usually start from Fermi's Golden rule.

$$\boxed{\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{m}{2\pi\hbar^2} \right)^2 \frac{k'}{k} \sum_{\lambda', \sigma'} \sum_{\lambda, \sigma} p_\lambda p_\sigma |\langle \vec{k}', \vec{\sigma}', \lambda' | \hat{U} | \vec{k}, \vec{\sigma}, \lambda \rangle|^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'})} \quad (2.6)$$

where $|\lambda\rangle$ and $|\lambda'\rangle$ are initial and final states with energy E_λ and $E_{\lambda'}$, respectively. $\vec{\sigma}$ and $\vec{\sigma}'$ represent the initial and final spin states of neutron while p_σ shows the polarization probability. $\hat{U}$ denotes the interaction operator of the neutron with the sample.

We can reach a general form of the partial differential cross-section by three substitutions. First, we can replace the potential $\hat{U}$ with the Fermi pseudo potential for nuclei at fixed

positions $\hat{R}_j$.

$$\hat{U}(\vec{r}) = \frac{2\pi\hbar^2}{m} \sum_j b_j \delta(\vec{r} - \vec{R}_j) \quad (2.7)$$

where b_j represents the scattering length of a nucleus with the order of 10^{-12} cm. Therefore, the cross-section typically has the order of 10^{-24} cm² = 1 barn. It is worth mentioning that b_j is a complex number. The real part is related to the energy-independent scattering, while the imaginary part is associated with the energy-dependent absorption. Second, the incident and scattered neutron states can be treated using the plane wave expression.

$$\begin{aligned} |\vec{k}\rangle &= e^{i\vec{k}\cdot\vec{r}} \\ |\vec{k}'\rangle &= e^{i\vec{k}'\cdot\vec{r}} \end{aligned} \quad (2.8)$$

$$\boxed{\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{jj'} b_j b_{j'} \int_{-\infty}^{\infty} \langle e^{-\vec{Q}\cdot\vec{R}_{j'}(0)} e^{\vec{Q}\cdot\vec{R}_j(t)} \rangle e^{-i\omega t} dt} \quad (2.9)$$

Correlation functions

Correlation functions describe how the scattering signal from a sample varies with time or distance. In Eq. 2.9, the operator part corresponds to the intermediate pair correlation function:

$$I(\vec{Q}, t) = \frac{1}{N} \sum_{jj'} \int_{-\infty}^{\infty} \langle e^{-\vec{Q}\cdot\vec{R}_{j'}(0)} e^{\vec{Q}\cdot\vec{R}_j(t)} \rangle e^{-i\omega t} \quad (2.10)$$

where N is the number of atoms in the system. The Fourier transformation with respect to $\vec{Q}$ yields the space-time pair correlation function introduced by van Hove in 1954.

$$G(\vec{r}, t) = \frac{1}{(2\pi)^3} \int I(\vec{Q}, t) e^{-i\vec{Q}\cdot\vec{r}} d\vec{Q} \quad (2.11)$$

Similarly, the dynamical structure factor is obtained by taking the Fourier transformation with respect to t .

$$S(\vec{Q}, \omega) = \frac{1}{(2\pi)^3} \int I(\vec{Q}, t) e^{-i\omega t} dt \quad (2.12)$$

Coherent and incoherent scattering

In neutron scattering, coherent scattering refers to the process in which a neutron interacts with a whole nucleus or a group of nuclei in a crystal so that the neutron's wavelength and phase are preserved. This results in the neutron scattering coherently and constructively with other atoms in the material, producing diffraction patterns that contain information about the material's crystal structure.

In contrast, incoherent scattering refers to the process in which a neutron interacts with individual atoms in a material, causing them to vibrate or recoil. This process results in the neutron losing its phase coherence with other atoms in the material, and the scattered neutrons no longer form a coherent diffraction pattern. Incoherent scattering can provide information about the dynamics and thermal motion of individual atoms in a material, but it is generally less useful for determining the crystal structure of a material than coherent scattering.

We now start from the cross-section Eq. 2.9. Since there is no correlation between scattering lengths b_j and $b_{j'}$ of the nuclei. Therefore, the sum over j and j' has to be average over the sample volume.

$$\begin{aligned} \text{for } j \neq j': \langle b_j b_{j'} \rangle &= \langle b_j \rangle \langle b_{j'} \rangle = \langle b \rangle^2 \\ \text{for } j = j': \langle b_j b_{j'} \rangle &= \langle b_j^2 \rangle = \langle b^2 \rangle \end{aligned} \quad (2.13)$$

The cross-section Eq. 2.9 can be written as

$$\boxed{\frac{d^2\sigma}{d\Omega d\omega} = N \frac{k'}{k} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int d\vec{r} e^{i\vec{Q} \cdot \vec{r}} (\langle b \rangle^2 G(\vec{r}, t) + [\langle b^2 \rangle - \langle b \rangle^2] G_s(\vec{r}, t))} \quad (2.14)$$

where $G(\vec{r}, t) = G_s(\vec{r}, t) + G_d(\vec{r}, t)$. The two terms in Eq. 2.14 are called coherent and incoherent neutron scattering cross-sections.

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{coh} = N \frac{k'}{k} \langle b \rangle^2 S_{coh}(\vec{Q}, \omega) \quad (2.15)$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{inc} = N \frac{k'}{k} [\langle b^2 \rangle - \langle b \rangle^2] S_{inc}(\vec{Q}, \omega) \quad (2.16)$$

For coherent scattering, the total cross-section is the square of the averaged scattering lengths.

$$\sigma_{coh} = 4\pi \left(\frac{1}{N} \sum_j b_j \right)^2 = 4\pi \langle b \rangle^2 \quad (2.17)$$

while the total incoherent scattering is given by the disorder of the scattering lengths.

$$\sigma_{inc} = 4\pi (\langle b^2 \rangle - \langle b \rangle^2) \quad (2.18)$$

Principle of detailed balance

In neutron scattering experiments, neutrons can loss or gain energy. The $\hbar\omega$ in Eq. 2.2 can be positive or negative depending on the neutron loss or gain energy. It is therefore important to investigate the effect of time reversal ($\omega \rightarrow -\omega$) operation acting on $S(\vec{Q}, \omega)$. Readers can refer to [28, 29] for deriving the detailed balance principle. Here we only discuss the conclusion of the principle. The principle of detailed balance is

$$\boxed{S(-\vec{Q}, -\omega) = e^{-\frac{\hbar\omega}{k_B T}} S(\vec{Q}, \omega)} \quad (2.19)$$

which unambiguously relates the neutron energy-gain and energy-loss processes. The most important consequence is the fact that the neutron scattering structure factor for energy-gain neutrons relates to the structure factor of energy-loss neutron scaled by the temperature-dependent Boltzmann factor $e^{-\hbar\omega/(k_B T)}$ [Fig. 2.2]. The principle of detailed balance is beneficial for neutron scattering experiments. For example, we can confirm the excitation by checking the positive and negative energies. Moreover, the Boltzmann factor in Eq. 2.19 allows us to determine the sample temperature precisely by comparing the measured intensities of structure factors at $\pm\hbar\omega$.

Magnetic scattering

Neutron scattering is the most direct technique to probe the magnetic properties of materials. Here, we start with the Fermi's Golden rule (Eq. 2.6) to discuss the magnetic scattering of neutrons. In Eq. 2.6, the interaction operator $\hat{U}$ can be described by the

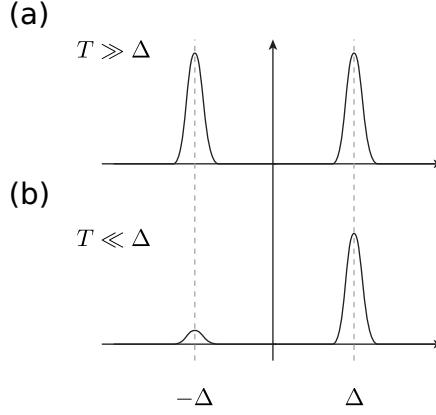


Figure 2.2: Schematic illustration of the temperature dependence of inelastic scattering. Δ is the energy difference between the ground state and the first excited state. (a) $T \gg \Delta$. (b) $T \ll \Delta$.

interaction of a neutron with the magnetic field $\vec{H}$ associated with the sample.

$$\hat{U} = \hat{\mu} \cdot \vec{H} = -\gamma \mu_N \hat{\sigma} \cdot \vec{H} \quad (2.20)$$

where $\hat{\mu}$ is the magnetic moment operator of the neutron, γ represents the gyromagnetic ratio, μ_N is the nuclear magneton, and $\hat{\sigma}$ is a Pauli spin operator. Since unpaired electrons generate the magnetic field associated with the sample, the magnetic field term can be described by the moving with velocity $\vec{v}_e$.

$$\vec{H} = \nabla \times \left(\frac{\vec{\mu}_e \times \vec{R}}{|\vec{R}|^3} \right) - \frac{e}{c} \frac{\vec{v}_e \times \vec{R}}{|\vec{R}|^3} \quad (2.21)$$

where $\vec{R}$ is the distance from the electron to the point at which the magnetic field is measured. The magnetic moment of electron is $\vec{\mu}_e = -2\mu_B \vec{s}$, μ_B is the Bohr magneton and $\vec{s}$ is the spin operator of the electron. Therefore, the first term in Eq. 2.21 is generated by electron spin, and the second term comes from its orbital motion. Readers can refer to [28, 29] for details. The cross-section for unpolarized neutron beam and spin-only scattering is

$$\boxed{\frac{d^2\sigma}{d\Omega d\omega} = (\gamma r_0)^2 \frac{k'}{k} F^2(\vec{Q}) e^{-2W(\vec{Q})} \sum_{\alpha, \beta} \left(\delta_{\alpha\beta} - \frac{Q_\alpha Q_\beta}{Q^2} \right) S^{\alpha\beta}(\vec{Q}, \omega)} \quad (2.22)$$

where $S^{\alpha\beta}(\vec{Q}, \omega)$ is the magnetic scattering function:

$$S^{\alpha\beta}(\vec{Q}, \omega) = \sum_{j,j'} e^{i\vec{Q} \cdot (\vec{R}_j - \vec{R}_{j'})} \sum_{\lambda, \lambda'} p_{\lambda} \langle \lambda | \hat{S}_{j'}^{\alpha} | \lambda' \rangle \langle \lambda' | \hat{S}_j^{\beta} | \lambda \rangle \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) \quad (2.23)$$

$F(\vec{Q})$ is the magnetic form factor defined by the Fourier transform of the normalized spin density associated with magnetic ions. $e^{-2W(\vec{Q})}$ denotes the Debye-Waller factor and $\hat{S}_j^{\alpha}$ shows the spin operator of j -th ion on the j -site $\vec{R}_j$.

The cross-section of magnetic scattering in Eq. 2.22 is governed by three factors: (1) the form factor $F(\vec{Q})$. (2) the polarization factor $\delta_{\alpha\beta} - Q_{\alpha}Q_{\beta}/Q^2$. (3) the magnetic scattering function $S^{\alpha\beta}(\vec{Q}, \omega)$. The magnetic form factor $F(\vec{Q})$ usually falls off with increasing modulus of the scattering vector $\vec{Q}$. While the polarization factor $\delta_{\alpha\beta} - Q_{\alpha}Q_{\beta}/Q^2$ indicates neutrons can only couple to magnetic moments or spin fluctuations perpendicular to $\vec{Q}$, which allows to determine directions or to distinguish between different polarizations of spin fluctuations.

It is worth mentioning that when the spin-orbit coupling is strong in a system, the orbital sector is no longer quenched. Therefore, the simplest treatment is to assume $\vec{\mu} = -\mu_B(\vec{L} + 2\vec{S})$, which is a combination of spin and orbital moments. Therefore, we replace the spin operator $\hat{S}_j^{\alpha}$ by

$$\hat{S}_j^{\alpha} = \frac{1}{2}g\hat{J}_j^{\alpha} \quad (2.24)$$

where

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (2.25)$$

is the Landé g-factor and $\hat{J}_j^{\alpha}$ is an effective angular momentum operator.

The physical explanation of the magnetic scattering function, $S^{\alpha\beta}(\vec{Q}, \omega)$, is rather complicate. However, we can quote the result for $Q \rightarrow 0$ for simplicity because the form factor drops as increasing Q . The scattering function can be written as

$$S^{\alpha\beta}(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \sum_{j,j'} \int_{-\infty}^{\infty} e^{i\vec{Q} \cdot (\vec{R}_j - \vec{R}_{j'})} \langle \hat{S}_j^{\alpha}(0) \hat{S}_{j'}^{\beta}(t) \rangle e^{-i\omega t} dt \quad (2.26)$$

where $\langle \hat{S}_j^\alpha(0) \hat{S}_{j'}^\beta(t) \rangle$ is the thermal average of time-dependent spin operators and refers to the pair correlation function. A neutron scattering experiment measures the Fourier transform of the pair correlation function in space and time, which is clearly just what is needed to describe a magnetic system on an atomic scale.

Phonon scattering

Neutron scattering measures not only the magnetic property on an atomic scale but also the collective atomic motion in the crystal. That is the dispersion of the phonon spectrum, which is largely unknown before the advent of neutron scattering. Here we discuss essential concepts to understand the experimental results from inelastic neutron scattering.

Cross-section for one-phonon scattering

We start from Eq. 2.9 and assume the position $\hat{R}_j(t)$ has the form:

$$\hat{R}_j(t) = \vec{l}_j + \hat{u}_j(t) \quad (2.27)$$

where $\vec{l}_j$ is the equilibrium position and $\hat{u}_j(t)$ denotes a small displacement from $\vec{l}_j$. Then we can use harmonic approximation to represent the $\hat{u}_j(t)$ by normal modes:

$$\hat{u}_j(t) = \sqrt{\frac{\hbar}{2MN}} \sum_{s, \vec{q}} \frac{\vec{e}_s(\vec{q})}{\sqrt{\omega_s(\vec{q})}} \left(\hat{a}_s(\vec{q}) e^{i[\vec{q} \cdot \vec{l}_j - \omega_s(\vec{q})t]} + \hat{a}_s^\dagger(\vec{q}) e^{-i[\vec{q} \cdot \vec{l}_j - \omega_s(\vec{q})t]} \right) \quad (2.28)$$

where M is the atomic mass, $\vec{q}$ is the wavevector of the normal mode. While $\omega_s(\vec{q})$ and $\vec{e}_s(\vec{q})$ are eigenvalue and eigenvector, respectively. The sum extends N values of $\vec{q}$ in the first Brillouin zone. $\hat{a}_s$ and $\hat{a}_s^\dagger$ are phonon annihilation and creation operators. Now we define abbreviations to emphasize the key physical picture for the phonon scattering cross-section. We define operators $\hat{A}$ and $\hat{B}$ as follows:

$$\hat{A} = -i\vec{Q} \cdot \hat{u}_{j'}(0) = -i \sum_{s, \vec{q}} \left(\alpha_s(\vec{q}) \hat{a}_s(\vec{q}) + \alpha_s^*(\vec{q}) \hat{a}_s^\dagger(\vec{q}) \right) \quad (2.29)$$

$$\hat{B} = i\vec{Q} \cdot \hat{u}_j(0) = i \sum_{s, \vec{q}} \left(\beta_s(\vec{q}) \hat{a}_s(\vec{q}) + \beta_s^*(\vec{q}) \hat{a}_s^\dagger(\vec{q}) \right) \quad (2.30)$$

with

$$\alpha_s(\vec{q}) = \sqrt{\frac{\hbar}{2MN}} \sum_{s,\vec{q}} \frac{\vec{Q} \cdot \vec{e}_s(\vec{q})}{\sqrt{\omega_s(\vec{q})}} e^{i\vec{q} \cdot \vec{l}_{j'}} \quad (2.31)$$

$$\beta_s(\vec{q}) = \sqrt{\frac{\hbar}{2MN}} \sum_{s,\vec{q}} \frac{\vec{Q} \cdot \vec{e}_s(\vec{q})}{\sqrt{\omega_s(\vec{q})}} e^{[i\vec{q} \cdot \vec{l}_j - \omega_q(\vec{q})t]} \quad (2.32)$$

the cross-section can be written as

$$\boxed{\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{1}{2\pi\hbar} e^{-2W(\vec{Q})} \sum_{j,j'} b_j b_{j'} e^{i\vec{Q} \cdot (\vec{l}_j - \vec{l}_{j'})} \int_{-\infty}^{\infty} e^{\langle \hat{A}\hat{B} \rangle} e^{-i\omega t} dt} \quad (2.33)$$

where $e^{-2W(\vec{Q})} = e^{\hat{A}^2}$ is the Debye-Waller factor. Since we assumed $\hat{u}_j(t)$ is a small displacement, we can deal with the $e^{\langle \hat{A}\hat{B} \rangle}$ using Taylor expansion:

$$e^{\langle \hat{A}\hat{B} \rangle} = 1 + \langle \hat{A}\hat{B} \rangle + \frac{1}{2} \langle \hat{A}\hat{B} \rangle^2 + \dots + \frac{1}{n!} \langle \hat{A}\hat{B} \rangle^n + \dots \quad (2.34)$$

the first term corresponds to elastic scattering. Here we only consider the linear term $\langle \hat{A}\hat{B} \rangle$, and the final expression of the cross-section is

$$\begin{aligned} \frac{d^2}{d\Omega d\omega} = \frac{4\pi^3}{v_0} \frac{k'}{k} \sum_{s,\vec{q}} \frac{1}{\omega_s(\vec{q})} & \left| \sum_{\vec{d}} \frac{\langle b_d \rangle}{\sqrt{M_d}} e^{-W_d(\vec{Q})} e^{i\vec{Q} \cdot \vec{d}} (\vec{Q} \cdot \vec{e}_{\vec{d},s}(\vec{q})) \right|^2 \\ & \times \left[(n_s(\vec{q}) + 1) \delta(\omega - \omega_s(\vec{q})) \sum_{\vec{\tau}} \delta(\vec{Q} - \vec{q} - \vec{\tau}) \right. \\ & \left. + n_s(\vec{q}) \delta(\omega + \omega_s(\vec{q})) \sum_{\vec{\tau}} \delta(\vec{Q} + \vec{q} - \vec{\tau}) \right] \quad (2.35) \end{aligned}$$

The cross-section contains two δ -functions related to positive and negative energy transfers. The term with $\delta(\omega - \omega_s(\vec{q}))$ refers to the phonon emission, and the second term with $\delta(\omega + \omega_s(\vec{q}))$ refers to the phonon absorption induced by neutron scattering process. These processes are known as Stokes and anti-Stokes, corresponding to neutron energy loss and energy gain during the scattering. From the cross-section for one-phonon scattering in Eq. 2.35, we can see the rules for energy and momentum conservation:

$$\pm \hbar \omega_s(\vec{q}) = \hbar \omega = \frac{\hbar^2}{2m} (|\vec{k}|^2 - |\vec{k}'|^2) \quad (2.36)$$

$$\pm \vec{q} = \vec{Q} - \vec{\tau} = \vec{k} - \vec{k}' - \vec{\tau} \quad (2.37)$$

Phonon density of states

The measurements of phonon density of states are related to incoherent phonon scattering. We can see more insights by evaluating the incoherent scattering term in Eq. 2.33 with $j = j'$.

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{1}{2\pi\hbar} e^{-2W(\vec{Q})} \sum_j b_j^2 \int_{-\infty}^{\infty} e^{\langle \hat{A}\hat{B} \rangle} e^{-i\omega t} dt \quad (2.38)$$

here we encounter the $e^{\langle \hat{A}\hat{B} \rangle}$ term again. For one-phonon scattering situation, we only consider the $\langle \hat{A}\hat{B} \rangle$ term in Taylor expansion (Eq. 2.34), ignoring the elastic and higher order multi-phonon contributions. Using the assumption we have discussed for one-phonon scattering and introduce the normal mode expansion. We obtain

$$\langle \hat{A}\hat{B} \rangle = \frac{\hbar}{2MN} \sum_{s,\vec{q}} \frac{(\vec{Q} \cdot \vec{e}_s(\vec{q}))^2}{\omega_s(\vec{q})} \left[e^{i\omega_s(\vec{q})t} (n_s(\vec{q}) + 1) + e^{-i\omega_s(\vec{q})t} n_s(\vec{q}) \right] \quad (2.39)$$

therefore, the cross-section can be written as

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{2M} \frac{k'}{k} (\langle b^2 \rangle - \langle b \rangle^2) e^{-2W(\vec{Q})} \sum_{s,\vec{q}} \frac{(\vec{Q} \cdot \vec{e}_s(\vec{q}))^2}{\omega_s(\vec{q})} \\ \times [(n_s(\vec{q}) + 1)\delta(\omega - \omega_s(\vec{q})) + n_s(\vec{q})\delta(\omega + \omega_s(\vec{q}))] \end{aligned} \quad (2.40)$$

again, we can see the physical picture from two terms associated with δ -functions, emission, and absorption. However, the cross-section now has no constraint on the momentum transfer. As a result, all phonons with energy ω_s contribute to the scattering cross-section, regardless of their wavevectors. Here, we can bring out the phonon density of states $g(\omega)$, which describes the number of phonons per energy interval.

$$\int_{-\infty}^{\infty} g(\omega) d\omega = 3N \quad (2.41)$$

where N is the number of atoms in a 3-dimensional lattice. The phonon scattering cross-

section in Eq. 2.40 can be written as

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{4M} \frac{k'}{k} (\langle b^2 \rangle - \langle b \rangle^2) e^{-W(\vec{Q})} \langle (\vec{Q} \cdot \vec{e}_s(\vec{q}))^2 \rangle \cdot \frac{g(\omega)}{\omega} \cdot \left[\coth \frac{\hbar\omega}{2k_B T} \pm 1 \right] \quad (2.42)$$

where $\left[\coth \frac{\hbar\omega}{2k_B T} \pm 1 \right] / 2$ stands for the Bose-Einstein occupation for phonon emission $n_s(\vec{q}) + 1$ and absorption $n_s(\vec{q})$. Experimentally, this representation becomes useful for samples that have dominating incoherent scattering because the momentum-dependent term can be quite complicated. However, in a cubic lattice, the term can be written as $\langle (\vec{Q} \cdot \vec{e}_s(\vec{q}))^2 \rangle = \frac{1}{3} Q^2$. Therefore, the phonon cross-section for a cubic Bravais lattice is

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{12M} \frac{k'}{k} (\langle b^2 \rangle - \langle b \rangle^2) e^{-W(\vec{Q})} Q^2 \cdot \frac{g(\omega)}{\omega} \cdot \left[\coth \frac{\hbar\omega}{2k_B T} \pm 1 \right] \quad (2.43)$$

It is clear that the phonon cross-section becomes more prominent at higher Q , contradicting the magnetic scattering, which decays with increasing Q . This feature is handy for differentiating the magnetic and phonon scatterings in actual experiments.

2.2.2 X-ray Scattering

X-ray scattering is complementary to neutron scattering because of the trend of atomic scattering lengths differs from neutron scattering. This is due to photons mainly interact with electrons in materials, while neutrons is more sensitive to nuclei in neutron scatterings.

Form factor and structure factor

In order to describe the x-ray scattering of a crystal, we start with the scattering from an atom. Classically, the electron number density surrounding an atom can be described as $\rho(\vec{r})$. Therefore, the charge in a volume element $d\vec{r}$, at $\vec{r}$ is $-e\rho(\vec{r})d\vec{r}$. The atomic form factor is defined as

$$f^0(\vec{Q}) = \int \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r} = \begin{cases} Z, & \text{for } Q \rightarrow 0 \\ 0, & \text{for } Q \rightarrow \infty. \end{cases} \quad (2.44)$$

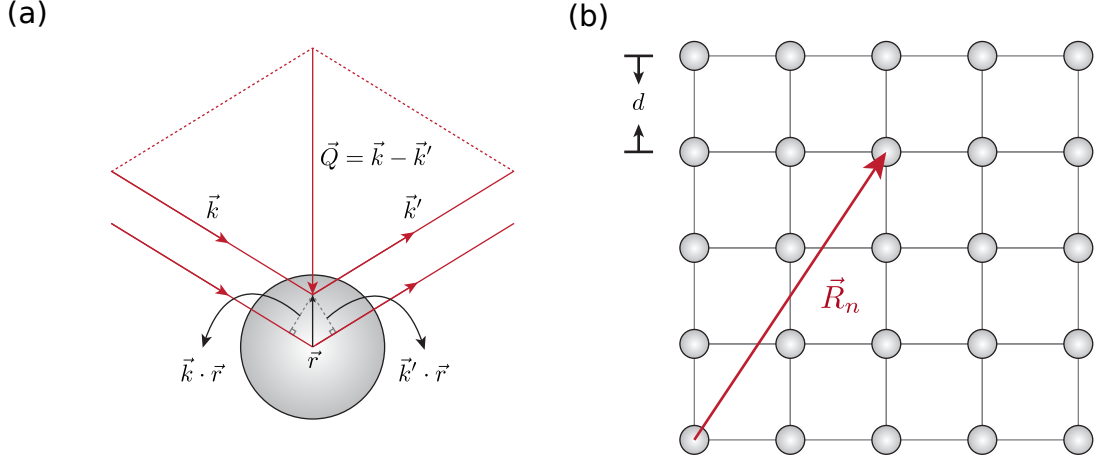


Figure 2.3: Scattering from an atom and a crystal. (a) Scattering from an atom. $k = k'$ for an elastic scattering. The momentum transfer is defined by $\vec{Q} = \vec{k} - \vec{k}'$. (b) Scattering from a crystal. The atomic sites are defined by the position vector $\vec{R}_n$.

where Z is atomic number. The physical meaning becomes clear in two limits. Fig. 2.3 (a) shows the scattering process of a single atom. When $Q \rightarrow 0$, the momentum transfer of scattered photon is zero, while the phase difference between scattered photons $\Delta\phi(\vec{r}) = (\vec{k} - \vec{k}') \cdot \vec{r} = 0$. Therefore, the integration is the total electron number (Z) of the atom. On the other hand, when Q gradually increases, the interference between scattered photons becomes out of phase. As $Q \rightarrow \infty$, the atomic form factor $f^0(\vec{Q}) \rightarrow 0$.

Now we can extend the calculation to a crystal as Fig. 2.3 (b) shown. We define $\vec{R}_n$ as lattice vectors which describe the position of lattice and $\vec{r}_j$ are positions of atoms to any particular lattice site. Based on the definitions, the position of any atom in the crystal is given by $\vec{R}_n + \vec{r}_j$. The scattering amplitude of a crystal is the sum of the contributions from each atoms, which has the form:

$$F^{crystal}(\vec{Q}) = \sum_j f_j(\vec{Q}) e^{i\vec{Q} \cdot \vec{r}_j} \sum_n e^{i\vec{Q} \cdot \vec{R}_n} \quad (2.45)$$

where the first term is the unit cell structure factor while the second term is a sum over lattice sites. The sum of the second term becomes of order N if it fulfills

$$\vec{Q} \cdot \vec{R}_n = 2\pi \times \text{integer} \quad (2.46)$$

where $\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, and $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ are the basis vectors of the lattice and (n_1, n_2, n_3) are integers [Fig. 2.3 (b)]. By introducing the concept of reciprocal lattice, the lattice site in the reciprocal lattice is

$$\vec{G} = h \vec{a}_1^* + k \vec{a}_2^* + l \vec{a}_3^* \quad (2.47)$$

where $(\vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^*)$ are basis vectors for the reciprocal lattice, and (h, k, l) are Miller indices which are integers. The scalar product therefore becomes

$$\vec{G} \cdot \vec{R}_n = 2\pi(hn_1 + kn_2 + ln_3) = 2\pi \times \text{integer} \quad (2.48)$$

therefore, the condition for $\vec{Q}$ to have a non-vanishing value of $F^{crystal}(\vec{Q})$ is

$$\boxed{\vec{Q} = \vec{G}} \quad (2.49)$$

This is so-called the Laue condition for the diffraction of a crystal, and is completely equivalent to Bragg's law. On the other hand, the intensity in each point fulfills the Laue condition is given by the absolute square of unit cell structure factor in Eq. 2.45. From a (large) set of intensities from a given crystal it is possible to deduce the positions of the atoms in the unit cell. This is the foundation of the x-ray crystallography which is one of scattering techniques used in this thesis. We will have more detailed discussion in the later of this chapter.

The lattice sum $S_N(\vec{Q})$

In order to calculate the scattering intensity in Eq. 2.45, the lattice sum is required.

$$S_N(\vec{Q}) = \sum_n e^{i\vec{Q} \cdot \vec{R}_n} \quad (2.50)$$

The simplest example is a one-dimensional crystal which the lattice points are specified by $R_n = na$, where n is an integer and a is the lattice constant. The lattice sum can be written as

$$S_N(Q) = \sum_{n=0}^{N-1} e^{iQna} \quad (2.51)$$

which sum over N unit cells. The geometric series can be solved as

$$|S_N(Q)| = \frac{\sin NQa/2}{\sin Qa/2} \quad (2.52)$$

For large N , $|S_N(Q)|$ has sharply defined peaks whenever the denominator is equal to zero. The condition $Qa/2 = \pi \times (\text{integer})$ or $Q = (\text{integer}) \times (2\pi/a) = G_h$, where G_h is a reciprocal lattice vector. Eq. 2.52 can be further generalized by introducing the reciprocal lattice a^* and the δ -function, the detail derivation can be found in the reference book [30].

$$|S_N(Q)|^2 \rightarrow N a^* \sum_{G_h} \delta(Q - G_h) \quad (2.53)$$

For two dimensions, the reciprocal lattice vector is $\vec{G} = h \vec{a}_1^* + k \vec{a}_2^*$, and we can extend the unit cell scattering amplitude as

$$|S_N(\vec{Q})|^2 \rightarrow N A^* \sum_{\vec{G}} \delta(\vec{Q} - \vec{G}) \quad (2.54)$$

where A^* is the area of the unit cell in reciprocal space, and $N = N_1 N_2$ is the number of the unit cells. For three dimensions, $\vec{G} = h \vec{a}_1^* + k \vec{a}_2^* + l \vec{a}_3^*$, we obtain

$$|S_N(\vec{Q})|^2 \rightarrow N \nu_c^* \sum_{\vec{G}} \delta(\vec{Q} - \vec{G}) \quad (2.55)$$

where ν_c^* is the volume of the unit cell in reciprocal space.

The unit cell structure factor $F(\vec{Q})$

Now we turn to evaluate the term of unit cell structure factor in Eq. 2.45

$$F(\vec{Q}) = \sum_j f_j(\vec{q}) e^{i\vec{Q} \cdot \vec{r}_j} \quad (2.56)$$

For a face centered cubic cell, the reciprocal lattice is a body center cubic in reciprocal space [Fig. 2.4]. The basis vectors for four atoms in a primitive cell are

$$\vec{r}_1 = 0, \vec{r}_2 = \frac{1}{2}(\vec{a}_1 + \vec{a}_2), \vec{r}_3 = \frac{1}{2}(\vec{a}_2 + \vec{a}_3), \vec{r}_4 = \frac{1}{2}(\vec{a}_3 + \vec{a}_1) \quad (2.57)$$

which are shown in Fig. 2.4 (a). The reciprocal lattice of a FCC lattice is a BCC cell with

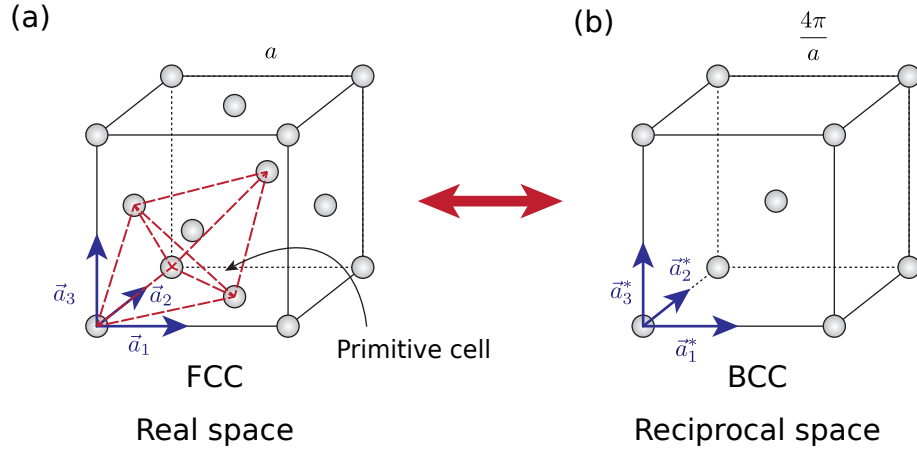


Figure 2.4: (a) Face center cubic unit cell. (b) Body center cubic lattice in reciprocal space.

lattice spacing of $2\pi/a$ and the reciprocal lattice vector is of the form $\vec{G} = (\frac{2\pi}{a})(h, k, l)$ [Fig. 2.4 (b)]. Therefore, the unit cell structure factor is the sum over all atoms with corresponding phase factor.

$$F_{hkl}^{FCC} = f(\vec{G}) \sum_j e^{i\vec{G} \cdot \vec{r}_j} \quad (2.58)$$

$$= f(\vec{G})(1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}) \quad (2.59)$$

$$= \begin{cases} 4, & \text{if all } h, k, l \text{ are all even or odd} \\ 0, & \text{otherwise} \end{cases} \quad (2.60)$$

this simple example shows the idea of calculating the unit cell structure factor. For more complicated systems, group theory analysis becomes a useful tool to determine the structure from diffraction measurements. This concept is also the cornerstone of modern x-ray crystallography.

Debye-Waller factor and thermal diffuse scattering

Here we discuss the effect of lattice vibrations on the scattering intensity. There are two types of mechanisms of lattice vibrations. The first is quantum mechanical vibrations which is driven by the uncertainty principle and the vibrations are independent from

temperature. Another type is thermally-excited lattice vibration (phonon), which is the collective motion of atoms in a lattice. The most common way to deal with the vibration problems is to assume a small displacement from the equilibrium position, $\vec{R}_n \rightarrow \vec{R}_n + \vec{u}_n$, where $\vec{R}_n$ and $\vec{u}_n$ are equilibrium position and small displacement. The scattered intensity is given by the temporal average of the scattering amplitude.

$$I = \left\langle \sum_m f(\vec{Q}) e^{i\vec{Q} \cdot (\vec{R}_m + \vec{u}_m)} \sum_n f^*(\vec{Q}) e^{-i\vec{Q} \cdot (\vec{R}_n + \vec{u}_n)} \right\rangle \quad (2.61)$$

$$= \sum_m \sum_n f(\vec{Q}) f^*(\vec{Q}) e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_n)} \langle e^{i\vec{Q} \cdot (\vec{u}_m - \vec{u}_n)} \rangle \quad (2.62)$$

the temporal average term can be further simplified using the Baker-Hausdorff theorem

$$\langle e^{ix} \rangle = e^{-\frac{1}{2}\langle x^2 \rangle} \quad (2.63)$$

if x is described by a Gaussian distribution. Therefore, the temporal average term becomes

$$\langle e^{iQ(u_{Qm} - u_{Qn})} \rangle = e^{-\frac{1}{2}\langle Q^2(u_{Qm} - u_{Qn})^2 \rangle} \quad (2.64)$$

$$= e^{-\frac{1}{2}Q^2\langle (u_{Qm} - u_{Qn})^2 \rangle} \quad (2.65)$$

$$= e^{-\frac{1}{2}Q^2\langle u_{Qm}^2 \rangle} e^{-\frac{1}{2}Q^2\langle u_{Qn}^2 \rangle} e^{Q^2\langle u_{Qm}u_{Qn} \rangle} \quad (2.66)$$

here we simplified the notation of inner product terms, $\vec{Q} \cdot (\vec{u}_m - \vec{u}_n) \rightarrow Q(u_{Qm} - u_{Qn})$.

As the consequence of the translational symmetry, we have $\langle u_{Qm}^2 \rangle = \langle u_{Qn}^2 \rangle \equiv \langle u_Q^2 \rangle$. The final form of the scattering intensity can be separated into two terms

$$I = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q} \cdot \vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q} \cdot \vec{R}_n} \quad (2.67)$$

$$+ \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q} \cdot \vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q} \cdot \vec{R}_n} \left[e^{Q^2\langle u_{Qm}u_{Qn} \rangle} - 1 \right] \quad (2.68)$$

The first term is the elastic scattering from a lattice and the form factor now is

$$\boxed{f^{atom} = f(\vec{Q}) e^{-\frac{1}{2}Q^2\langle u_Q^2 \rangle} \equiv f(\vec{Q}) e^{-M}} \quad (2.69)$$

where the exponential term is known as the Debye-Waller factor. The important message

is that the elastic Bragg reflection is reduced in density by atomic vibrations, but its width is not increased. It is distinct to the second term in Eq. 2.67, which has a width determined by $\langle u_{Qm}u_{Qn} \rangle$ in the last factor. This correlation term is significant only over few lattice sites, and the width is much larger than the width of a Bragg reflection. This is known as the thermal diffuse scattering.

2.3 Experimental Techniques

This section contains the technical information for (1) Synchrotron crystallography, (2) Total scattering measurement, (3) Inelastic neutron scattering, and (4) High-pressure diamond anvil cell. The subsection of each technique provides the basic concept, important parameters, data analysis, and experimental setup based on author's experiences on those experimental techniques.

2.3.1 Crystallography

The idea of X-ray crystallography is to obtain atomic positions and corresponding thermal parameters from the measurement of scattering amplitude over large amount of Bragg reflections. In a diffraction measurement, the reflection of x-ray correspond to the Bragg's peak in reciprocal space. Therefore, the real space information (atomic positions, electronic orbitals) is the Fourier transform of the signals we obtained through a x-ray detector. To this end, the relative intensity of each Bragg reflection is the most important experimental information to obtain a reliable solution for a crystal structure.

Typically, the sample size of a synchrotron crystallography measurement is around 5 μm , but should be as small as possible to avoid the twinned structure and x-ray absorption of crystal itself. The small crystal is mounted on a fused quartz fiber with epoxy and taking reflection images over $\phi = 0 \rightarrow 360$ degrees. The step size can be small but not a definitive factor for the resolution of the experiment. In contrast to a typical x-ray diffraction measuring the rocking curve through a Bragg reflection with a high resolution,

the maximum coverage of the reciprocal space is more important for a crystallography experiment. Therefore the selection of the sample to area detector distance is crucial for the resolution of a crystallography experiment.

X-ray crystallography has a well-developed routine for data analysis. The general procedures are as the following. First, we integrate all images in to momentum space and determine the unit cell of the crystal, which refers to the process of indexing reflections (Bruker APEX). After the unit cell is determined and all reflections are properly indexed, we are allowed to generate the list of intensities of each (h, k, l) reflection with absorption correction (SADABS or TWINABS). The list of reflections is used for determine the space group using the symmetry operations of space groups (XPREP). Then the structure solution and refinement are carried out by SHELX and Olex2.

ChemMatCARS (15-ID) at Advanced photon source

In this thesis, all crystallography experiments were performed at the ChemMatCARS beamline at advanced photon source at Argonne national laboratory. The beamline utilizes a large CdTe area x-ray detector (Pilatus3 X 1M) with an optimized synchrotron beam at 30 keV ($\lambda = 0.4122 \text{ \AA}$). The cryojet N_2/He cool stream is used for sample cooling [Fig. 2.5]. Depending on the absorption and the scattering power of the sample, the measurements can be done in few minutes or hours.

2.3.2 Total Scattering Method

The pair distribution function (PDF) contains the information about structural correlation in materials. The PDF, $G(r)$, shows the probability of finding pairs of atoms separated by a distance r . Experimentally, PDF measurement is similar to traditional diffraction experiments, but optimizing in the way that the diffraction image covers large $Q \equiv 4\pi \sin\theta/\lambda$, where λ is the wavelength of the incident beam. Therefore, the incident beam energy is usually higher in order to maximize measured Q for PDF measurements. The theoretical description starts from the coherent scattering intensity for the collection

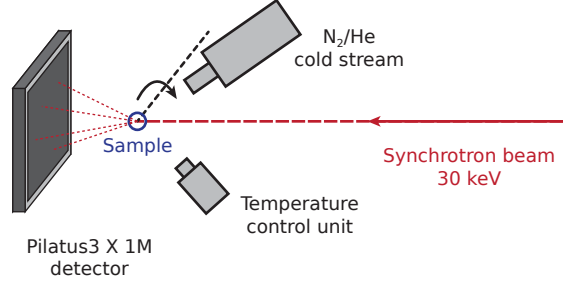


Figure 2.5: Schematic illustration of the ChemMatCARS beamline for advanced crystallography at advanced photon source. The incident x-ray beam has the energy of 30 keV, which balances the resolution and the coverage of reciprocal space. The sample to detector distance is 6 to 8 cm, depending on the required resolution for experiment.

of atoms

$$I_c(Q) = \int_0^\infty \sum_{i,j} b_i^* b_j \delta(r - r_{ij}) \frac{\sin Qr}{Qr} dr \quad (2.70)$$

where b_i is the scattering length of atom i . The total scattering structure function $S(Q)$ is given by (see [31] for details)

$$S(Q) = \frac{I_c(Q)}{N\langle b \rangle^2} + \frac{\langle b \rangle^2 - \langle b^2 \rangle}{\langle b \rangle^2} \quad (2.71)$$

Then the PDF is defined by

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin Qr dQ \quad (2.72)$$

where $Q[S(Q) - 1] = F(Q)$ is the reduced total scattering structure function, which is distinct to the crystallographic structure factor we have discussed in previous section.

The data process of PDF experiment has three major steps. First, the powder diffraction data is unwrap into one-dimensional $S(Q)$ using PyFAI package [32]. Then $F(Q)$ and $G(r)$ are obtained using PDFgetX3 or ADDIE packages [33, 34]. Finally, we can perform model-independent or -dependent analysis to extract the information for local correlation in the material.

Experimentally, the particle size of the powder sample has to be small enough ($< 20 \mu m$) for synchrotron PDF, because the sample tube is usually fixed and can not rotate

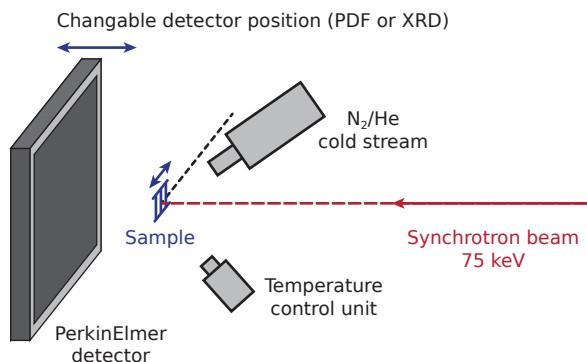


Figure 2.6: Schematic illustration of the experimental setup at 28-ID-1 at NSLS-II. The beamline uses a high-energy monochromatic incident beam, maximizing the Q_{max} to achieve a high-resolution pair distribution function. The detector position can change for traditional XRD and PDF measurements for each temperature, probing the average and local structure of the measured material.

along the sample axis to average out the reflection from small crystals in the sample. Further, a larger particle can saturate the detector image and cause the discrepancy of the relative diffraction intensities.

NSLS-II 28-1-ID

The 28-1-ID beamline at NSLS-II is designed for pair distribution function (PDF) measurements. The large PerkinElmer area detector covers a wide range of solid angles for diffraction measurements. The detector-to-sample distance is changeable for collecting traditional XRD and PDF at the same setup. The high-energy 75 keV incident synchrotron beam is used to reach higher momentum transfer, improving PDF resolution. The sample mount can hold three capillary samples for serial measurements on different samples. The cold helium and nitrogen streams are used for the sample cooling. The schematic of the experimental design is shown in Fig. 2.6.

NOMAD diffractometer

The Nanoscale Ordered Materials Diffractometer (NOMAD) is a neutron time-of-flight diffractometer designed to measure pair distribution functions of materials. The high

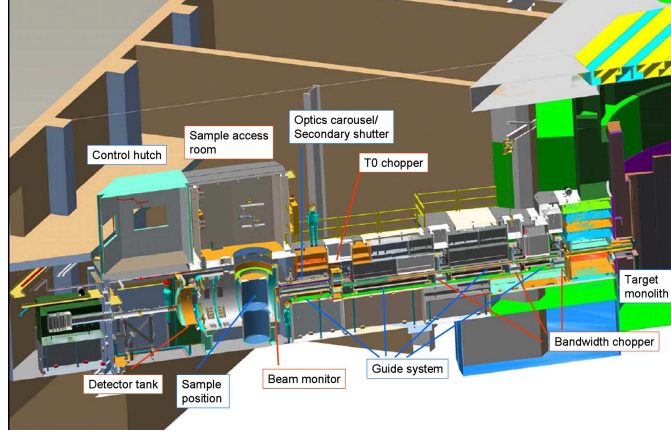


Figure 2.7: Schematic illustration of NOMAD beamline at SNS. The figure is adopted from the source [35].

neutron flux of spallation neutron source enhances the capability for measuring the high- Q diffraction signals. In addition, the large solid angle coverage of detector banks is designed to reach $Q_{max} = 50 \text{ \AA}^{-1}$, corresponding to $0.126 \text{ \AA}$ spatial resolution for PDFs. The schematic of NOMAD beamline is shown in Fig. 2.7.

2.3.3 Inelastic Neutron Scattering

Neutron source

There are major two types of neutron sources for scattering experiments. First is the fission source, which contains the fission of the uranium isotope 235 by slow neutron capture. The other one is a spallation neutron source, which uses a sequence of protons bombarding the target to generate neutrons. The difference between two methods starting from the incident particle hitting the target. In a nuclear fission process, the incident particle are slow neutrons. The fission of the compound nucleus, promotes the chain reaction and creates ore neutrons. On the other hand, the spallation technique uses high-energy ($\approx 1 \text{ GeV}$) protons bombarding the target. The proton first merged to the nucleus of the target, and whole nucleus becomes unstable. Eventually neutrons evaporate from the unstable nucleus. This process takes less than 10^{-15} s after the nucleus was hit, therefore, the time

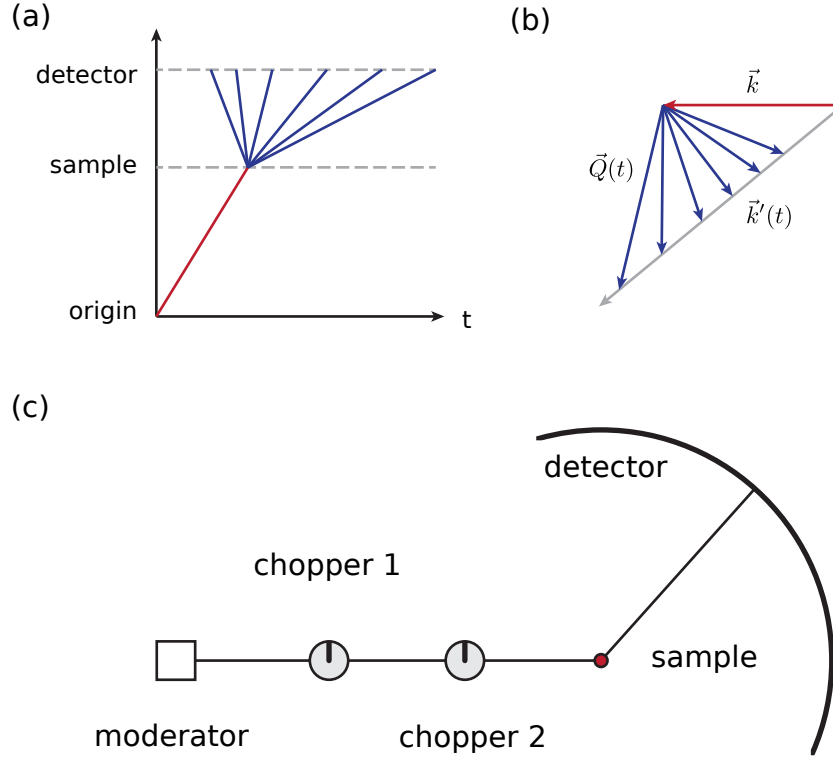


Figure 2.8: (a) Phase-space diagram and (b) Momentum representation of direct time-of-flight technique. (c) Schematic illustration of possible instrumental realization of a direct geometry chopper spectrometer.

distribution of spallation neutrons is exclusively determined by the time distribution of the driving particle pulse.

Time-of-flight spectrometers

Time-of-flight neutron spectrometers measure the energy of a neutron by recording the time neutron travels from the sample to a detector. The travel time and the sample-to-detector distance are used to calculate the energy of a scattered neutron. The measurement of momentum transfer is achieved by recording the position of the neutron hitting the detector. The schematic phase-space diagram and corresponding momentum representation are shown in Fig. 2.8 (a) and (b). The incident neutron beam energy (velocity) is selected by properly phasing two rotating neutron-absorbing choppers [Fig. 2.8 (c)].

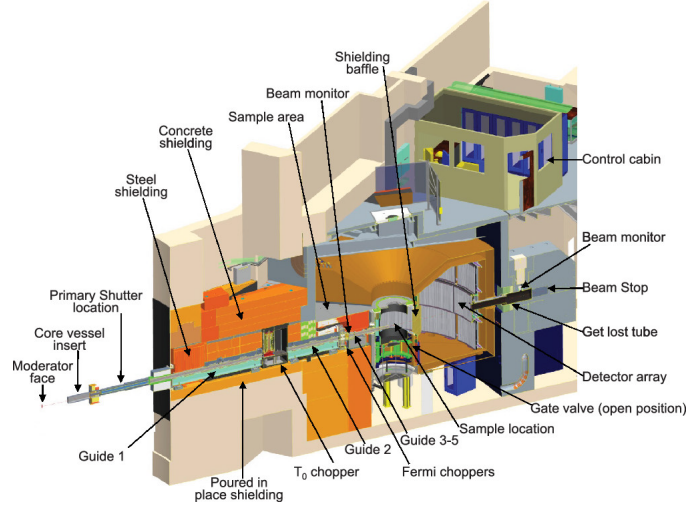


Figure 2.9: Schematic illustration of ARCS beamline. The figure is adopted from the source [36].

SEQUOIA and ARCS spectrometers

The direct geometry chopper spectrometer (DGCS) is a type of inelastic neutron scattering design that involves the use of rotating choppers to the incident energy of neutrons from the source [Fig. 2.8]. These neutrons are then scattered from a sample, and their final energy and momentum are determined using time-of-flight techniques and conservation principles based on their final velocity and scattering angle. At spallation neutron sources, three DGCS instruments are used in this thesis.

Wide Angular-Range Chopper Spectrometer (ARCS) and Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) are two direct geometry spectrometers at SNS. ARCS and SEQUOIA are complementary to each other. ARCS has a more intense incident neutron flux due to a short source-to-sample distance (13.6 m). The detector bank coverage of ARCS is from -28° to 135° with the energy resolution 3% to 5% E_i . On the other hand, SEQUOIA has a larger source-to-sample (20 m) and sample-to-detector distance (5.53m); therefore, the energy and momentum resolution is better than ARCS, but with a smaller detector band coverage (-30° to 60°). The schematic illustrations of ARCS and SEQUOIA are shown in Fig. 2.9 and Fig. 2.10, respectively.

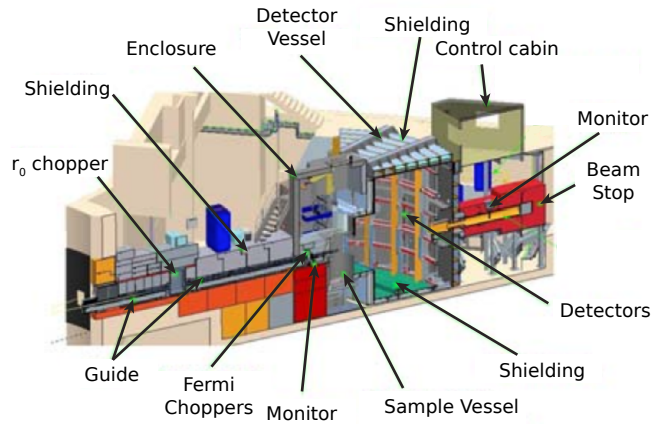


Figure 2.10: Schematic illustration of SEQUOIA beamline. The figure is adopted from the source [37].

2.3.4 High-pressure Diamond Anvil Cell

A diamond anvil cell (DAC) is a device used to create extremely high-pressure environments to study the behavior of materials under those conditions. It consists of two opposing diamond anvils, which are cut to have flat faces that are then brought into contact with each other [Fig. 2.11 (a)]. A sample is placed on one of the faces, and the anvils are then pressed together using a metallic membrane driven by high-pressure helium gas, generating high pressures in the chamber filled with pressure medium. With a DAC, pressures above hundred GPa can be achieved, allowing us to investigate a wide range of phenomena, including structural phase transition, insulator-metal phase transitions, metal-superconductor transition, and the behavior of materials under extreme conditions.

Experimental setup

The high-pressure experiments conducted in this thesis involved the use of a Diacell Bragg-LT(G) DAC from Almax-easyLab, with a stainless steel gas membrane serving as the pressure mechanism. To prepare for the x-ray experiment using the DAC, a series of steps must be followed. While more detailed discussions can be found later in this section, the general procedures are outlined below.

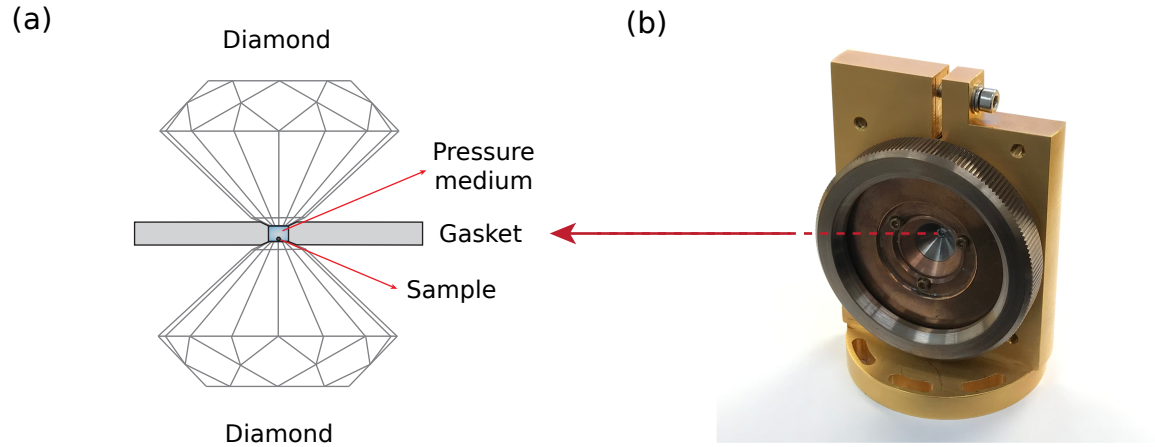


Figure 2.11: Schematic and pictures of diamond anvil cell (DAC). (a) Components of a DAC. The sample is sealed in a chamber filled with pressure medium. (b) Diamond alignment.

- Check diamonds alignment and clean the surfaces
- Prepare the gasket
- Mount the sample
- Mount a small piece of silver foil for pressure calibration
- Install the prepared gasket
- Fill the cell with pressure medium
- Close the DAC and tighten four screws
- Check if the cell is filled with pressure medium
- Mount the DAC on the diffractometer along with the gas membrane
- Purge the helium gas line if necessary
- Increase the applied pressure
- Start the experiment

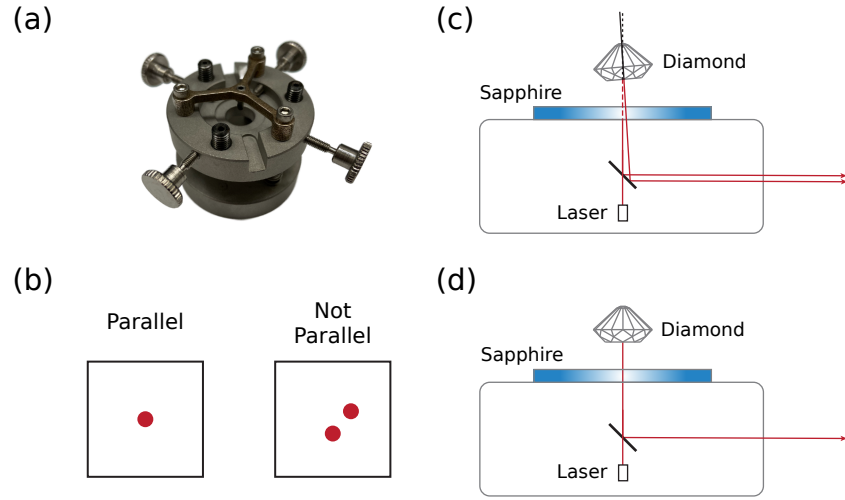


Figure 2.12: Alignment of diamond anvil. The laser unit and a flat sapphire plate are used for aligning the diamond anvil. (a) The diamond is not parallel to the sapphire. (b) Aligned diamond anvil. (c) Schematic illustration of reflected laser beams for parallel and not parallel cases. (d) The device for diamond anvil alignment.

Alignment of Diamonds

First, we glue a diamond on a tungsten carbide seat with Stycast epoxy. A laser unit, a flat sapphire disc, and an alignment tool [Fig. 2.12 (a)] are used for the checking procedures. By adjusting four screws, we can fine tune the diamond position on a anvil by overlapping the reflected laser beams from air-sapphire and air-diamond interfaces [Fig. 2.12] (b)-(d).

To check two diamonds are parallel, we bring two diamonds as close as possible. This is the most risky step for entire procedures, because diamonds can break due to a small collision. Therefore, I usually put a small piece of sticky tag between the cell and the piston to provide an extra resistance for bringing two diamonds closer. Once two diamonds are close enough, we can see fringes on the diamond using the optical microscope [Fig. 2.13]. Newton's rings which are a series of concentric circular fringes of light and dark that are produced by the interference of light waves reflected from the top and bottom surfaces of a thin air film trapped between two diamond surfaces, the rings vanish only if two diamond surfaces are perfectly parallel.

Gaskets

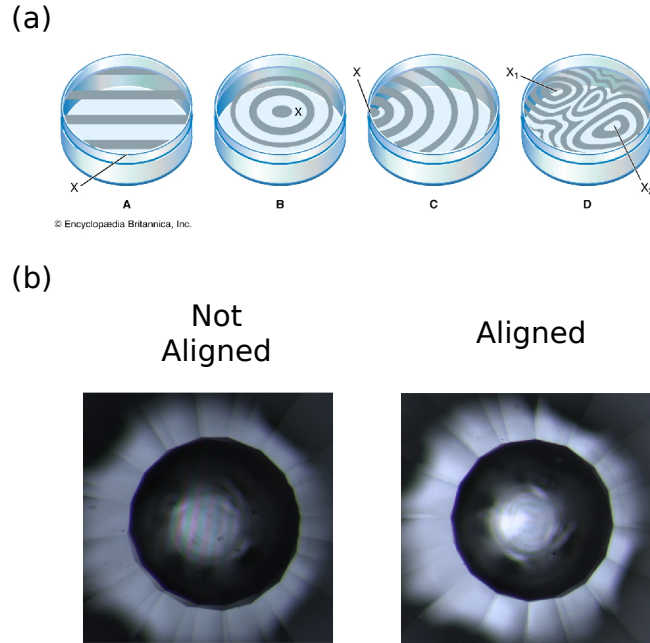


Figure 2.13: Alignment of two diamonds. When two diamond surfaces contact, we can use the Newton's rings to check the alignment of two diamond surfaces. (a) The Newton rings when two surfaces have contact [Figure: Encyclopedia Britannica, Inc]. (b) Examples for not aligned and aligned diamonds.

The gasket plays a crucial role in the DAC by performing several essential functions, including supporting the pressure through friction with the anvil, and enclosing the sample. In some cases, the gasket may also act as a window for x-ray and neutron scatterings, or as an outlet for transport measurements. Typically, gaskets are made of high-strength metals, and they must have some level of ductility to allow for the volume reduction that corresponds to the increase in pressure within the sample chamber.

The choice of gasket material is determined by the desired pressure level. Typically, harder gasket materials are capable of withstanding higher pressures, while softer ones can handle lower pressures. For this thesis, CuBe gaskets have been employed for pressures under 8 MPa, while stainless steel 301 gaskets have been utilized for higher pressure ranges.

Electrical discharge machining (EDM) drill is utilized to make a flawless hole. This is crucial for a successful experiment, because the crack or non-centered hole can cause leaks of the pressure medium resulting damaged diamonds. The settings of the EDM drill

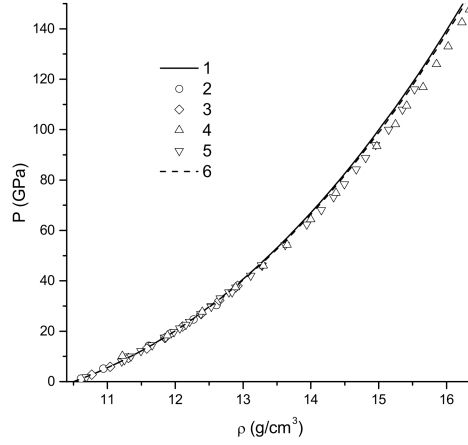


Figure 2.14: Equation of state of silver at 300 K, 1: [39], 2: [40], 3: [41], 4: [42], 5: [38], 6: fit of the Vinet equation to data [39]. Figure (d) is adopted from the source [39].

depends on the material of the gasket. Our EDM drill can adjust the current and the criteria for finishing the drilling process.

Pressure calibration

To measure the pressure in the cell, we load a small piece of silver foil near the sample. The equation of state (EoS) of silver is well studied, and can be described by Vinet equation of state formalism.

$$P = 3K_0 \left(\frac{V}{V_0} \right)^{-2/3} \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \exp \left\{ \frac{3}{2} (K'_0 - 1) \times \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \right\} \quad (2.73)$$

The three parameters of a Vinet EoS are thus the volume V_0 , the isothermal bulk modulus K_0 and its pressure derivative K'_0 at ambient pressure. The parameters K_0 and K'_0 obtained by fitting this EoS to the experimental data. The parameters for silver are $V_0 = 17.021$, $K_0 = 101$, and $K'_0 = 5.97$, experimental results are shown in Fig. 2.11, more details can be found in [38].

Chapter 3

Computational Methods

3.1 Introduction

This chapter provides a brief overview of the theoretical basis of density functional theory (DFT), as well as frozen phonon mode calculation and group theory analysis. The primary application of those methods is to analyze the structure distortion and lattice dynamics in lacunar spinels. However, it should be noted that the electronic structure of these materials cannot be accurately simulated using DFT alone. Spin-orbit coupling (SOC), electronic correlation (U), and complete active space self-consistent field (CASSCF) approach are required to reproduce correct electronic structure [43–46].

3.2 Density Functional Theory

Since its inception in 1965, Density Functional Theory (DFT) has gained widespread use in the field of condensed matter physics. DFT is based on the idea that the properties of the ground state can be described by a functional of the charge density of the system. The main task of DFT is to determine the electron density of the ground state of a system, which is accomplished by solving self-consistent Kohn-Sham equations.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}[\rho] \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (3.1)$$

where $\psi_i(\mathbf{r})$ is the i -th eigenstate of the system with energy ϵ_i , $V_{\text{eff}}[\rho]$ is the effective potential that depends on the electron density $\rho(\mathbf{r})$. The effective potential is given by:

$$V_{\text{eff}}[\rho] = V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}[\rho] \quad (3.2)$$

where $V_{\text{ext}}(\mathbf{r})$ is the external potential, $\int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$ is the Hartree potential, and $V_{\text{xc}}[\rho]$ is the exchange-correlation term. This is essential in DFT because now the many-electron problem is approximated to an effective single electron Hamiltonian. The exchange correlation potential $V_{\text{xc}}(\rho)$ takes into account the many-electron interactions and it is non-trivial. The most common approximations for the exchange-correlation are local density approximation (LDA) and generalized gradient approximation (GGA), while other advanced functionals are out of the scope of this thesis.

The Kohn-Sham equations are solved self-consistently, meaning that the electron density is used to calculate the effective potential, which in turn is used to solve for the new electron density, and so on, until the solution converges to a stable electron density. The resulting electron density can be used to calculate physical properties of the system, including the total energy, band structure, electronic density of states, and atomic forces for structural optimization.

For lacunar spinels, we employed the plane-wave basis projector augmented wave (PAW) method [47] in the framework of DFT within the GGA in the Perdew–Burke–Ernzerhof (PBE) [48] as implemented in the QuantumESPRESSO code [49]. This selection of the exchange-correlation and pseudopotential accurately reproduces the dynamic properties for lacunar spinel [50]. For electronic calculation, we implemented the spin-orbit coupling with non-collinear spin interactions, and the density of states is projected into a relativistic spin-orbital basis.

3.3 First principles phonon calculation

In order to obtain more insights into the dynamic properties of lacunar spinels, we employed first principles phonon calculations to directly compare the phonon density of states obtained from inelastic neutron scatterings. Two steps achieve the phonon calculation: (1) Calculate the atomic forces of distorted structures using DFT. (2) Analyze the forces associated with a systematic set of displacements to obtain a series of phonon frequencies using Phonopy package [51].

Here we brief discuss the theoretical behind the **Phonopy** package, detailed discussion can be found in theoretical works on first principle phonon calculation [51–53]. The lattice vibration is associated with the crystallographic symmetry, and the vibrational normal modes are constrained by the space group of the lattice. For each irreducible representaion, we assume the equilibrium positions $\vec{r}(l\kappa)$ with small displacement $\vec{u}(l\kappa)$, where l and κ are the labels of unit cells and atoms in each unit cell, respectively. The crystal potential energy Φ can be written as

$$\Phi = \Phi_0 + \sum_{l\kappa} \sum_{\alpha} \Phi_{\alpha}(l\kappa) u_{\alpha}(l\kappa) \quad (3.3)$$

$$+ \frac{1}{2} \sum_{ll'\kappa\kappa'} \sum_{\alpha\beta} \Phi_{\alpha\beta}(l\kappa, l'\kappa') u_{\alpha}(l\kappa) u_{\beta}(l'\kappa') \quad (3.4)$$

$$+ \frac{1}{3!} \sum_{ll''\kappa\kappa'\kappa''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'') u_{\alpha}(l\kappa) u_{\beta}(l'\kappa') u_{\gamma}(l''\kappa'') + \dots \quad (3.5)$$

where $\alpha, \beta, \dots$ are Cartesian indices. Φ_0 , $\Phi_{\alpha}(l\kappa)$, $\Phi_{\alpha\beta}(l\kappa, l'\kappa')$, and $\Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'')$ correspond to the zeroth, first, second, and third order force constants. Since we assume the displacement $\vec{u}(l\kappa)$ is small, the higher-order terms can be treated by the perturbation theory. Here we focus our discussion on the second-order harmonic term. Starting with the force from the crystal potential

$$F_{\alpha}(l\kappa) = -\frac{\partial\Phi}{\partial u_{\alpha}(l\kappa)} \quad (3.6)$$

the second-order force constant is

$$\Phi_{\alpha\beta}(l\kappa, l'\kappa') = \frac{\partial^2 \Phi}{\partial u_\alpha(l\kappa) \partial u_\beta(l'\kappa')} = -\frac{\partial F_\beta(l'\kappa')}{\partial u_\alpha(l\kappa)} \quad (3.7)$$

the computational cost can be reduced by introducing the crystal symmetry for calculating the force constants. The dynamical property of atoms in the harmonic approximation is obtained by solving eigenvalue problem of dynamical matrix

$$D(\vec{q})\hat{e}_{\vec{q}j} = \omega_{\vec{q}j}^2 \hat{e}_{\vec{q}j} \quad (3.8)$$

or

$$\sum_{\beta\kappa'} D_{\kappa\kappa'}^{\alpha\beta}(\vec{q}) e_{\vec{q}j}^{\beta\kappa'} = \omega_{\vec{q}j}^2 e_{\vec{q}j}^{\alpha\kappa} \quad (3.9)$$

with

$$D_{\kappa\kappa'}^{\alpha\beta}(\vec{q}) = \sum_{l'} \frac{\Phi_{\alpha\beta}(0\kappa, l'\kappa')}{\sqrt{m_\kappa m_{\kappa'}}} e^{i\vec{q} \cdot [\vec{r}(l'\kappa') - \vec{r}(0\kappa)]} \quad (3.10)$$

where m_κ is the mass of the atom κ , $\vec{q}$ is the wave vector, and j is the band index. $\omega_{\vec{q}j}$ and $\hat{e}_{\vec{q}j}$ are eigenvalue and eigenvector for mode $\{\vec{q}j\}$, corresponding to phonon frequency and polarization vector of the lattice. The phonon DOS is defined as

$$g(\omega) = \frac{1}{N} \sum_{\vec{q}j} \delta(\omega - \omega_{\vec{q}j}) \quad (3.11)$$

where N is the number of unit cells in crystal. Therefore, $g(\omega)$ is normalized so that the total number of phonon states is $3n_a$ for three-dimensional lattice, where n_a is the number of atoms. Atom specific phonon DOS projected along a unit direction vector $\hat{n}$ is defined as

$$g_\kappa(\omega, \hat{n}) = \frac{1}{N} \sum_{\vec{q}j} \delta(\omega - \omega_{\vec{q}j}) |\hat{n} \cdot \hat{e}_{\vec{q}j}^\kappa|^2 \quad (3.12)$$

where κ is selected for a specific atomic site and allows us to project the phonon DOS to a specific type of atoms.

Chapter 4

Synthesis of Lacunar Spinel

This chapter provides the detailed procedures of synthesizing lacunar spinels GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}, \text{X}=\text{S}, \text{Se}$). The solid-state reaction and chemical vapor transport methods are used in this thesis. This chapter organizes as follows. The methods and parameters are discussed in the first half of this chapter. In the second half, powder x-ray diffraction of the powder samples and crystallography of single crystal samples are presented.

4.1 Introduction

The synthesis of high-quality samples is crucial for successful experiments. In this thesis, our experiments cover the entire series of d^1 lacunar spinels in synchrotron and neutron scatterings. The form of the sample can be powder or single crystals, and each has its advantages. The difficulty in synthesizing powder material is that the sample is usually mixed with impurities from the residual of the starting materials. On the other hand, the major challenge for synthesizing single crystal samples is to obtain the optimal condition maximizing the crystal size. The synthesis methods have been discussed in many papers [16, 18, 24, 54]. Here, I only demonstrate the synthesizing methods and parameters I used in this thesis.

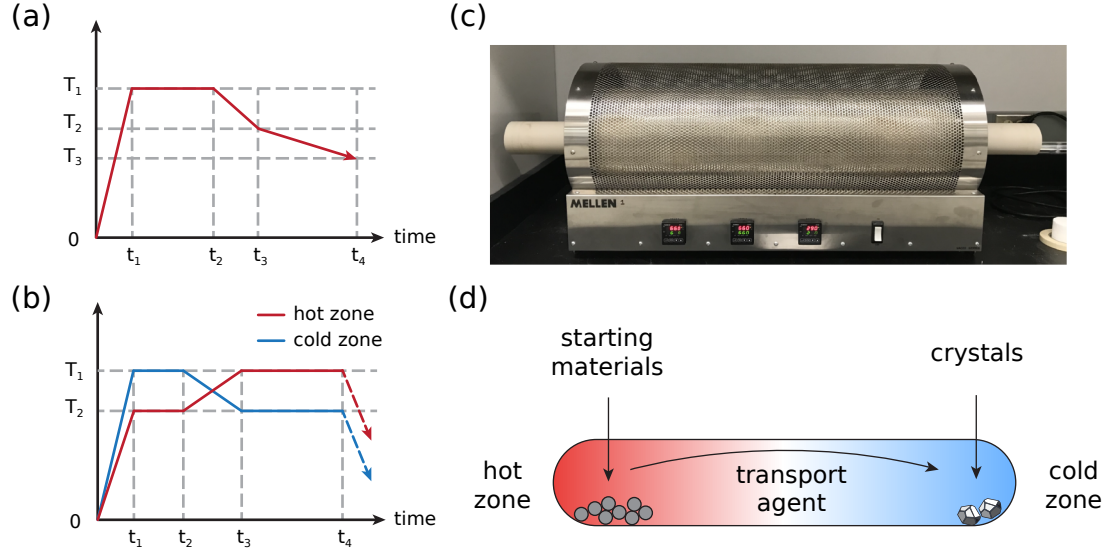


Figure 4.1: Synthesis of lacunar spinels. (a) The temperature profile of solid-state reaction. (b) The temperature profile of two-zone chemical vapor transport. (c) The three-zone furnace in our laboratory. (d) Schematic illustration for chemical vapor transport. The entire sealed quartz tube is filled with a transport agent (iodine gas).

Table 4.1: Parameters of the synthesis of lacunar spinels. The corresponding procedures are shown in Fig. 4.1 (a).

	GaV ₄ S ₈	GaV ₄ Se ₈	GaNb ₄ S ₈	GaNb ₄ Se ₈	GaTa ₄ Se ₈
T ₁ (°C)	950	1000	1000	1050	1050
T ₂ (°C)	20	20	20	970	950
T ₃ (°C)	N/A	N/A	N/A	850	800
t ₁ (hrs)	15	15	15	8	8
t ₂ - t ₁ (hrs)	24	24	24	24	24
t ₃ - t ₂ (hrs)	quench	quench	quench	6	6
t ₄ - t ₃ (hrs)	N/A	N/A	N/A	120	150

Table 4.2: Parameters of the synthesis of lacunar spinels. The corresponding procedures are shown in Fig. 4.1 (b).

	GaNb ₄ S ₈	GaNb ₄ Se ₈
T ₁ (°C)	950	1000
T ₂ (°C)	900	950
t ₁ (hrs)	8	8
t ₂ - t ₁ (hrs)	8	8
t ₃ - t ₂ (hrs)	15	15
t ₄ - t ₃ (days)	21	21

4.2 Methods

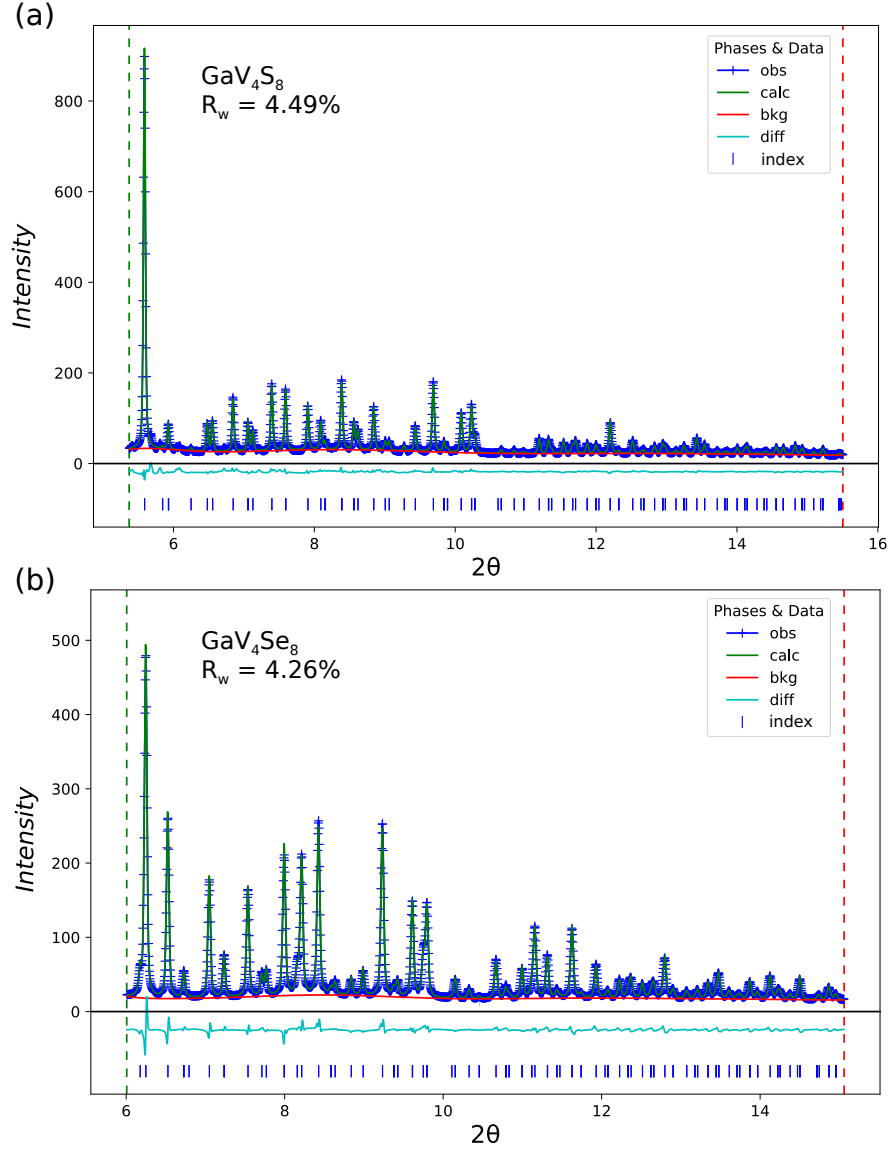
High-purity (>99.99%) starting materials from Alfa Aesar were used for all synthesis. The crystalline GaV_4S_8 , GaV_4Se_8 , GaNb_4S_8 , and GaNb_4Se_8 samples are prepared by loading stoichiometric raw materials into a $\varnothing$ 10 mm, 100 mm long fused silica tube in an argon-filled glovebox, evacuated, and flame sealed. The ampules were placed in a box furnace, and the temperature profiles and corresponding parameters for each sample are shown in Fig. 4.1 (a) and Table 4.1. Three heating and regrinding repetitions were required to obtain the single-phase powder.

Single crystal samples of GaTa_4Se_8 were synthesized by solid-state reaction. About 1.5 g of stoichiometric raw materials were loaded into a $\varnothing$ 10 mm, 170 mm long fused silica tube in an argon-filled glovebox, evacuated, and flame sealed. The temperature profile for GaTa_4Se_8 is slightly different from other lacunar spinels in this thesis, which requires a slower cooling rate (1°C/hr) to obtain single crystals [Fig. 4.1 (a) and Table 4.1]. On the other hand, single crystal samples of GaNb_4S_8 and GaNb_4Se_8 are synthesized by chemical vapor transport with iodine as the transport agent. The total 1.5 g of single-phase crystalline material was sealed in a $\varnothing$ 10 mm, 220 mm long fused silica tube in an argon-filled glovebox with 75 mg iodine, evacuated, and sealed. The ampule was placed in a two-zone furnace with 50°C temperature gradient. The temperature profile and related parameters are shown in Fig. 4.1 (b) and Table 4.2.

4.3 Results

For powder samples, the refinement results for GaV_4S_8 and GaV_4Se_8 at room temperature are shown in Fig. 4.2. The powder diffraction data have an excellent refinement to the cubic phase, with the $R_w = 4.49\%$ and 4.26% for GaV_4S_8 and GaV_4Se_8 , respectively. The refinements indicate the resulting powder samples are in single-phase.

The resulting single crystal samples of GaTa_4Se_8 are shown in Fig. 4.3. Surprisingly, solid-state reaction works much better than chemical vapor transport for synthesizing

Figure 4.2: Powder XRD for GaV_4S_8 and GaV_4Se_8 .

GaTa_4Se_8 single crystals. As a result, we could obtain more than 2 g single crystals with sizes larger than $250 \mu\text{m}$ in a single batch [Fig. 4.3]. The larger single crystals are used for neutron scattering, and smaller samples are used in x-ray experiments. The details of synchrotron crystallography results are listed in Table 4.3.

The reconstruction of reciprocal space from synchrotron x-ray crystallography measurements of GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 indicate the high quality of single crystal samples,

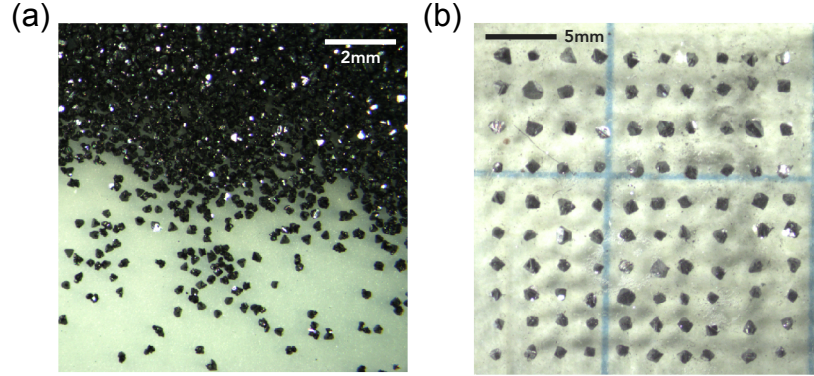


Figure 4.3: GaTa_4Se_8 single crystals from a single batch.

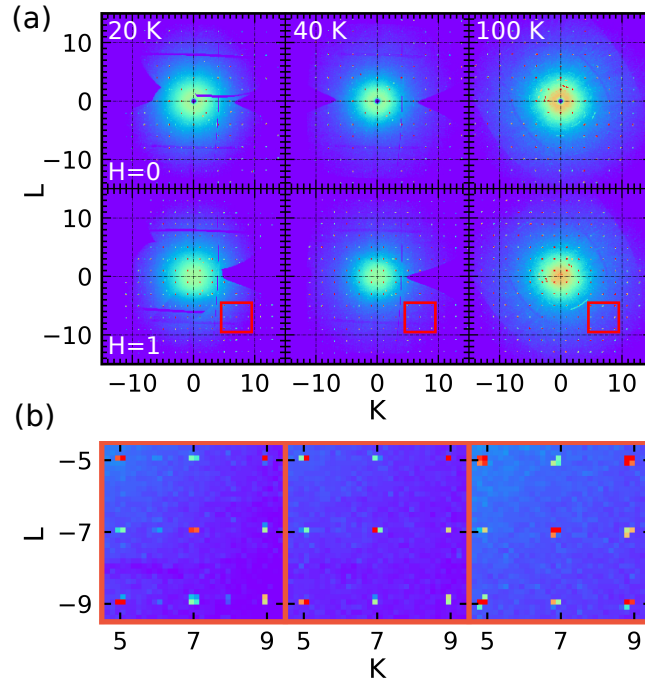


Figure 4.4: Reconstruction of the reciprocal space for GaNb_4S_8 single crystal.

and all crystallography refinements obtain $R_w \leq 1\%$ [Fig. 4.4, 4.5, 4.6]. The details of synchrotron crystallography results are listed in Table 4.3.

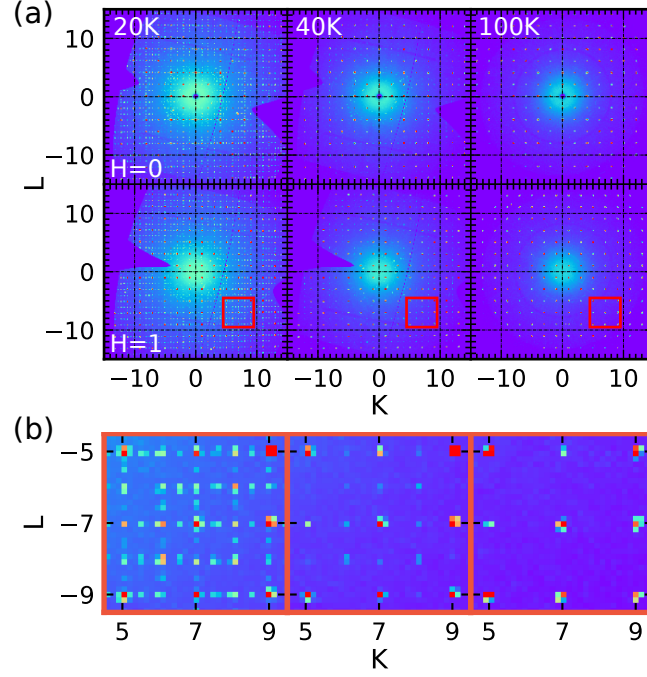


Figure 4.5: Reconstruction of the reciprocal space for GaNb₄Se₈ single crystal.

4.4 Conclusion

In conclusion, high-quality powder and single-crystal samples of lacunar spinels are prepared using solid-state reaction and chemical vapor transport. Especially in GaTa₄Se₈, we could obtain a massive amount of single crystals in a relatively short time compared to the chemical vapor transport for synthesizing single crystals. This allows us to prepare a sample for neutron scattering experiments which usually require a large amount of materials.

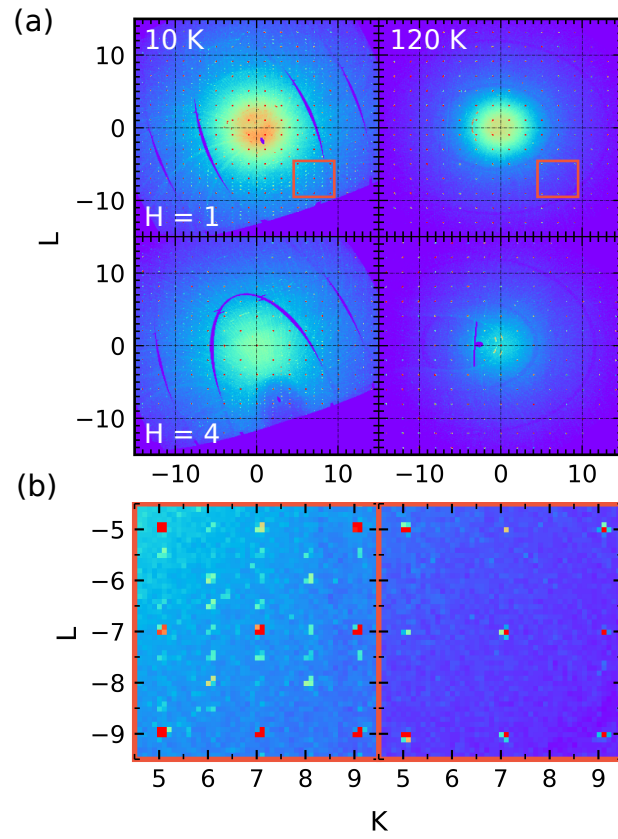


Figure 4.6: Reconstruction of the reciprocal space for GaTa₄Se₈ single crystal.

Table 4.3: Crystallographic refinement results for GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 .

Sample	GaNb_4S_8	GaNb_4Se_8	GaTa_4Se_8
Temperature (K)	100	100	250
Crystal system	cubic	cubic	cubic
Space group	$F\bar{4}3m$	$F\bar{4}3m$	$F\bar{4}3m$
a ($\text{\AA}$)	9.9806(3)	10.40910(10)	10.2640(3)
Diffractometer	15-ID-D, APS	15-ID-D, APS	15-ID-D, APS
Abs. correction	Multiscan	Multiscan	Multiscan
Reflections collected	12063	13368	7066
Indep. reflections	401 ($R_{int}=5.09\%$)	464 ($R_{int}=3.40\%$)	472 ($R_{int}=3.56\%$)
F(000)	1292.0	1868.0	2380.0
λ ($\text{\AA}$, synchrotron)	0.41328	0.41328	0.41328
2θ range(deg)	4.11 to 47.57	3.94 to 47.77	6.876 to 90.26
Index ranges	$-19 \leq h \leq 17$ $-17 \leq k \leq 19$ $-17 \leq l \leq 19$	$-17 \leq h \leq 15$ $-19 \leq k \leq 17$ $-17 \leq l \leq 19$	$-19 \leq h \leq 17$ $-15 \leq k \leq 19$ $-16 \leq l \leq 16$
Data, restr., param.	401/0/13	464/0/12	472/0/13
Goodness of fit	1.154	1.190	1.036
R_1 , $wR_2(I \geq 2\sigma)$	0.0126, 0.0217	0.0088, 0.0200	0.0088, 0.0150
R_1 , $wR_2(\text{all})$	0.0133, 0.0217	0.0088, 0.0200	0.0092, 0.0151
Max diff. peak/hole	0.58/-0.74	0.98/-0.96	0.61/-0.59

Chapter 5

Bond Ordering and Molecular Spin-Orbital Fluctuations in the Cluster Mott Insulator GaTa_4Se_8

This chapter contains our observations of bond ordering and spin-orbital fluctuations in GaTa_4Se_8 . The chapter is organized as follows. First, the crystallography at cubic and tetragonal phases of GaTa_4Se_8 single crystal are reported. Second, I present our x-ray and neutron total scattering measurements which uncover the temperature-dependent local structure distortions. Third, the inelastic neutron scattering measurements of phonon density of states and the density functional theory calculations of frozen phonon mode are presented. The supplemental information of data analysis is included in the final section. The work presented in this chapter has been published on T.-H. Yang, S. Kawamoto, T. Higo, S. G. Wang, M. B. Stone, J. Neufeind, J. P. C. Ruff, A. M. M. Abeykoon, Y.-S. Chen, S. Nakatsuji, and K. W. Plumb, Phys. Rev. Research 4, 033123 (2022).

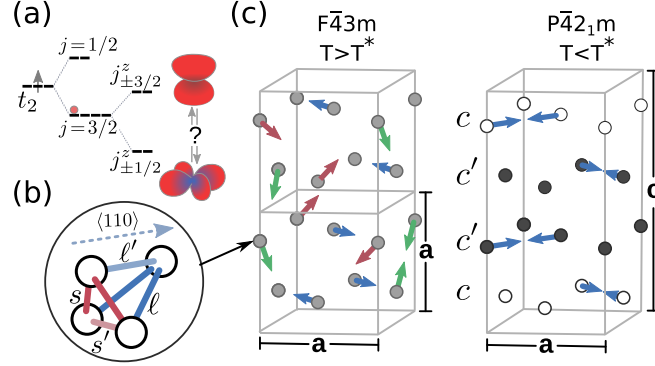


Figure 5.1: Unit cell doubling and intercluster dimers in GaTa_4Se_8 . (a) Spin-orbit coupling driven $j = 3/2$ states on Ta_4 cluster molecular orbitals. j^z spin-orbital states are Jahn-Teller degenerate. (b) Monoclinically distorted Ta_4 clusters with four inequivalent Ta-Ta distances $\ell > \ell' > s' > s$ point along local $\langle 110 \rangle$ axis. (c) Local distortions of Ta_4 clusters on FCC lattice fluctuate among $\langle 110 \rangle$ directions for $T > T^*$, shown as colored arrows. Intercluster interactions select a global rotational symmetry breaking below T^* . Unit cell doubling occurs through a formation of two inequivalent Ta_4 stacked in a $c - c' - c' - c$ pattern.

5.1 Introduction

For materials where spin-orbit coupling is competitive with electronic correlations, the spatially anisotropic spin-orbital wavefunctions can stabilize degenerate states that lead to many and diverse quantum phases of matter. Here, we find evidence for a dynamical spin-orbital state preceding a $T^* = 50$ K order-disorder spin-orbital ordering transition in the $j = 3/2$ lacunar spinel GaTa_4Se_8 . Above T^* , GaTa_4Se_8 has an average cubic crystal structure, but total scattering measurements indicate local non-cubic distortions of Ta_4 tetrahedral clusters for all measured temperatures $2 < T < 300$ K. Inelastic neutron scattering measurements reveal the dynamic nature of these local distortions through symmetry forbidden optical phonon modes that modulate $j = 3/2$ molecular orbital occupation as well as intercluster Ta-Se bonds. Spin-orbital ordering at T^* cannot be attributed to a classic Jahn-Teller mechanism and based on our findings, we propose that intercluster interactions acting on the scale of T^* act to break global symmetry. The resulting staggered intercluster dimerization pattern doubles the unit cell, reflecting a spin-orbital valence bond ground state.

5.2 Methods

Sample Synthesis

Single crystal samples of GaTa_4Se_8 were synthesized by solid-state reaction. About 1.5 g of stoichiometric quantities of Ga, Ta, and Se were loaded into a I.D. = 10 mm, 170 mm long quartz ampules under an argon glovebox, evacuated, and sealed. The ampules were heated to 1050 °C with 80 °C/hour ramping rate and stayed at 1050 °C for 24 hours. Then cooled to 850 °C with 1 °C/hour cooling rate before air quenching. We were able to obtain thousands of high-quality single crystals with a dimension above 200 microns in a single batch. The quality of single crystals was confirmed by x-ray diffraction ($\text{Ag K}\alpha$ radiation). The composition was confirmed by powder x-ray diffraction with ground crystals (Bruker $\text{Cu K}\alpha$ radiation).

Synchrotron x-ray crystallography

Temperature-dependent synchrotron x-ray diffraction measurements were carried out on the QM2 beamline at Cornell High Energy Synchrotron source using an x-ray energy of 20.67 keV (0.5998 Å), and the Pilatus 300K area detector positioned 56.2 cm from the sample. The single crystal sample was mounted on a Cu post on the coldfinger of a closed cycle cryostat for measurements in reflection geometry between 3 and 300 K.

Synchrotron x-ray crystallography measurements were carried out on 15-ID at Advanced Photon Source, Argonne National Laboratory using an x-ray energy of 30.00 keV (0.4133 Å) and Pilatus CdTe detector positioned at 7 cm from the sample. The 20 μm single crystal was mounted on a quartz capillary, and measurements were carried out between 10 K and 300 K using a He cryostream. Diffraction peaks were indexed, the unit cell, and UB matrix of each tetragonal domain were determined in reciprocal lattice and CELLNOW software for six domains. All frames were integrated using Bruker SAINT software, and multidomain absorption corrections were performed through TWINABS. The crystal structure was solved by direct methods and least-square method refinements on F^2 were carried out

using SHELXTL [55] and Olex2 [56] packages. The converged solution using full single domain reflection data and all Ga, Ta and Se atoms were modeled by isotropic atomic displacement parameters (ADPs). We checked $1 \times 1 \times 2$, $2 \times 2 \times 1$ and $2 \times 2 \times 2$ superlattices in -4 and $-42m$ tetragonal lattice classes. Based on the extinction rules of x-ray reflection, we find the $P\bar{4}2_1m$ space group with $1 \times 1 \times 2$ superlattice is the most consistent with our data. Details of the crystallographic analysis are provided in Section 5.8.

Pair distribution function measurements

Synchrotron total scattering measurements (xPDF) were conducted on 28-ID-1 (PDF) beamline at the National Synchrotron Light Source-II at Brookhaven National Laboratory. The sample was loaded in a 1 mm I.D. kapton capillary, mounted in a He cryostat, and data was collected between 5 K and 330 K on warming in 5 K steps. Measurements were carried out using an x-ray energy of 74.46 keV (0.1665 Å). We used an amorphous silicon PerkinElmer area detector with a sample to detector distance of 1008 mm for diffraction and 204 mm for PDF. Detector position was determined by calibration using a Ni standard. The two dimensional diffraction data were integrated using PyFAI [32] and then corrected, normalized, and Fourier transformed to obtain the atomic pair distribution function (PDF), $G(r)$, using PDFgetX3 [33] and a $Q_{max} = 27 \text{ Å}^{-1}$.

Neutron total scattering measurements (nPDF) were carried out on the NOMAD beamline at Spallation Neutron Source at Oak Ridge National Laboratory. A 4.2 g sample was loaded into a vandadium sample can and mounted on the coldfinger of a He cryostat. Data was collected for 160 minutes at 5 K, 55 K and 300 K, and 80 minutes for intermediate temperatures. The structure factor $S(Q)$ was checked to determine the Q_{max} for each temperature. Background subtracted time-of-flight data were reduced and transformed to PDF using a $Q_{max} = 34.5 \text{ Å}^{-1}$ and ADDIE available at NOMAD [34]. xPDF and nPDF refinements were carried out using PDFgui and DIFFPY-CMI modeling platforms [57].

Inelastic neutron scattering

Inelastic neutron scattering measurements were carried out on the SEQUIOA spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. A 5 g polycrystalline sample was loaded into an Al sample can and mounted on the coldfinger of a closed cycle cryostat to achieve a base temperature of 5 K. Measurements were conducted using a fixed incident energy $E_i = 60$ meV and the coarse Fermi chopper rotating at 300 Hz, providing an energy resolution at the elastic line of 3.1 meV. All data was normalized and reduced using algorithms in the MANTID analysis software [58]. The normalized neutron intensities were converted into neutron weighted phonon density of states by integrating over Q (0.2 to 5 $\text{\AA}^{-1}$) and corrected for multiphonon and multiscattering processes within the incoherent approximation [59].

5.3 X-ray crystallography and unit cell doubling

GaTa_4Se_8 has a single magnetic and structural transition at $T^*=50$ K where the magnetic susceptibility abruptly drops and the unit cell doubles, as indicated by the sudden appearance of structural superlattice Bragg reflections at $[1/2, 0, 0]$ positions [Fig. 5.2 (a)]. As shown in Fig. 5.2 (b), a bifurcation of cubic $[h, 0, 0]$ reflections and abrupt volume decrease at T^* indicate a first-order cubic to tetragonal transition, but with no detectable hysteresis or phase coexistence. Above T^* , single crystal XRD consistently refines to the cubic space group $F\bar{4}3m$. Below T^* , the $[1/2, 0, 0]$ reflections indicate a unit cell doubling along a unique cubic axis and we observed all $[1/2, 0, 0]$ reflections consistent with six domains of the tetragonal cell. We did not find any additional peak splitting or evidence for an orthorhombic distortion. We have evaluated our $T=10$ K single crystal XRD data against all subgroups of the cubic cell that are consistent with a $k = [1/2, 0, 0]$ distortion; body centered space groups are ruled out by the observation of reflections with $h+k+l \neq 2n$ and based on the absence of any $[2n+1, 0, 0]$ reflections we ruled out all possible primitive groups except for $P\bar{4}2_1m$, more details are described in Section 5.8.

We obtain high fidelity refinements for $P\bar{4}2_1m$ with $a = b = 10.3437$ and $c = 20.6878$ ($R_1 = 0.0879$ for 13104 reflections). Within the tetragonal cell there are two distinct Ta_4 clusters labeled c and c' in Fig. 5.1 (c), each having the same symmetry, but different Ta-Ta bond lengths. The symmetry of tetrahedral clusters is reduced to monoclinic and retains a single mirror plane. Each cluster contains four different bond lengths shown in Fig. 5.1 (b) and listed in table 5.3, with three long-bonds, labeled ℓ and ℓ' ($\ell > \ell'$), and three short-bonds labeled s and s' ($s < s'$) resulting in a characteristic elongation of tetrahedra along cubic *face diagonals*. Each Ta_4 cluster points along $\langle 110 \rangle$ towards a single neighboring cluster, forming an intercluster dimer motif as illustrated [Fig.5.1 (b) and (c)]. The cubic unit cell doubling occurs through a $c-c'-c'-c$ stacking arrangement of Ta clusters along the c-axis, giving rise to $[1/2, 0, 0]$ reflections from six domains of the tetragonal cell.

The structural transition in GaTa_4Se_8 is distinct from reports in other lacunar spinels. For $\text{Ga}(\text{V},\text{Nb})_4(\text{S},\text{Se})_8$, the Jahn-Teller active M_4 clusters undergo a rhombahedral distortion, displacing along the cubic *body diagonals*, in a ferrodistorptive pattern for vanadium based compounds [17, 21, 23, 43, 60] and antiferrodistorptive pattern for the niobium compounds [15, 25]. A primary mode analysis GaNb_4S_8 found a single Jahn-Teller active mode within irreducible representation X_5 and dominated by displacements of the Nb_4 tetrahedra [15]. In contrast, we find that the distortion in GaTa_4Se_8 is described by a superposition of modes within many irreducible representations. The most dominant distortions belong to X_5 (subgroup $P\bar{4}2_1m$, amplitude= 0.12 Å) and X_3 (subgroup $P\bar{4}m2$, amplitude= 0.07 Å) representations, both modes involving nearly equivalent displacements of Ta and Se atoms [61–63]. Unit cell doubling is affected through a combination of W_4 and Δ_1 modes with amplitudes of 0.02 Å and nearly equivalent Ta/Se displacements [63]. Thus, we cannot attribute the transition in GaTa_4Se_8 to a classic Jahn-Teller mechanism acting through a single normal mode of the cell. The intercluster dimer motif, unit cell doubling, mode mixing, and equivalent contributions from displacements of metal and ligand ions implicates the complex spin-orbital wavefunction and a mechanism likely

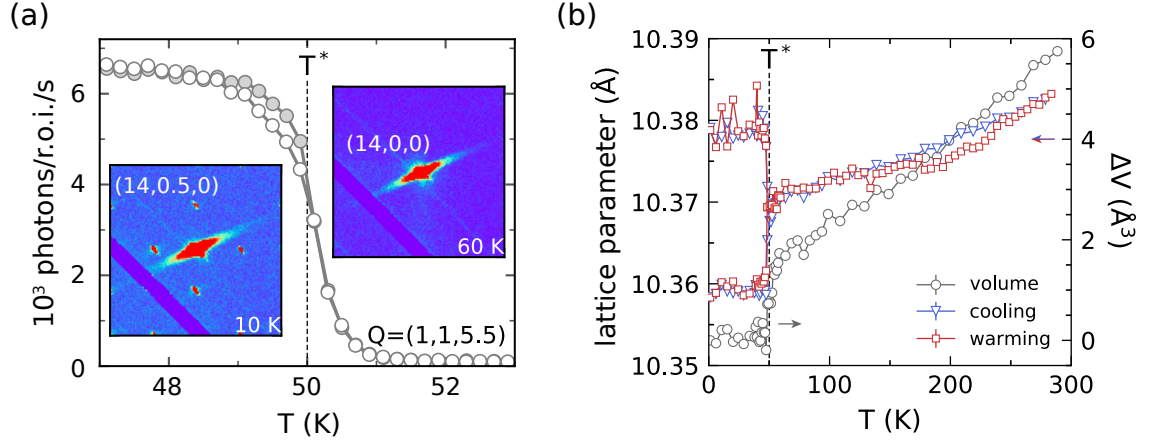


Figure 5.2: (a) X-ray diffraction reveals a first-order onset of superlattice $[1/2, 0, 0]$ at T^* . (b) Temperature dependence of lattice parameter and cell volume extracted from the $[12, 0, 0]$ reflection. There is a sharp decrease in volume at T^* but no measurable hysteresis.

involving intersite interactions, are at play in GaTa_4Se_8 .

5.4 Local distortions and dynamic orbital degeneracy breaking

Having established the low temperature space group in GaTa_4Se_8 , we now turn to atomic pair distribution analysis (PDF) to provide detailed insight into the evolution of atomic correlations across different length-scales through T^* . Temperature dependent x-ray (xPDF) and neutron (nPDF) PDF measurements shown in Fig. 5.3 provide a histogram of atomic pair correlations from which atomic pair separations can be read off independent of a specific structural model. The PDF data for GaTa_4Se_8 have two striking features. First, the double-peak structure around 3 Å indicates at least two intercluster Ta-Ta distances between 2.9 and 3.1 Å for temperatures up to 300 K. Thus, the local crystal structure of GaTa_4Se_8 is not cubic well into the temperature regime where the average structure is cubic. Second, nPDF and xPDF data do not show any discernible qualitative changes across all measured temperatures beyond thermal broadening. The absence of any change in the local structure is highlighted in Fig. 5.4 (a) that shows a negligible difference in

nPDF across T^* and in Fig. 5.4 (b) that shows the normalized PDF peak intensities for inter and intra-cluster pair separations

$$x(r', T) = \frac{G(r', T) - G(r', 300)}{G(r', 5) - G(r', 300)}, \quad (5.1)$$

where $G(r, T)$ is the PDF intensity at distance r . x acts as an effective local order parameter for displacive transitions [64]. The smooth evolution of x with temperature for all pair separations is consistent with thermal disorder (Debye-Waller) and directly implicates an order-disorder transition at T^* . Local distortions in GaTa_4Se_8 are present but uncorrelated across length scales beyond one unit cell at least up to 300 K. At T^* , global cubic symmetry is broken as the distorted units select a unique $\langle 110 \rangle$ axis and stack in a $c - c' - c' - c$, forming the cell doubled tetragonal structure of Fig. 5.1 (b).

In Fig. 5.5 and 5.6, we show a model dependent analysis of the PDF data, covering broad length and temperature scales. A cubic model fails to account for the observed local structure ($r < 5 \text{ \AA}$) for all measured temperatures $T < 300 \text{ K}$. In particular, the cubic structure cannot capture the two Ta-Ta distances around $3 \text{ \AA}$ and overestimates the PDF weight for Se-Se pairs at $3.5 \text{ \AA}$. This local structure is reproduced at all measured temperatures by the tetragonal $P\bar{4}2_1m$ lattice that includes four intercluster Ta-Ta bond lengths $\ell > \ell' > s' > s$. Within the accuracy of our measurements, the degree of local distortion in GaTa_4Se_8 as measured by the bond length difference $\ell - s$ does not depend on temperature, indicating local distortions of Ta clusters are fully set in up to at least $T=300 \text{ K}$. On the other hand, the PDF data for $r > 5 \text{ \AA}$ are equally well described by the cubic and tetragonal models at all temperatures because the tetragonal cell is metrically cubic ($c/2 \sim a$). We find that within experimentally achievable resolution, the average structures of cubic and tetragonal cells are only distinguished in a PDF measurement through a small anomalous upturn in thermal parameters upon cooling through T^* . Details are described in Section 5.8.

Ta_4 tetrahedral clusters in GaTa_4Se_8 are distorted at all measured temperatures, indicating that local, and potentially dynamic, Jahn-Teller distortions are already present

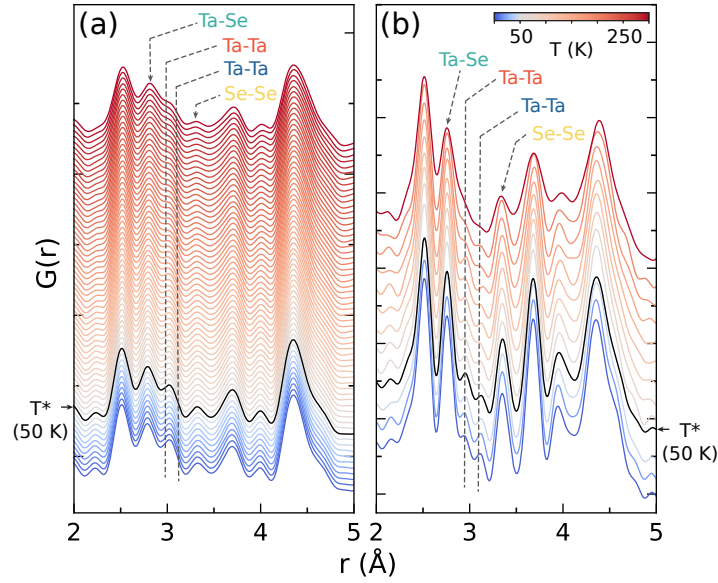


Figure 5.3: Temperature dependence of atomic pair separation in GaTa₄Se₈. (a) Temperature dependent xPDF and (b) nPDF measurements show local distortions of Ta₄ clusters exist well above the transition through two distinct intercluster Ta-Ta distances, $s = 2.95$ Å and $\ell = 3.06$ Å observed at all measured temperatures. Real space resolutions of PDF data are $\delta r = 0.233$ Å for xPDF and $\delta r = 0.182$ Å for nPDF.

at 300 K. Local distortions preceding an orbital ordering structural transition are common in transition metal compounds, but global symmetry breaking is generally also apparent in total scattering measurements through the appearance of a new length-scale or an abrupt change in bond lengths as atoms displace through the transition [64–71]. The structural transition in GaTa₄Se₈ is unique in this respect. An absence of any detectable redistribution in PDF intensity though T^* demonstrates that no length-scale, or further local symmetry breaking, is introduced at the structural transition on the scale of our measurements. Instead, a global six-fold discrete rotational symmetry breaking occurs at T^* , where already distorted Ta₄ clusters select a particular $\langle 110 \rangle$ axis [Fig. 5.1 (b)]. Superlattice reflections in a diffraction measurement are a consequence of this global rotational symmetry breaking.

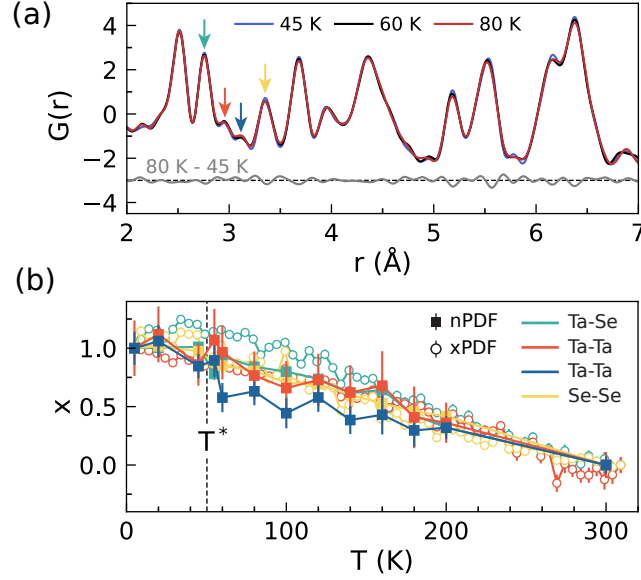


Figure 5.4: (a) Detailed comparison of small r nPDF above and below T^* . 45 - 80 K difference data show no measurable change in atomic pair displacements through the transition. (b) Temperature dependence of normalized inter-Ta₄ cluster PDF peak intensities x showing the continuous and smooth evolution of atomic distances with temperature. Filled symbols are from nPDF and open from xPDF.

5.5 Phonon density of states and dynamic distortions

The energy integrated diffraction measurements presented above find an average cubic structure for GaTa₄Se₈ at $T > T^*$, implying that local distortions are incoherently fluctuating in space, time, or both. In Fig. 5.7 we show the measured phonon density of states (PDOS) as a function of temperature that provide direct evidence for the dynamic nature of local distortions above T^* through the appearance of a symmetry forbidden optical phonon mode (13 meV) well into the cubic phase.

Measured PDOS at select temperatures are shown in Fig. 5.7 (a). The most striking feature of this data is a temperature dependent 13 meV phonon intensity appearing above background below $T=200$ K. This mode is visible in the raw neutron scattering data as a non-dispersive feature with an intensity that increases quadratically with momentum transfer, ruling out a magnetic origin (see Appendix 5.8). In Fig. 5.7 (c) we show the temperature dependent integrated intensity of the 13 meV mode, corrected for the Bose

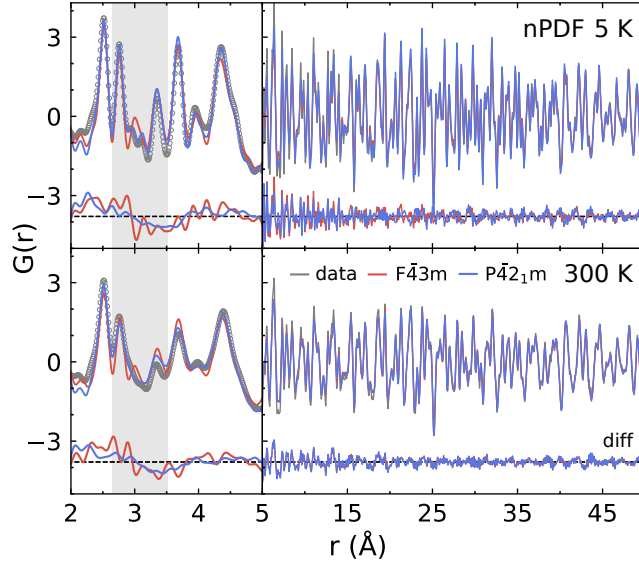


Figure 5.5: Local and average structures of GaTa_4Se_8 . Model fits to neutron pair distribution function measurements at $T = 5$ K and $T = 300$ K for (a) nPDF and (b) xPDF. At all temperatures the tetragonal cell ($P\bar{4}2_1m$) with distorted tetrahedra provides a significantly improved description of the local structure for $r < 5\text{\AA}$, while the average structure is equally well described using the cubic or tetragonal cell.

factor, and normalized to its intensity at $T=10$ K. Above 200 K it was not possible to reliably resolve the 13 meV intensity from the adjacent modes at 10 and 15 meV. We find that the integrated intensity increases linearly with decreasing temperature from 200 K and saturates at T^* while the energy position and width are constant and set by the energy resolution of the spectrometer (see section 5.8).

We have carried out first principles calculations of the neutron weighted PDOS for GaTa_4Se_8 in order to obtain insight into the origin of the 13 meV intensity. The results of these calculations for both $F\bar{4}3m$ and $P\bar{4}2_1m$ space groups are shown in Fig. 5.7 (b) and are in excellent agreement with the measured spectra. There is a notable absence of phonon modes around 13 meV for the cubic cell; but, significant 13 meV PDOS weight arising from optical phonons in the tetragonal cell. Indeed, the 13 meV phonon intensity is the primary qualitative distinction between the cubic and tetragonal PDOS. The appearance of this optical phonon intensity for $T > T^*$, where the average structure is cubic, directly

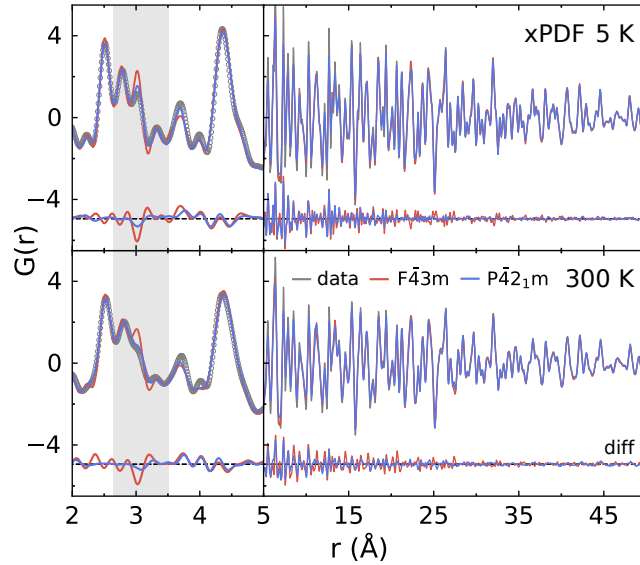


Figure 5.6: Local and average structures of GaTa_4Se_8 . Model fits to neutron pair distribution function measurements at $T = 5 \text{ K}$ and $T = 300 \text{ K}$ for (a) nPDF and (b) xPDF. At all temperatures the tetragonal cell ($P4_21m$) with distorted tetrahedra provides a significantly improved description of the local structure for $r < 5 \text{ \AA}$, while the average structure is equally well described using the cubic or tetragonal cell.

reflects the dynamic structural fluctuations associated with the local symmetry breaking for $T > T^*$ in GaTa_4Se_8 as schematically illustrated in Fig. 5.1 (b). We have evaluated the partial contributions of Ga, Ta, and Se to the PDOS of the tetragonal cell and find the dominant contribution is from Se with additional secondary contributions from Ta and Ga [Fig. 5.7 (b)]. Optical A_1 , A_2 , B_1 , B_2 , and E phonon modes all contribute the PDOS between 12 to 14 meV and our data are not consistent with the assignment of a unique Jahn-Teller phonon mode on Ta_4 clusters to this feature of the PDOS.

It is instructive to compare the temperature dependent phonon spectra in GaTa_4Se_8 measured by INS with that measured by infrared spectroscopy (IR). The PDOS as measured by INS contains the full spectrum of predicted vibrational modes, while IR measurements only find a subset of the symmetry allowed modes all attributed to vibrations on the ligand sites [72]. Such a discrepancy must arise as a result of a substantial screening of vibrational modes from electron delocalization over Ta_4 tetrahedral units in insulating

GaTa₄Se₈. Neutrons interact directly with nuclear cores and are not subject to electronic screening. Such an electronic delocalization is most apparent in GaTa₄Se₈ because of the spatially extended nature of Ta d orbitals. The apparently metallic Ta₄ clusters are at odds with local Jahn-Teller mechanisms generally accepted as the origin of structural transitions in Lacunar spinels and evidence that a picture from mean field arguments for M₄ molecular clusters should be revisited, especially in the case of Ta and Nb compounds [73–75]. For GaTa₄Se₈, a minimal description should involve active and hybridized Ta and Se molecular orbitals on cubane clusters, spin-orbit coupling on the molecular orbitals, as well as interactions between clusters. The mixed character of dynamic distortions and decomposition of the structural transition into a superposition of irreducible representations implicate a degeneracy among possible Jahn-Teller distortions in GaTa₄Se₈. This is likely a consequence of spin-orbit coupling, covalency, and configurational mixing on the Ta₄ clusters [74, 76]. Ultimately, additional interactions between clusters acting on the scale of T* select a unique valence bond state and quench the structural fluctuations.

5.6 Discussion

We find that local and dynamic distortions are present up to at least 300 K in GaTa₄Se₈. These reduce tetrahedral symmetry of the Ta₄ clusters and dynamically break orbital degeneracy. Heat capacity measurements have found an entropy change associated with T* approaching ln(4) [26, 27] indicating that the orbital and spin degrees of freedom simultaneously freeze out at T*. In other words, T* corresponds to a collective, order-disorder, spin-orbital ordering between two insulating phases. A discrete six-fold rotational symmetry on the FCC lattice is broken through T* and we propose this order is selected through intercluster spin-orbital interactions that act on the scale of T*.

Interestingly, diffraction measurements indirectly implicate dynamic structural fluctuations above global structural transitions in other lacunar spinels [15, 19, 43]. However, the nature of structural and magnetic transitions, local distortions of transition metal clusters,

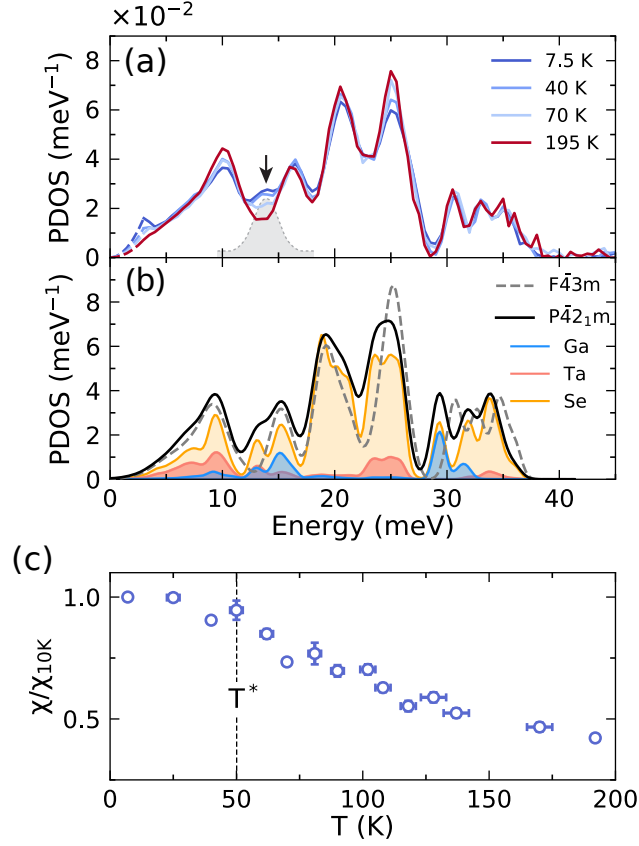


Figure 5.7: Dynamic symmetry breaking in GaTa_4Se_8 . (a) Measured neutron weighted phonon density of states in GaTa_4Se_8 . A representative Lorentzian fit to the cubic symmetry forbidden optical phonon intensity at 13.8 meV is shown as the grey shaded area. (b) DFT calculated neutron weighted phonon DOS for the cubic ($F\bar{4}3m$) and tetragonal ($P\bar{4}2_1m$) cells. Partial contributions to the tetragonal cell DOS are also shown. (c) Temperature dependence of the 13.8 meV intensity extracted from Lorentzian fits to the dynamic susceptibility.

low temperature crystal structure, and magnetic state are unique in GaTa_4Se_8 among the family of d^1 Lacunar spinels. $\text{GaV}_4(\text{S,Se})_8$ and GaNb_4Se_8 exhibit a typical separation of spin and orbital energy scales with rhombahedral structural distortions that quench orbital moments occurring at high temperatures preceding lower temperature spin only magnetic transitions [21, 26, 43, 54, 77, 78]. GaNb_4S_8 exhibits a unit cell doubling spin-orbital transition that is similar to GaTa_4Se_8 , but the symmetry of the low temperature structure is further reduced from $P\bar{4}2_1m$ to $P2_12_12_1$ with Nb_4 clusters distorting along

cubic body diagonal directions in an antiferro pattern [15, 25, 79]. The material trend implicates both spatially extended electron density and spin orbit coupling as these both increase from V→Nb→Ta and can respectively act to drastically alter Jahn-Teller physics [11, 14]. In particular, for $j = 3/2$ degrees of freedom, spin orbit coupling can lead to a degeneracy among different types of possible Jahn-Teller distortions [14]. The symmetry forbidden phonon intensity we observe above T^* in GaTa_4Se_8 is consistent with such a degeneracy that is ultimately broken by additional interactions.

Above T^* , GaTa_4Se_8 is a correlated Mott insulator [80, 81], containing an odd number of electrons in the cubic cell. While the Tetragonal unit cell below T^* contains four formula units and an even number of valence electrons, our band structure calculations find a metallic state for this structure, supporting the Mott insulating picture. The absence of magnetic ordering must then indicate a valence bond solid type ground state. The structural dimerization suggests a staggered valence bond covering shown in Fig. 5.1 (b). Such a sharp reduction in magnetic susceptibility and dimerized superstructure below T^* is remarkably similar to the orbitally induced Peierls metal-insulator transitions observed in spinels [66, 82, 83] and other orbitally degenerate compounds exhibiting temperature dependent metal insulator transitions [84, 85]. However, in GaTa_4Se_8 the transition is between two insulating states.

Resonant inelastic x-ray scattering found that at the level of DFT the molecular orbital state in GaTa_4Se_8 is molecular analog of the atomic $j = 3/2$ [20]. Although, covalency, configurational interactions between molecular orbitals, and local distortions alter the pure $j = 3/2$ description [74–76], it may still stand as an approximate description of the magnetism. In this case GaTa_4Se_8 may realize a spin-orbital dimer ground state proposed for Mott insulators on an FCC lattice with d^1 filling and large spin-orbit coupling [86]. Our measurement show how the lattice degrees of freedom can act to select an ordered valence bond solid from the glassy spin-orbit dimer covering proposed in [86].

Our measurements implicate an essential role played by cluster orientational ordering to affect a Peierls like intercluster dimerization at T^* . This ordering is likely driven by

intercluster spin-orbit interactions that break the degeneracy of orbital configurations. The importance of such interactions is further underscored by the primary involvement of both Ta and Se ions across intercluster bonds through the structural transition. Despite the large intercluster separation, closest Ta-Ta distance 4.274 Å closest Ta-Se distance 2.744 Å, there is strong evidence that intercluster exchange is a relevant energy scale in lacunar spinels. For example, recent inelastic neutron scattering measurements of spin waves in magnetically ordered GaV_4S_8 suggest exchange interactions between the clusters on the order of 20 K [87]. A more spatially extended electron density on Ta 5d orbitals should give rise to enhanced interactions compared with the V compounds so that exchange interactions on the scale of $T^* = 50$ K are not unreasonable. In GaTa_4Se_8 the broken symmetry at T^* involves both spin and orbital degrees of freedom and such spin-orbital exchange may be mediated through lattice vibrations [88, 89]. The 13 meV mode we observe distorts Ta_4 clusters, simultaneously modulating orbital occupancy, intercluster distances, and Ta-Se bond angles to influence intercluster interactions. In this respect, the optical phonon response we observe in GaTa_4Se_8 is reminiscent of spin Peierls compound CuGeO_3 [90, 91], but in the case of GaTa_4Se_8 , lattice vibrations affect a complex spin-orbital exchange. Further theoretical effort investigating the role of optical phonons in generating effective spin-orbital interactions in cluster Mott insulators is required [92, 93]. Our results provide empirical insight on the microscopic mechanisms that may generate such orbital interactions.

5.7 Conclusion

In summary, we have used a combination of single crystal diffraction, total scattering, and inelastic neutron scattering measurements to show that Ta_4 tetrahedral clusters in GaTa_4Se_8 are locally and dynamically distorted up to temperatures of at least 300 K. We resolve the optical phonon modes associated with lattice fluctuations between degenerate orbital configurations on the FCC lattice. We propose that the degeneracy of these

configurations is broken through inter-cluster spin-orbit exchange interactions. A collective order-disorder spin-orbital transition in GaTa_4Se_8 is characterized by the long range orientational ordering of distorted Ta_4 clusters to form weak structural dimers aligned along $\langle 110 \rangle$ directions. This suggests that a spin-orbital valence bond solid ground state may be realized in GaTa_4Se_8 .

5.8 Supplementary information for data analysis

Crystal Structure Solution

We performed temperature dependent x-ray diffraction measurements on a four-circle geometry diffractometer in our laboratory at Brown University. We used a microfocused $\text{Ag K}\alpha$ x-ray source and collected the data using a GaAs photon counting area detector (256×256 pixels) with $55 \times 55 \mu\text{m}^2$ pixel size. The temperature-dependence of a $[12, 0, 0]$ longitudinal scan and representative fits are shown in Fig. 5.8 and Fig. 5.9, respectively. Our lab based Ag x-ray source contains contributions from two wavelengths, $\text{Ag K}\alpha_1$ ($0.5594 \text{ \AA}$) and $\text{K}\alpha_2$ ($0.5638 \text{ \AA}$), these cannot be separated by our focusing optics, but the Bragg reflections from each wavelength are spatially resolved on our area detector so that the contribution from each wavelength can be fit simultaneously. Scans at select

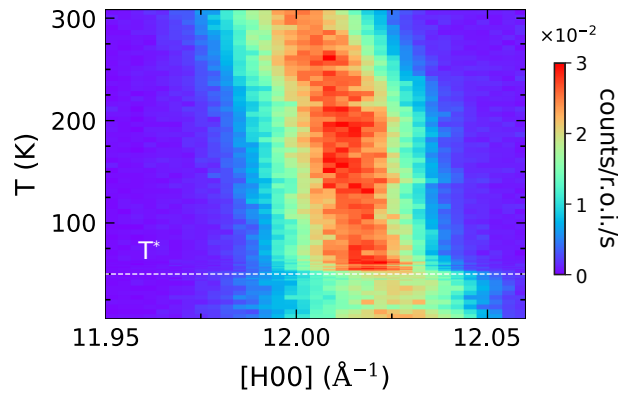


Figure 5.8: Temperature-dependent longitudinal cut through $[12, 0, 0]$ reflection. The peak shows a sudden broadening across T^* , indicating a cubic to tetragonal structural transition.

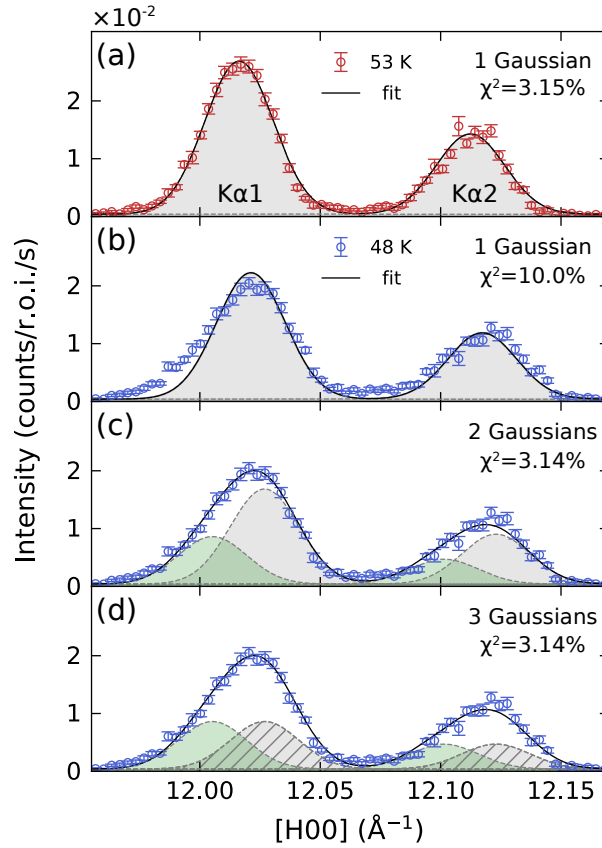


Figure 5.9: Gaussian fits above, and below T^* on $[12, 0, 0]$ reflection. (a) $T = 53$ K, the widths of $K\alpha 1$ and $K\alpha 2$ reflections are constrained. In (b), (c), and (d), $T = 48$ K, the widths of Gaussians were fixed to the fitted width at $T = 53$ K. (b) Single Gaussian for each $K\alpha 1$ and $K\alpha 2$ reflection. (c) Two-Gaussian fit with 2:1 peak intensities for tetragonal scenario. (d) Three-Gaussian fit with 1:1:1 peak intensities for orthorhombic scenario. Two Gaussians overlap in the hatched area.

temperatures above T^* are shown in Fig. 5.8. The peak widths are consistent above T^* , but abruptly increase below 50 K. Peaks were fit with single, double, and triple Gaussians with constrained peak widths at 52 K ($\sigma=0.01399$), shown in Fig. 5.9. Data below T^* are most consistent with two Gaussian components with a 2:1 relative intensity, indicative a cubic-tetragonal structural transition, shown in Fig. 5.2 (b) of the main text.

Representative two-dimensional slices from data used for crystallographic refinement are shown in Fig. 5.10 (a) and (b). The space-group of the low-temperature structure can be constrained by examining the systematically absent reflections for a tetragonal cell.

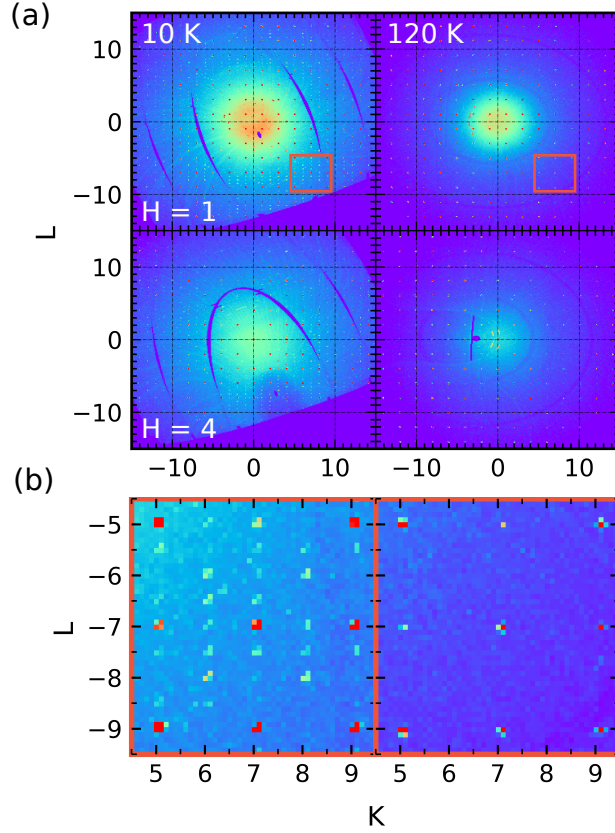


Figure 5.10: (a) Crystallographic measurements at 10 K and 120 K. H=1 and H=4 K-L slices are shown. Below T^* , superlattice peaks at half-integer positions appeared. (b) Magnified figures for the red box areas in (a).

Body-centered tetragonal space groups are ruled out by the appearance of reflections with $h+k+l \neq 2n$, indexed in the tetragonal cell. The absence of $[h, 0, 0]$, $h=2n+1$, rules out all primitive tetragonal space groups excepting $P\bar{4}2_1m$. Accordingly, $P\bar{4}2_1m$ is the most plausible space group for the low temperature structure, which is also a maximal subgroup of $F\bar{4}3m$ with a given unit cell doubled tetragonal structure.

Multiple twin laws and intensity corrections are necessary for crystallographic refinement to account for non-merohedral twinning of the tetragonal cell. We followed general procedures used for other systems with non-Merohedral twinning [94]. We applied three twin laws: (1) Original tetragonal cell (2) rotate (1) against $[1, 0, 0]$ axis with -90 degrees (3) rotate (1) against $[0, 1, 0]$ with -90 degrees, as shown in Fig. 5.11. For

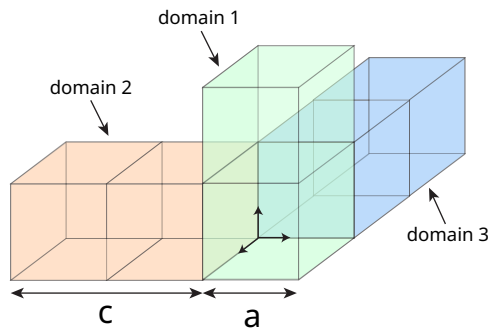


Figure 5.11: Twin laws of low-temperature structure. Each domain has its inversion domain; therefore, there are six domains at low temperatures.

each domain, we applied an additional inversion twin law to account for the inversion twinning. Therefore, six domains are considered in our crystallographic analysis. The peak intensities were integrated by Bruker SAINT software with multiple domains, and the domain population determined using the TWINABS package based on $4/mmm$ symmetry and $P\bar{4}2_1m$ space group. Finally, we used a total of 13104 reflections (single domain) for structure refinement with SHELXL [55] and Olex2 [56]. We were not able to stabilize the structure with full anisotropic thermal parameters, probably due to the disorder of the multi-domain structure. As a consequence, within isotropic thermal parameters, we obtained the crystal structure for a single domain that has $R=8.79\%$, $wR_2=10.18\%$ with 99.9% completeness of data set for $P\bar{4}2_1m$ structure. The details of the crystallographic refinement are summarized in Table 5.1.

Primary Mode Analysis

A primary mode analysis for a $k = (1/2, 0, 0)$ structural transition between $F\bar{4}3m$ and $P\bar{4}2_1m$ spacegroups described in the main text was performed on the Bilbao crystallographic server [61, 62, 95]. Details of mode amplitudes are shown in Fig. 5.13 and Table 5.2. Atomic displacements are listed in Appendix.

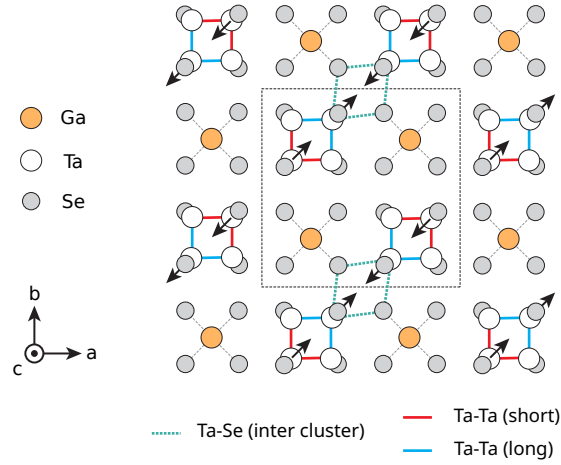


Figure 5.12: The refined structure shows distorted Ta_4 clusters and the formation of cluster dimers below T^* . Arrows indicate the shifts of Ta atoms along $\langle 110 \rangle$ direction.

Table 5.1: Crystallographic refinement for single domain.

Temperature (K)	10
Crystal system	Tetragonal
Space group	$P\bar{4}_21m$
a ($\text{\AA}$)	10.34370(14)
b ($\text{\AA}$)	10.34370(14)
c ($\text{\AA}$)	20.6878(5)
Data collection diffractometer	15-ID-D, APS
Absorption correction	Multiscan
Reflections collected	13104
Independent reflections	1952 ($R_{int}=0.0281$)
F(000)	4760.0
Radiation	Synchrotron, $\lambda=0.41328 \text{ \AA}$
2θ range for data collection (deg)	3.932 to 90.234
Index ranges	$0 \leq h \leq 10, 0 \leq k \leq 14, 0 \leq l \leq 29$
Refinement method	Full-matrix least squares on F^2
Data, restraints, parameters	1952/0/63
Goodness of fit	1.198
$R_1, wR_2(I \geq 2\sigma)$	0.0879, 0.1018
$R_1, wR_2(\text{all})$	0.0990, 0.1046
Largest diff. peak/hole	3.98/-5.61

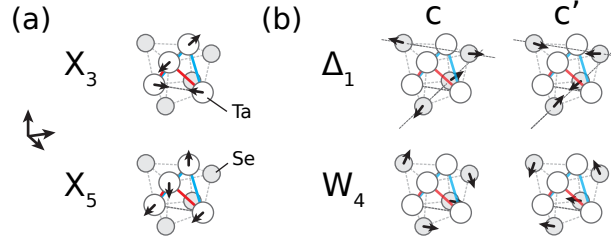


Figure 5.13: Primary distortion modes at 10 K. (a) X_3 and X_5 modes. (b) Δ_1 and W_4 modes double the unit cell along c-axis. Δ_1 mode produces the large and small Ta_4Se_4 in c and c' layer, respectively.

Table 5.2: Irreducible representation of distortion modes.

$\vec{K}$	Irrep	Direction	Isotropy SG	Amp. ($\text{\AA}$)
(0,0,0)	Γ_1	(a)	$F\bar{4}3m$	0.0171
(0,0,0)	Γ_3	(a,0)	$I\bar{4}m2$	0.0055
$(0, \frac{1}{2}, 0)$	Δ_1	$(0,0,0,0,a,-a)$	$P\bar{4}m2$	0.0600
(0,1,0)	X_3	(0,a,0)	$P\bar{4}m2$	0.2033
(0,1,0)	X_5	$(0,0,0,a,0,0)$	$P\bar{4}2_1m$	0.3383
$(\frac{1}{2}, 1, 0)$	W_4	$(0,a,0,0,0,0)$	$I\bar{4}2m$	0.0736

Supporting Data for Pair Distribution Analysis

In Fig. 5.14, we compared simulations of the PDF intensity with our neutron PDF results. The thermal parameters at 60 K and 45 K were used for $F\bar{4}3m$ and $P\bar{4}2_1m$ structure, respectively. The instrumental $Q_{broad}=0.018$ and $Q_{damp}=0.019$ were used in all simulations. The simulations show that in the large- r regime $F\bar{4}3m$ and $P\bar{4}2_1m$ structures are not distinguishable, except a slight change in peak widths that resembles thermal broadening. To search for this effect in our data, the temperature-dependent thermal parameters were extracted using $F\bar{4}3m$ cubic structure against the large- r regime (30 to 60 $\text{\AA}$). In order to minimize the parameter space, we constrained the model to isotropic thermal parameters and assumed each species of atom had the same value. The result shown in in Fig. 5.15 reveals a small upturn in the Ta thermal parameters across T^* , consistent with expectations from the simulated PDFs.

In order to track the temperature dependence of local distortions independent of any structural model, we fit data in the region $r < 5 \text{ \AA}$ to five and six Gaussian functions

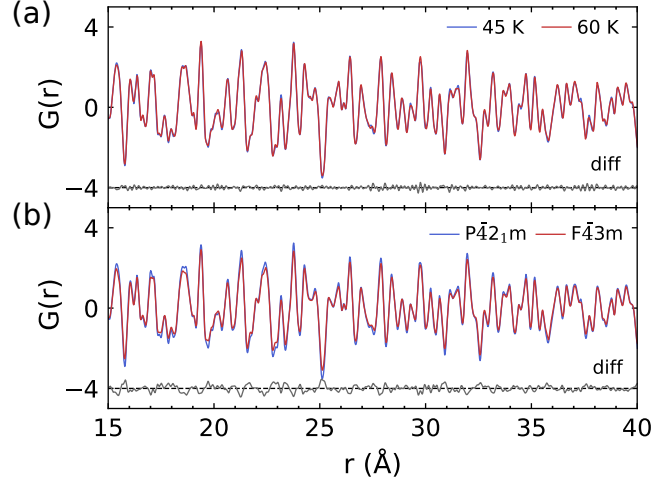


Figure 5.14: Experimental and simulated PDFs in large- r range. (a) Neutron PDF at 45 K and 60 K. (b) Simulations for $F\bar{4}3m$ and $P\bar{4}2_1m$ structures. $Q_{damp}=0.018$ and $Q_{broad}=0.019$ were used for simulations.

for xPDF and nPDF, respectively, as shown in Fig. 5.16. From our fits we extract a normalized PDF intensity $x(r', T)$ shown in Fig. 5.4. Fig. 5.17 shows the temperature-dependent interatomic distances extracted from the same fits.

Supporting Data for Inelastic neutron scattering and phonon modes

To compare inelastic neutron scattering data across a large range of temperatures, we weight the measured intensity by the Bose factor and plot a dynamic susceptibility $\chi''(Q, E)$ in in Fig. 5.18. The 13 meV mode is readily visible in the region highlighted in the dashed box of Fig. 5.18. Fig. 5.19 shows the representative $\chi''(E)$ integrated over $0.38 < Q < 5.5 \text{ \AA}^{-1}$. We concentrated on data between energy transfers of 9 and 28 meV and found that this region was adequately described by a fit to 5 Gaussian functions with a constant background. Fig. 5.19 (b) and Fig. 5.19 (c) show the fit results at 7 K and 192 K, respectively. Temperature-dependent phonon mode intensities extracted from the Gaussian fits are shown in Fig. 5.20 (a). All Bose factor corrected phonon mode intensities are consistent across measured temperatures except for the 13 meV intensity that displays a prominent temperature dependence. Fig. 5.20 (b) shows the temperature-dependent energy and

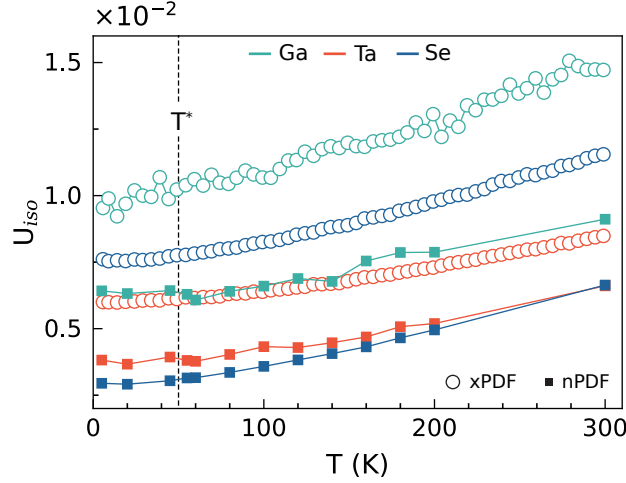


Figure 5.15: Thermal parameters extracted from PDF refinements with $F\bar{4}3m$ cubic structure. We only observed a slight upturn in thermal parameters across T^* . The errorbars of the fits are within the symbol size.

width of 13 meV phonon mode are constant in the measured temperature range.

Electronic Structure

We carried out density functional theory (DFT) calculations of the electronic structure of $P\bar{4}2_1m$ $GaTa_4Se_8$ without (PAW-PBE) and with spin-orbit coupling (PBE+SOC). We used a 680 eV (PAW-PBE) and 620 eV (PBE+SOC) cutoffs for plane-wave energy with $6 \times 6 \times 6$ (cubic) and $5 \times 5 \times 3$ (tetragonal) Monkhorst-Pack k-point mesh for self-consistent-field calculations. The projector-augmented-wave (PAW) method [47] and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [48] were used for all calculations. All calculations were performed using Quantum ESPRESSO [49, 96]. Cell parameters were restricted by $P\bar{4}2_1m$ space group and the force threshold was set to 4×10^{-5} a.u.. The criteria of equivalent atomic positions was 1×10^{-5} Å. The optimized structures are consistent with Ta_4 cluster distortions and intercluster dimerizations along $\langle 110 \rangle$ as we observed in x-ray diffraction. Details of the Ta_4 clusters are presented in Fig. 5.21 and the inter and intracluster bond lengths for PAW-PBE (PBE), PBE+SOC (SOC), and experimentally determined values are presented in table 5.3. The optimized structures display a slightly

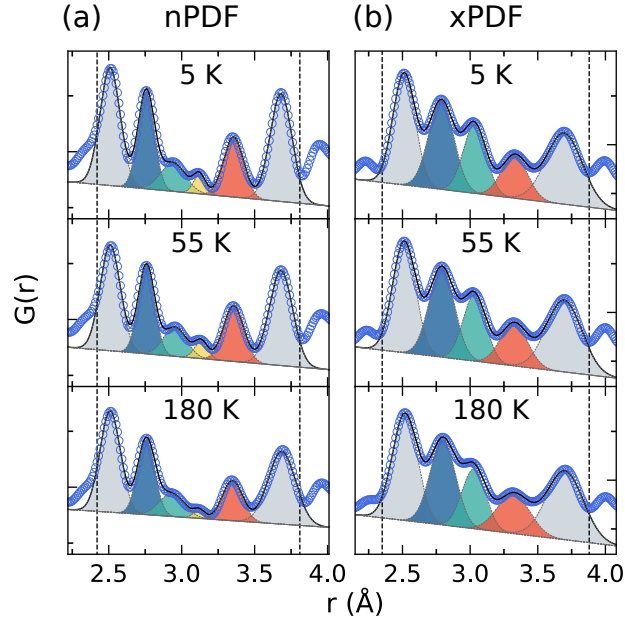


Figure 5.16: Representative Gaussian temperature-dependent peak intensity fits at 5 K, 55 K, and 180 K, for (a) nPDF data, and (b) xPDF data.

elongated c -axis ($c > 2a$), which also agrees with our experimental result. In addition, we find that PAW-PBE overestimated the unit cell size ($a = 10.4677$ Å, $c = 21.0086$ Å) as PBE+SOC ($a = 10.3988$ Å, $c = 20.8129$ Å) has smaller cell and slightly closer to experimentally determined values ($a = 10.3437$ Å, $c = 20.6878$ Å). Ta_4 clusters form dimers along $\langle 110 \rangle$ directions in both calculated structures.

Band structures and electronic density of states for PAW-PBE and PBE+SOC calculations

Table 5.3: Intra and intercluster distances in Å. The definition of bonds are shown in Fig. 5.21. c and c' denote the inequivalent clusters in $\text{P}\bar{4}2_1\text{m}$ tetragonal structure. PBE (PAW-PBE), SOC (PBE+SOC) are optimized structures from DFT.

	PBE (c)	PBE (c')	SOC (c)	SOC (c')	Exp (c)	Exp (c')
l	3.129	3.129	3.084	3.084	3.06	3.04
l'	3.086	3.086	3.053	3.053	3.03	3.03
s'	2.939	2.939	2.951	2.951	2.97	2.97
s	2.927	2.927	2.935	2.935	2.95	2.95
d_l	4.358	4.357	4.331	4.332	4.30	4.29
d_s	4.283	4.282	4.273	4.273	4.28	4.27

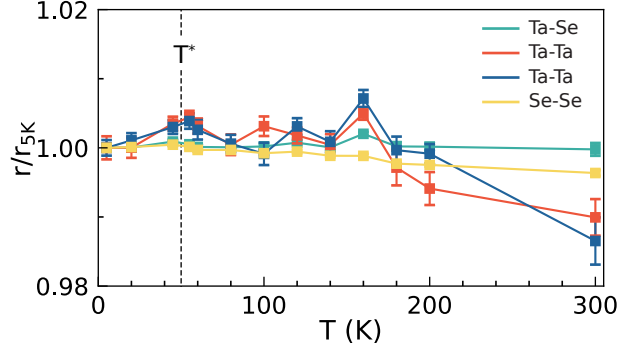


Figure 5.17: Temperature-dependent interatomic distances extracted from nPDF. The interatomic distances are normalized by their value at 5 K.

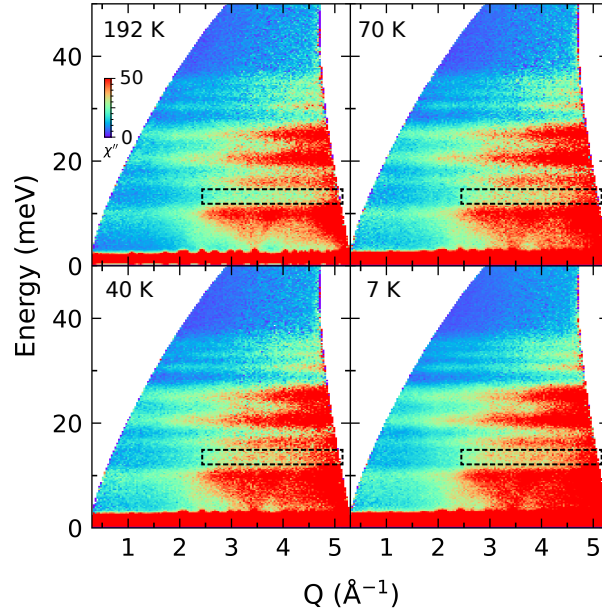


Figure 5.18: Measured dynamic susceptibility $\chi''(Q, E)$ at 192 K, 70 K, 40 K and 7 K. Dashed boxes highlight the phonon mode at 13 meV.

are shown in Fig. 5.22 and Fig. 5.23. In both calculations, the density of electronic states at the E_F is drastically reduced from that of the cubic cell. Without spin-orbit coupling, the unit cell doubled structure opens a small gap since the total electron count is even in a primitive cell. However, with spin-orbit coupling, the splitting of the electronic bands retains a metallic state in the unit cell doubled structure. A large Coulomb interaction, U , is required to open an insulating gap and our band structure calculations indicate that

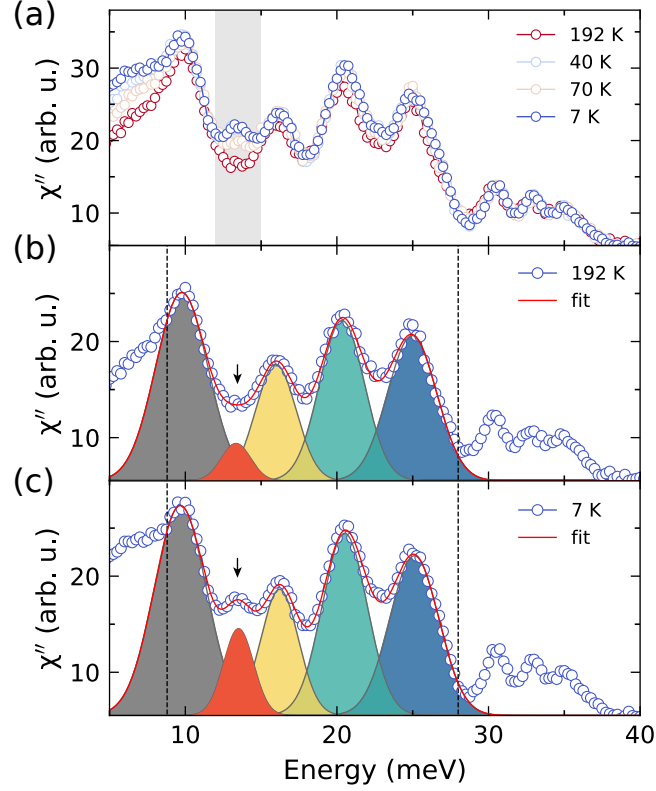


Figure 5.19: (a) Temperature-dependent $\chi''(E)$ integrated over $Q=0.38$ to $5.5 \text{ \AA}^{-1}$. (b) The fit for 7 K data. (c) The fit for 192 K data. The shaded area highlights the contribution of 13 meV mode, and two dashed lines indicate the fit range.

GaTa₄Se₈ is retains its Mott insulating nature at low temperatures.

Phonon calculations

We used Phonopy package [97] for ab-initio phonon calculations and Quantum ESPRESSO [49, 96] as the force calculator. For phonon calculations, we used 680 eV cutoff for plane-wave energy with a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh for self-consistent-field calculations. We checked the total energy convergence with the cutoff energy and k-point mesh for calculations. The minimal k-point were used for the cell with 104 atoms. To compare with the results measured by inelastic neutron scattering, the neutron weighted

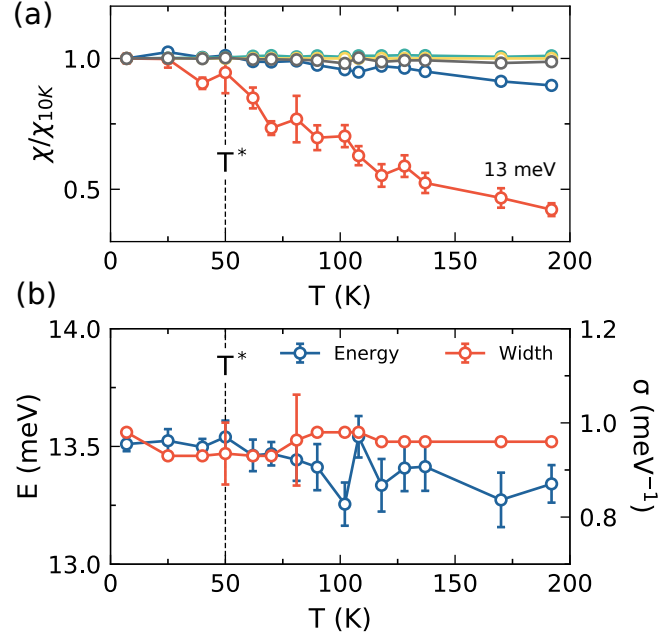


Figure 5.20: (a) Temperature-dependent mode intensity. χ is the amplitude of fitted Gaussian. Representative fits are shown in Fig. 5.19 (b) and (c). (b) Temperature-dependent energy and width of 13 meV mode. The peak energy and width are fairly consistent in measured temperature range.

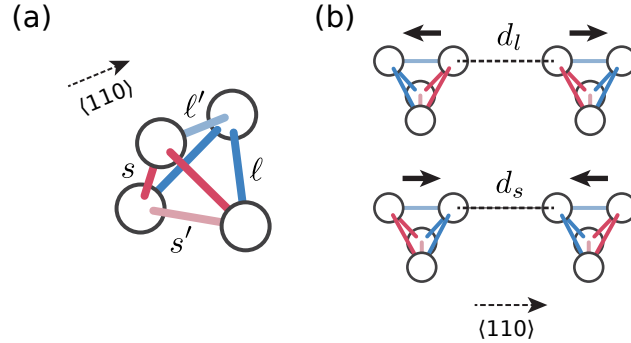


Figure 5.21: (a) Local distortion of Ta₄ clusters, $s < s' < \ell' < \ell$. (b) The inter-cluster distances. The bond lengths for the two inequivalent small clusters c and c' are shown in Table 5.3.

phonon DOS was calculated

$$PDOS(E) = \sum_i \sigma_i g_i(E), \quad (5.2)$$

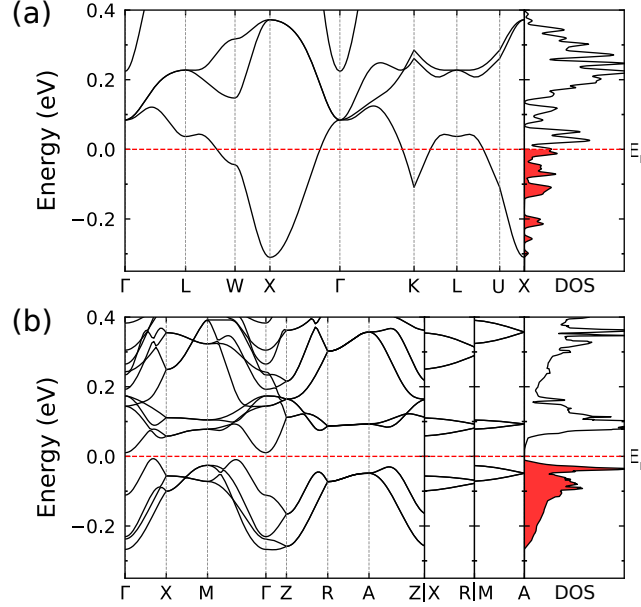


Figure 5.22: Electronic structure of GaTa_4Se_8 without SOC. (a) Cubic structure ($F\bar{4}3m$, $a=10.3849 \text{ \AA}$). (b) Tetragonal structure ($P\bar{4}2_1m$, $a=10.4677 \text{ \AA}$, $c=21.0086 \text{ \AA}$). In tetragonal structure the electronic density of states is reduced at the Fermi level and opens a small gap below T^* .

where σ_i and $g_i(E)$ are neutron cross-section and projected phonon density of states for each atomic species. To simulate the measured PDOS, we convolved the calculated PDOS with an empirical instrumental resolution function for SEQUOIA[37]

$$f(E) = 1.435 \times 10^{-6} \times E^3 + 3.885 \times 10^{-4} \times E^2 \quad (5.3)$$

$$- 7.882 \times 10^{-2} \times E + 4.295. \quad (5.4)$$

The irreducible representation of phonon modes can be calculated with the information of occupied Wyckoff positions (WPs). In $P\bar{4}2_1m$ tetragonal structure, Ga atoms occupy 4e WPs. Ta and Se atoms are on 4e and 8f WPs. Each atom on 4e site has $2A_1 + A_2 + B_1 + 2B_2 + 3E$ optical phonon modes, and $3A_1 + 3A_2 + 3B_1 + 3B_2 + 6E$ for atoms on 8f WPs. Therefore, the entire unit cell with 20 asymmetric atoms has $46A_1 + 32A_2 + 32B_1 + 46B_2 + 78E$ optical modes. As Fig. 5.7 in main text shows, the most distinguishable difference between cubic and tetragonal structure is the modes around 13 meV. From

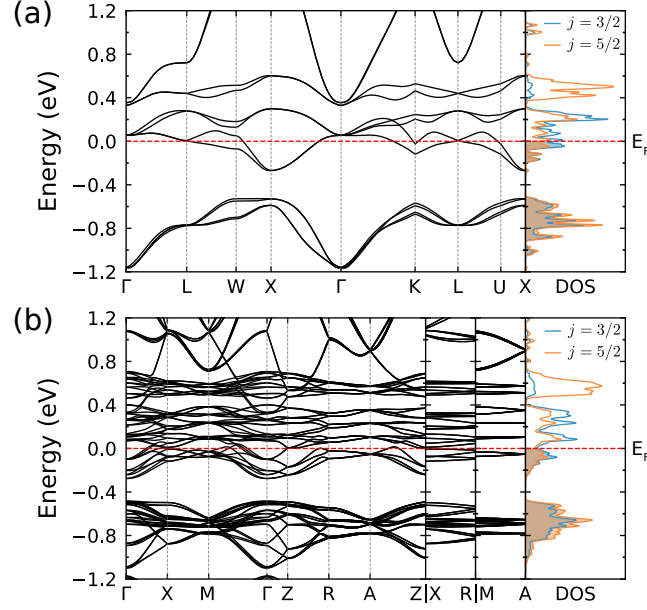


Figure 5.23: Electronic structure of GaTa_4Se_8 with SOC, with the density of states projected into atomic $j=3/2$ and $j=5/2$ basis shown in the side panel. (a) Cubic structure ($F\bar{4}3m$, $a=10.3260$ Å). (b) Tetragonal structure ($P4_21m$, $a=10.3988$ Å, $c=20.8129$ Å). Both structures require electronic correlation (U) to open a gap, therefore, retains a Mott insulator below T^* .

our DFT calculation, we assigned phonon modes between 12 and 14 meV to irreducible representation $2A_1 + 2A_2 + 2B_1 + 3B_2 + 4E$, which is the mixed modes of all Ga, Ta and Se atoms.

Chapter 6

Spin-orbital ordering and continuous phase transition in cluster Mott insulator GaNb_4Se_8

This chapter contains the x-ray diffraction experiments on GaNb_4Se_8 , which is the only member has two separated phase transitions with a substantial spin-orbit coupling. The chapter is organized as follows. First, the importance of this work is addressed. Second, the x-ray crystallography and refined structures at three phases are presented. Third, I discuss our discovery of the first-order spin-orbital dimer ordering and the second-order quadrupolar ordering phase. The preprint of this work will be available: T.-H. Yang, Tieyan Chang, Y-S Chen and K. W. Plumb (2023)

6.1 Introduction

The interplay of charge, spin, orbital, and lattice distortion (static or dynamic) is the foundation for novel material properties. However, those effects are usually independent due to the well-separated energy scales. In 4d or 5d transition metal materials, the spin-orbit coupling can be strong enough to alter the electronic ground state and arise novel

phases, for example, spin-orbit assisted Kiteav materials, topological superconductors, and spin-orbit liquid phase [86, 98–101]. In particular, $4d^1$ or $5d^1$ Mott insulators draw significant attention due to a single electron occupying the relativistic $j = 1/2$ or $j = 3/2$ ground state provides a rich playground for exploring fundamental physics.

Lacunar spinels with the chemical formula GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$) are a family of cluster Mott insulators that contain a single unpaired electron having the molecular t_2 ground state on each M_4 cluster site [46, 76]. The vast isostructural members provide an unprecedented opportunity to investigate the interplay of spin, orbit, and lattice [Fig. 6.1] In GaV_4S_8 and GaV_4Se_8 the structural and magnetic phase transitions are separate due to the dominating Jahn-Teller effect [43]. With a stronger spin-orbit coupling, GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 have magnetic singlet ground states [26, 58], implying the substantial spin-orbit coupling can influence the tendency of the Jahn-Teller effect and magnetic ground state. Recently, the spin-orbital disorder-order phase transition into the spin-orbital dimer state was observed in GaTa_4Se_8 [16]. In GaTa_4Se_8 , the correlation unit is a molecular $j_{eff} = 3/2$ [20, 46]. The phase transition is driven by the dominating spin-orbit coupling, while the Jahn-Teller effect (JTE) is suppressed. The ground state, therefore, fluctuates between $j^z = \pm 1/2$ and $j^z = \pm 3/2$, causing the lattice dynamics represented by the phonon anomaly far above the transition temperature. Under hydrostatic pressure, GaTa_4Se_8 has an insulator-metal transition and becomes topological superconducting at higher pressure [54, 100, 102]. GaNb_4Se_8 presents an intermediate structural phase before forming magnetic singlet dimers which distinct from GaNb_4S_8 and GaTa_4Se_8 . This intermediate state hints at the complex nature of the concurrent structural and magnetic phase transitions at T^* in strong spin-orbit coupling lacunar spinels. Therefore, it is crucial to provide thorough studies on the crystal structure, which enables a study of the most interesting regimes of the Mott transition with strong spin-orbit coupling in lacunar spinels.

In this work, we investigate crystal structures of GaNb_4Se_8 using single crystal x-ray diffractions and group theory analysis. Above $T_Q = 50$ K, GaNb_4Se_8 has a cubic

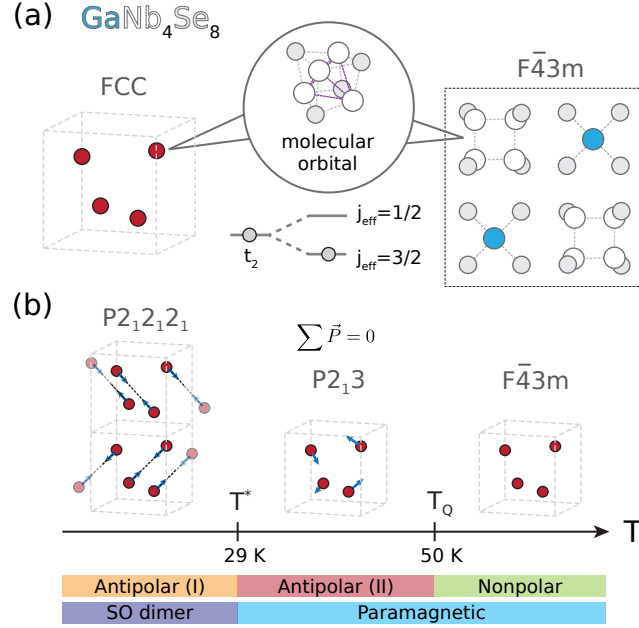


Figure 6.1: Crystal structure and the electronic ground state of GaNb_4Se_8 . (a) The correlation unit in GaNb_4Se_8 is a molecular $j_{\text{eff}} = 3/2$ orbital of Nb_4Se_4 cluster. Each cluster occupies an FCC lattice site. (b) Structure, electric and magnetic properties at different temperatures.

unit cell in a non-centrosymmetric space group $F\bar{4}3m$ [54]. Previous x-ray diffraction studies on powder samples suggested a $P2_13$ cubic structure at $T^* < T < T_Q$, and a $P2_12_12_1$ orthorhombic cell below T^* [26]. However, the detailed structures associated with the proposed antipolar and quadrupolar ordering phases are not reported due to the difficulty of solving the structure reliably. Therefore, reliable structure solutions are the most important information this work provides. Further, we find that two phase transitions have distinct mechanisms. At $T_Q = 50 \text{ K}$, we identify the second-order phase transition by the X_5 distortion mode. Furthermore, we find that the unit cell doubles and forms singlet dimers alternating along the c -axis at $T^* = 29 \text{ K}$, highlighting the crucial role of spin-orbit coupling in the emergence of these phenomena. Our work sheds light on the complex interplay between spin-orbit coupling and the Jahn-Teller effect in GaNb_4Se_8 and provides essential crystal structure information for further investigations into exotic properties.

6.2 Methods

Sample Synthesis

Polycrystalline samples of GaNb_4Se_8 were synthesized by solid-state reaction in box furnaces. About 1.5 g of stoichiometric quantities of high-purity raw materials (Gallium: Alfa Aesar, 99.999%; Niobium: Alfa Aesar, 99.99%; Selenium: Alfa Aesar, 99.999%) were loaded into a I.D. =10 mm, 100 mm long quartz ampules under an argon glovebox, evacuated, and sealed. The ampules were heated to 1050 °C with 80 °C/hour ramping rate, held for 24 hours and then air-quenched to room temperature. The resulting powder was reground in an argon glovebox, resealed under vacuum, and heated following the same procedure. Three heating and regrinding repetitions were required to obtain the single-phase powder. The composition was confirmed by powder x-ray diffraction (Bruker $\text{Cu K}\alpha$ radiation). Single crystal samples of GaNb_4Se_8 were prepared by chemical vapor transport. About 1.5 g of single-phase GaNb_4Se_8 powder and 75 mg iodine were sealed in a I.D. =10 mm, 210 mm long quartz ampules. The ampule was placed in a two-zone furnace with 950 °C and 1000 °C zone temperatures for 20 days. The quality of single crystals were checked by four-circle x-ray diffractometer ($\text{Ag K}\alpha$ radiation).

Synchrotron x-ray crystallography

Single crystal crystallography measurements were performed on 15 ID-D beamline at Advanced Photon Source at Argonne National Laboratory. The sample was mounted on a quartz fiber with epoxy adhesive. We used Dectris Pilatus3X 1M CdTe area detector with a sample to detector distance of 130 mm for 100 K and 120 mm for 40 K and 20 K measurements. Nitrogen and helium cryo-streams were used to control the sample temperature. For each temperature, we collected images, rotating the sample through 360 degrees with 0.3 and 0.1 degrees/step for 100 K and lower temperatures. The images were integrated into reciprocal space and indexed using Bruker APEX4 software. We used SADABS and TWINABS packages for absorption correction and checked the space group

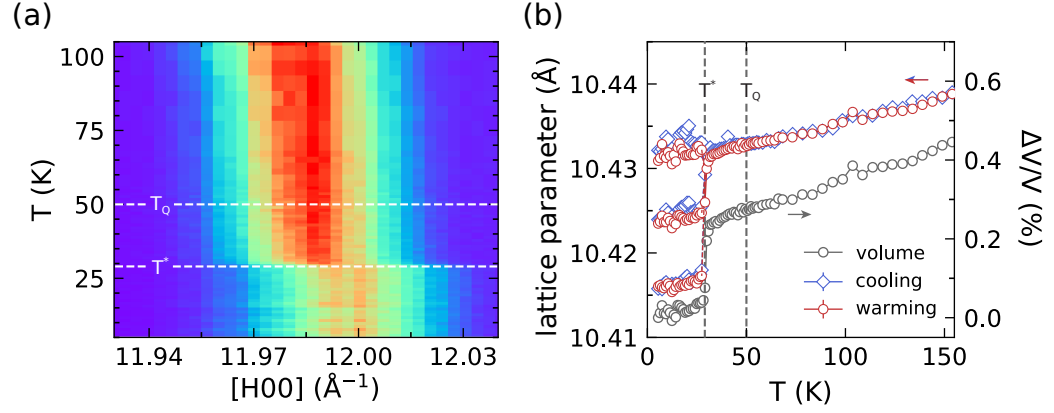


Figure 6.2: Temperature-dependent x-ray diffraction measurements on $[12,0,0]$ peak. (a) Temperature-dependent $[H00]$ cuts. The peak broadened below T^* in the orthorhombic cell phase. (b) Lattice parameter(s) extracted from $[12,0,0]$ peak.

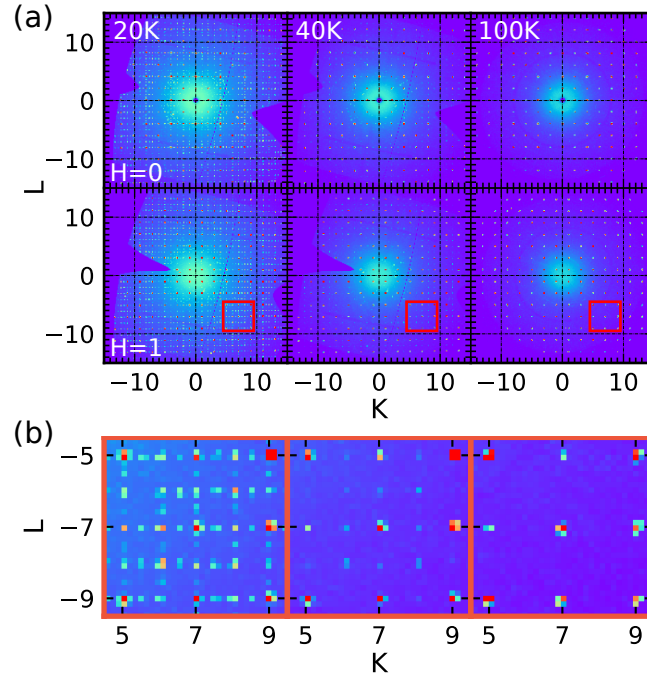


Figure 6.3: Synchrotron crystallography results at 20, 40 and 100 K. (a) The reconstruction of $(0kl)$ and $(1kl)$ planes in reciprocal space. (b) Zoomed areas in $(1kl)$ plane, indicated by red boxes in (a).

by XPREP package. The structure solution and refinements were performed on Shelx with Olex2 user interface [55, 56].

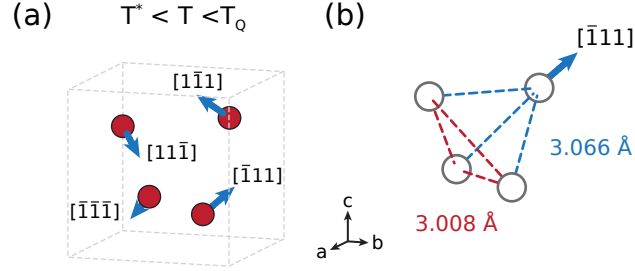


Figure 6.4: Refined crystal structure at 40 K. (a) Red circles represent Nb_4 clusters, and blue arrows show the overall distortion of each cluster. (b) The distorted bonds in an Nb_4 cluster. Each cluster elongates along cubic $[\bar{1}11]$ or equivalent direction in $P2_13$ space group.

6.3 Jahn-Teller driven continuous phase transition

We start by investigating the structural phase transition at $T_Q = 50$ K. The temperature-dependent diffraction measurements on $[12, 0, 0]$ peak show the broadening at $T^* = 29$ K, but no detectable change across T_Q [Fig. 6.2 (a)], which verifies the cubic-cubic phase transition at T_Q . The lattice parameter and crystal volume extracted from the Gaussian fit of the longitudinal cut through $[12, 0, 0]$ peak shows no sudden change, which is usually observed in an orbital ordering phase transition [Fig. 6.2 (b)].

Our synchrotron x-ray crystallography shows the crystal structure at 40 K is a primitive cubic cell with $P2_13$ space group, and the refined structure supports the proposed antipolar and quadrupolar ordering in previous studies [26, 103]. Fig. 6.3 shows the appearance of reflections breaking the reflection conditions: $h + k = 2n$; $h + l = 2n$; $k + l = 2n$ for a face-center-cubic (FCC) cell, indicating a primitive cubic unit cell at 40 K. Our refinement gives the best fit to the $P2_13$ space group with $R_1 = 0.0442$ ($I \geq 2\sigma$), and the Nb atoms on 16e Wyckoff position (WP) split into 4a and 12b WPs in $P2_13$ resulting the Nb_4 tetrahedron elongates along the cubic $\langle \bar{1}11 \rangle$ or one of the equivalent directions [Fig. 6.4]. The parameters of the refinement are listed in Table 6.3 and the refined atomic positions are listed in Appendix.

The primary distortion mode is a Jahn-Teller activate X_5 mode from our group theory analysis performed on Bilbao crystallographic server [104–106]. The mode amplitudes and

isotropy space groups are listed in Table 6.1 and the atomic distortions for each symmetry mode are listed in Appendix. Two primary distortion modes, Γ_1 and X_5 , contribute to the structural transition, but the X_5 -mode is the only addition distortion mode required in the $F\bar{4}3m \rightarrow P2_13$ transition which is a *Jahn-Teller active mode*. Therefore, from the symmetry perspective, we conclude that this transition is mainly driven by the Jahn-Teller effect.

The phase transition at T_Q is a second-order phase transition due to the continuous change of X_5 distortion mode amplitude. The temperature-dependent $[8, 0, 1]$ peak intensity is shown in Fig. 6.5. The continuous change of the peak intensity can result from either the nucleation growth of the low-temperature phase or a gradual evolution of the structural distortion. The nucleation growth usually shows a strong hysteresis effect due to the formation of domains, creating an energy barrier for switching the structure from low to high symmetry and vice versa. On the other hand, the gradual change of the structure distortion does not create an energy barrier for symmetry breaking. Therefore, the transition can be smooth without a significant hysteresis. From our group theory analysis of crystallographic results, we identified that the X_5 is the only distortion mode that participates in the $F\bar{4}3m \rightarrow P2_13$ phase transition. Fig. 6.6 shows the simulated $[8, 0, 1]$ peak intensity versus the X_5 mode amplitude indicating the peak intensity increases as increasing mode amplitude which qualitatively agrees with the temperature-dependence of $[8, 0, 1]$ peak in Fig. 6.5.

Table 6.1: Irreducible representation of distortion modes for $F\bar{4}3m$ to $P2_13$ transition.

$\vec{K}$	Irrep	Direction	Isotropy SG	Amp. (Å)
(0,0,0)	Γ_1	(a)	$F\bar{4}3m$	0.0676
(0,1,0)	X_5	(a,a,a,a,a,a)	$P2_13$	0.1590

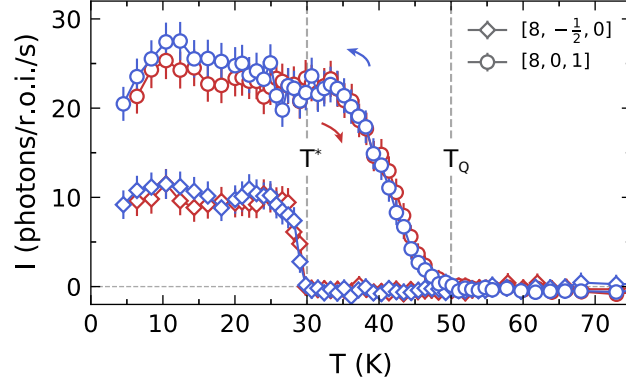


Figure 6.5: Temperature-dependent peak intensities for $[8, -1/2, 0]$ and $[8, 0, 1]$ reflections. The superlattice peak $[8, -1/2, 0]$ shows a first-order feature at T^* , while the $[8, 0, 1]$ structural peak has a second-order nature in $T^* < T < T_Q$.

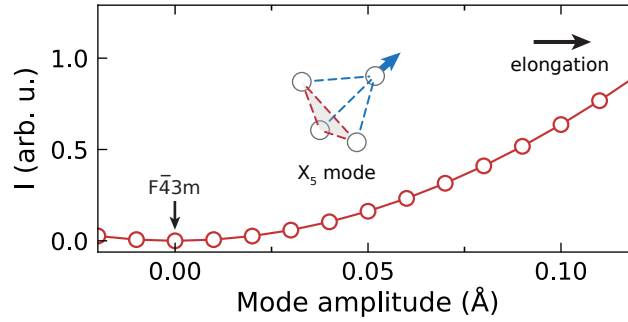


Figure 6.6: Simulated $[8, 0, 1]$ peak intensity versus X_5 distortion mode amplitude. The relative distortion of each atom in X_5 mode is extracted from the crystallography results. The mode amplitude is normalized to the primitive cell of high symmetry $F\bar{4}3m$ structure.

6.4 Singlet dimers in antipolar ordered phase

Now we are examining the first-order phase transition at $T^* = 29$ K. At T^* , GaNb_4Se_8 has simultaneous structural and magnetic transitions [26] and we observe the unit cell doubles along the c -axis. The unit cell doubling is indicated by the sudden appearance of structural superlattice Bragg reflections at $[1/2, 0, 0]$ positions [Fig. 6.3 and Fig. 6.5]. The domain structure is unavoidable with the $1 \times 1 \times 2$ unit cell. Therefore, we disentangle the domain structure by defining four twinned cells (rotates against the doubled axis for 0, 90, 180, and 270 degrees) for each doubled axes along a , b , or c ; accordingly, we define 12 domains in total. The intensities of Bragg peaks are corrected based on the symmetry

Table 6.2: Irreducible representation of distortion modes for $F\bar{4}3m$ to $P2_12_12_1$ transition.

$\vec{K}$	Irrep	Direction	Isotropy SG	Amp. ($\text{\AA}$)
(0,0,0)	Γ_1	(a)	F43m	0.1001
(0,0,0)	Γ_3	(a,b)	F222	0.0099
$(0, \frac{1}{2}, 0)$	$\Delta_3\Delta_4$	(0,0,0,0,a,b,0,0,0,0,-b,a)	C222 ₁	0.1976
(0,1,0)	X_3	(0,a,0)	P4m2	0.0834
(0,1,0)	X_4	(0,a,0)	P4n2	0.0120
(0,1,0)	X_5	(0,0,a,b,0,0)	P2 ₁ 2 ₁ 2	0.3233
$(\frac{1}{2}, 1, 0)$	W_1	(0,0,0,0,-a,a)	I42d	0.0573
$(\frac{1}{2}, 1, 0)$	W_2	(0,0,0,0,-a,a)	I42d	0.0836

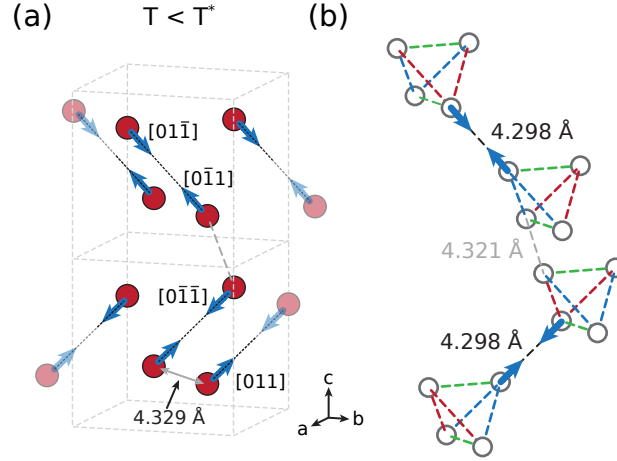


Figure 6.7: Refined crystal structure at 20 K. (a) The unit cell doubled $P2_12_12_1$ cell. Red circles represent Nb_4 clusters, and blue arrows show the overall distortion of each cluster. Black dashed lines indicate the closest distance between clusters, showing a dimerized structure. (b) The distorted bonds in an Nb_4 cluster. Each cluster has two long bonds (blue), two short bonds (red) and two intermediate bonds (green). The black dashed lines show the shortest intercluster distances, and the gray dashed line indicates the distance between two dimers.

operations using TWINABS for 12 domains. Our crystallographic data gives the best agreement with the unit cell doubled orthorhombic $P2_12_12_1$ space group with $R_1 = 0.0855$ ($I \geq 2\sigma$). The refinement parameters are listed in Table 6.3, and the refined structure is shown in Fig. 6.7.

We observe dimerized Nb_4 clusters below T^* , which form paired singlets along cubic $\langle 011 \rangle$ or $\langle 0\bar{1}1 \rangle$ direction. Fig. 6.7 show the refined crystal structure, and the refined atomic positions are listed in Appendix. The Nb_4 cluster elongates along cubic $\langle 011 \rangle$ or equivalent

direction and has three different bond lengths, represented by red, green and blue dashed lines in Fig. 6.7 (b). Combined with the previous results of magnetic singlet and electric antipolar orderings [26, 103], our result of the crystal structure confirms the paired nature of the ground state at $T < T^*$.

The unit cell doubled $P2_12_12_1$ structure is not a sub-spacegroup of the intermediate $P2_13$ structure, indicating the transition at T^* is not mainly driven by the same Jahn-Teller effect at T_Q . The $1 \times 1 \times 1$ orthorhombic $P2_12_12_1$ is the exclusive sub space group of the intermediate $P2_13$ structure while the appearance of superlattice peaks indicate the structure is a $1 \times 1 \times 2$ cell [Fig. 6.3]. Therefore, we calculate structure relation against the high temperature $F\bar{4}3m$ structure to obtain irreducible representations and distortion mode amplitudes listed in Table 6.2. The $\Delta_3\Delta_4$ mode contributes to the unit cell doubling with half-integer $\vec{K}$, and the distortions of the atoms are comparable to the Jahn-Teller active X_5 mode. The atomic distortions of irreducible representations are listed in the Appendix.

6.5 Discussion

We solve the GaNb_4Se_8 low temperature structures with high-fidelity x-ray crystallography and find distinct mechanisms, the Jahn-Teller effect and spin-orbit coupling, drive two transitions. At $T^* < T < T_Q$, we observe a second-order phase transition activated by the Jahn-Teller effect with irreducible representation X_5 distortion mode. At $T < T^*$, the unit cell doubles and forms a singlet dimer state, resembling the sibling compound GaTa_4Se_8 [16]. Compared to previous studies on heat capacity, magnetic susceptibility, and dielectric measurements [26, 103], our results complete the thus far missing structure information and provide insights into the fundamental mechanisms driving the possible spin-orbit and antipolar ordering phases.

It is instructive to compare the phase transitions in other isostructural and isoelectronic lacunar spinels. The low-temperature structures of GaM_4X_8 ($M=\text{V}, \text{Nb}, \text{Ta}$; $X=\text{S}, \text{Se}$) are

highly related to the relative strength of the Jahn-Teller effect and spin-orbit coupling. When the Jahn-Teller effect dominates ($M=V$), the orbital and magnetic sectors are distinct in GaV_4S_8 and GaV_4Se_8 , showing separate structural and magnetic transition at lower temperatures indicated by the appearance of rhombohedral reflections and the sudden change of magnetic susceptibility [17, 21–23]. On the other hand, GaV_4S_8 and GaV_4Se_8 demonstrate ferroelectricity with the charge dipole pointing along the cubic $\langle 111 \rangle$ direction as the result of the Jahn-Teller effect driven phase transition [17, 23]. Under a small external magnetic field, both compounds harbor skyrmion-type magnetic ground states [18, 24].

A dominating spin-orbit coupling can induce novel phases in lacunar spinels. For example, GaTa_4Se_8 is suggested to harbor a topological superconducting phase under pressure [100] and the spin-orbital fluctuations were observed by inelastic neutron scattering [16]. The dimerized $J_{eff} = 3/2$ ground state below the transition accompanied by a cubic ($F\bar{4}3m$) to unit cell doubled tetragonal ($P\bar{4}2_1m$) transition with a minimal Jahn-Teller effect which evidences the theoretical prediction of the suppression of Jahn-Teller effect by spin-orbit coupling [14, 16]. The M_4 ($M=\text{Nb, Ta}$) cluster size in GaNb_4Se_8 and GaTa_4Se_8 are almost identical with M-M distance around 3 Å. Therefore, the difference between GaNb_4Se_8 and GaTa_4Se_8 is mainly due to the strength of spin-orbit coupling and the bandwidth of d-electron states of Nb and Ta atoms. Both compounds have the nonmagnetic ground state below T^* along with antipolar ordering [103]. Although GaNb_4Se_8 and GaTa_4Se_8 have several similarities, only GaNb_4Se_8 has the intermediate cubic phase with a second-order phase transition at T_Q [Fig. 6.3]. The spin-orbit coupling in d_1 configuration can suppress the Jahn-Teller effect and create an effective Mexican hat potential of the lattice distortion. However, the intermediate cubic phase in GaNb_4Se_8 is solely driven by the Jahn-Teller effect from our group theory analysis, indicating the separation of SOC and the Jahn-Teller effect in GaNb_4Se_8 .

In GaNb_4S_8 and GaNb_4Se_8 , the competition between SOC and the JTE becomes delicate because the two effects are comparable. GaNb_4S_8 has a relatively strong JTE due

to the reduced Nb-Nb distances in Nb₄ cluster (≈ 2.7 Å) and the reported effective magnetic moment $\mu_{eff} \approx 1.67 \mu_B/f.u.$ which is comparable to the spin-only value ($1.73 \mu_B/f.u.$), indicating weaker SOC effect in GaNb₄S₈ [15]. Compared to GaNb₄Se₈, the crystal and cluster sizes are larger due to the substitution of S to Se and the reported effective magnetic moment $\mu_{eff} \approx 1.45 \mu_B/f.u.$ [26], which indicates a stronger SOC. Therefore, GaNb₄Se₈ has a more balanced SOC and JTE than GaNb₄S₈ and GaTa₄Se₈. To this end, the intermediate phase transition driven by JTE is crucial since it is separated from the SOC effect and indicates the concurrent structural and magnetic phase transition at T^* is induced by SOC. Unfortunately, by the time of this work, there is no reported low-temperature structure for GaNb₄S₈ to allow us to compare primary distortion modes in both compounds. However, the observation of the superlattice peaks in GaNb₄S₈ implies the possible long-range ordering of Nb₄ clusters [15], and more detailed studies of the crystal structure are required.

The fore-mentioned comparisons are complementary to each other. The clues from GaTa₄Se₈ (strong SOC) and GaNb₄S₈ (strong JTE) emphasize the pivot role of two separated phase transitions in GaNb₄Se₈. The separation of two mechanisms provides a rare-to-find opportunity to study the interplay between SOC, JTE, and lattice distortions.

6.6 Conclusion

To conclude, we have used a series of single crystal diffraction, crystallography and space group analysis to show that two phase transitions are related to the competition between the Jahn-Teller effect and spin-orbit coupling. We resolved the detailed structures in the low-temperature phases and used group theory analysis to decouple the contributions from two effects. At the quadrupolar order temperature, $T_Q = 50$ K, we found the phase transition is continuous and can be described by the irreducible representation X_5 mode, which is Jahn-Teller active. The structure of the spin-orbital ordered phase at $T^* = 29$ K is also provided, showing the unit cell doubles due to the canted order of spin-orbital dimers.

Table 6.3: Crystallographic refinement results at 20, 40 and 100 K.

Temperature (K)	20	40	100
Crystal system	orthorhombic	cubic	cubic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 3	F43m
a (Å)	10.4090(5)	10.4071(6)	10.40910(10)
b (Å)	10.4086(5)	-	-
c (Å)	20.8145(10)	-	-
Diffractometer	15-ID-D, APS	15-ID-D, APS	15-ID-D, APS
Abs. correction	Multiscan	Multiscan	Multiscan
Reflections collected	66929	17258	13368
Indep. reflections	16630 (R _{int} =4.22%)	2489 (R _{int} =2.73%)	464 (R _{int} =3.40%)
F(000)	3736.0	1401.0	1868.0
λ (Å, synchrotron)	0.41328	0.41328	0.41328
2 θ range(deg)	2.544 to 50.64	3.218 to 49.048	3.94 to 47.77
Index ranges	-18 $\leq h \leq$ 19 -19 $\leq k \leq$ 19 -38 $\leq l \leq$ 38	-18 $\leq h \leq$ 18 -13 $\leq k \leq$ 16 -15 $\leq l \leq$ 18	-17 $\leq h \leq$ 15 -19 $\leq k \leq$ 17 -17 $\leq l \leq$ 19
Data, restr., param.	16630/0/205	2489/0/41	464/0/12
Goodness of fit	1.088	1.272	1.190
R ₁ , wR ₂ (I $\geq$ 2 σ)	0.0855, 0.1777	0.0442, 0.0776	0.0088, 0.0200
R ₁ , wR ₂ (all)	0.0910, 0.1794	0.0470, 0.0789	0.0088, 0.0200
Max diff. peak/hole	8.10/-7.15	4.92/-2.54	0.98/-0.96

The phase transitions in GaNb₄Se₈ is distinct from other sibling compounds and allows the investigation of the interaction between multiple energy scales. Further theoretical studies are required to understand the unexplored new type molecular $J_{eff} = 3/2$ Mott insulators.

Chapter 7

Direct evidence of spin-orbital fluctuation in molecular Mott insulator GaM_4X_8

This chapter contains pair distribution function and inelastic neutron scattering experiments on lacunar spinels GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$). Investigating the entire series of d^1 lacunar spinels provides comprehensive studies for the competition between spin-orbit coupling, the Jahn-Teller effect, and the exchange-correlation. Combining our pair distribution function and inelastic neutron scattering measurements, we conclude that our result provides direct evidence of spin-orbital fluctuation in lacunar spinels with strong spin-orbit coupling. The preprint of this work is under preparation, T.-H. Yang, D. L. Abernathy, Gihan Kwon, A. M. Milinda Abeykoon, Emil Bozin and K. W. Plumb (2023).

7.1 Introduction

The research of novel phases in condensed matter relies on understanding the interactions between energy scales. The geometry, coordination, and arrangement of transition metal ions are crucial for the collective properties. In recent years, the ions arranged on a

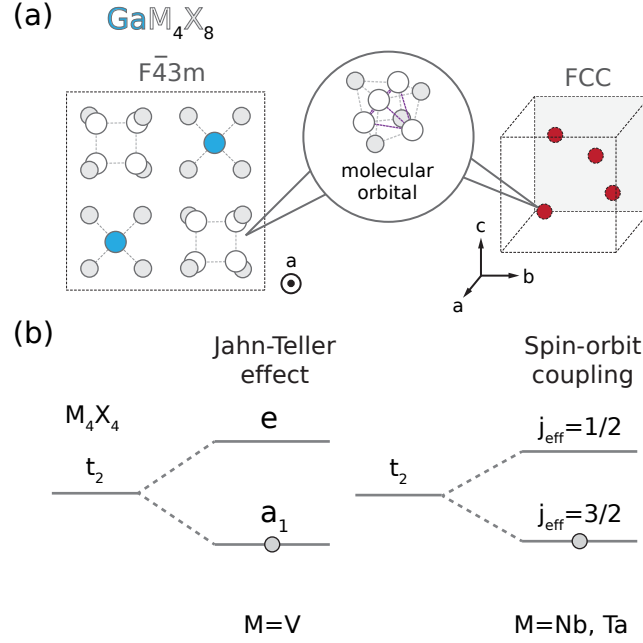


Figure 7.1: (a) Crystal structure of lacunar spinels in the $\bar{F}43m$ cubic phase. The correlation unit is a molecular orbital occupied by an unpaired t_2 electron. (b) The splitting of t_2 energy level due to the Jahn-Teller effect and spin-orbit coupling.

honeycomb or kagome lattice attracted intensive interest because the relativistic spin-orbit coupling induces the quantum state frustration in such systems [99]. However, spin-orbital frustration can appear when metallic ions occupy face-center-cubic (FCC) lattice sites. This frustration in a nominal FCC system is described by the Kugel-Khomskii model which the correlation units are spin-orbital quantum states.

Electron configuration plays an essential role in material properties. In transition metal compounds, the degeneracy of d-orbitals is usually lifted by the crystal field to reduce orbital frustrations, resulting in having energy separation of e_g and t_{2g} manifolds. The hierarchy of two manifolds is related to the coordination geometry. In an FCC lattice, the t_{2g} levels have lower energy due to the octahedral coordination of ions and ligand atoms.

In this work, we perform comprehensive studies on the d^1 lacunar spinels GaM_4X_8 ($\text{M}=\text{V, Nb, Ta}$; $\text{X}=\text{S, Se}$) using the pair distribution function, inelastic neutron scattering, and first principle phonon calculations. At room temperature, lacunar spinels have an FCC

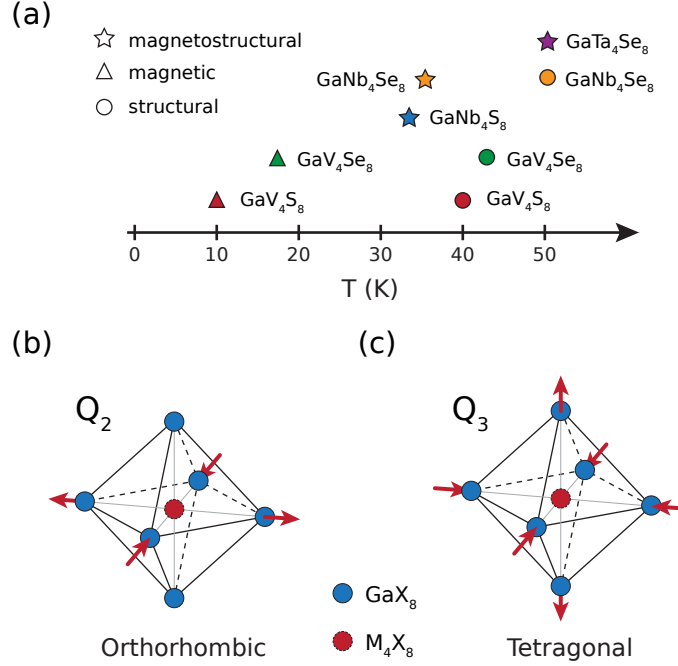


Figure 7.2: (a) Phase transitions of lacunar spinels. (b) Q_2 and (c) Q_2 vibrational modes of octahedrally coordinated ion.

cubic unit cell, and each FCC lattice site is occupied by an M_4X_4 cubane cluster [Fig. 7.1 (a)]. Each cluster contains a single t_{2g} electron, and the ground state is a molecular $S=1/2$ ($M=V$) or $J_{eff}=3/2$ ($M=Nb, Ta$) [Fig. 7.1 (b)]. The d^1 lacunar spinels have rich phases, for example, Néel-type skyrmion, spin-orbit singlet state, and topological superconductor phase [15, 18, 26, 100, 107]. Fig. 7.2 (a) shows the structural and magnetic phase transitions, and Table 7.1 lists the phase transitions and magnetic ground state. The wide varieties of the structural and magnetic phases provide a playground to explore the interplay between spin, orbital, and lattice dynamics in materials.

Table 7.1: Structural and magnetic phase transitions of lacunar spinels.

	T_s	T_N	LT structure	Θ_{CW}	Magnetism	Ref.
GaV ₄ S ₈	40	10	R3m		FM, Cyc, SkL, $s=1/2$	[18, 21, 22]
GaV ₄ Se ₈	42	18	R3m	-84.6	FM, Cyc, SkL, $s=1/2$	[23, 24]
GaNb ₄ S ₈	32	32	P2 ₁ 2 ₁ 2 ₁	-300	singlet, $j=3/2$	[19, 25]
GaNb ₄ Se ₈	32, 50	32	P2 ₁ 2 ₁ 2 ₁ , P2 ₁ 3	-139	singlet, $j=3/2$	[26]
GaTa ₄ Se ₈	50	50	P4 ₂ m	-285	singlet, $j=3/2$	[16, 27]

7.2 Methods

Sample Synthesis

Polycrystalline samples of GaV_4S_8 , GaV_4Se_8 , GaNb_4S_8 , GaNb_4Se_8 and GaTa_4Se_8 were synthesized by solid-state reaction in box furnaces. About 1.5 g of stoichiometric quantities of high-purity raw materials were loaded into a I.D. =10 mm, 100 mm long quartz ampules under an argon glovebox, evacuated, and sealed. The ampules were heated to 950 to 1050 °C with 80 °C/hour ramping rate and stayed at the same temperature for 24 hours. Then air-quenched to room temperature. The resulting powder was mixed in an argon glovebox and sealed for the same procedure. Three repetitions were required to obtain the single-phase powder. The composition was confirmed by powder x-ray diffraction with ground crystals (Bruker Cu $K\alpha$ radiation). Single crystal samples of GaNb_4S_8 and GaNb_4Se_8 were prepared by chemical vapor transport with 5% of total mass of iodine as the transport agent. About 1.5 g of single-phase powder was sealed in a I.D. =10 mm, 210 mm long quartz ampules with iodine. The ampule was placed in a two-zone furnace with 950 °C and 1000 °C zone temperatures for 20 days. The quality of single crystals were checked by four-circle x-ray diffractometer (Ag $K\alpha$ radiation).

X-ray pair distribution function

Synchrotron total scattering measurements (xPDF) were carried out on 28-ID-1 (PDF) beamline at the National Synchrotron Light Source-II at Brookhaven National Laboratory. The sample was loaded in a 1 mm I.D. kapton capillary, mounted in a He cryostat, and data was collected between 5 K and 330 K on warming in 5 K steps. Measurements were carried out using an x-ray energy of 74.46 keV (0.1665 Å). We used an amorphous silicon PerkinElmer area detector with a sample to detector distance of 1008 mm for diffraction and 204 mm for PDF. Detector position was determined by calibration using a Ni standard. The two dimensional diffraction data were integrated using PyFAI [32] and then corrected, normalized, and Fourier transformed to obtain the atomic pair distribution

function (PDF), $G(r)$, using PDFgetX3 [33] and a $Q_{max} = 27 \text{ \AA}^{-1}$.

Inelastic neutron scattering

Inelastic neutron scattering measurements were carried out on the ARCS spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. A 3 to 5 g polycrystalline sample was loaded into an aluminum sample can and mounted on the coldfinger of a closed cycle cryostat to achieve a base temperature of 5 K. Measurements were conducted using a fixed incident energy $E_i = 70(40) \text{ meV}$ and the coarse Fermi chopper rotating at 300 Hz, providing an energy resolution at the elastic line of $3.41(1.44) \text{ meV}$. All data was normalized and reduced using algorithms in the MANTID analysis software [58]. The normalized neutron intensities were converted into neutron weighted phonon density of states by integrating over Q (1 to $6 \text{ \AA}^{-1}$ and 2 to $12 \text{ \AA}^{-1}$ for $E_i = 40$ and 70 meV , respectively) and correcting for multiphonon and multiscattering processes within the incoherent approximation [59].

Density functional theory

We used Phonopy package [97] for ab-initio frozen phonon calculations and Quantum ESPRESSO [49, 96] as the force calculator. For phonon calculation, we used 680 eV cutoff for plane-wave energy with a $6 \times 6 \times 6$ and $4 \times 4 \times 2$ Monkhorst-Pack k-point mesh for the self-consistent-field calculations of cubic and tetragonal/orthorhombic structures. We checked the total energy convergence with the cutoff energy and k-point mesh for calculations. To compare with the results measured by inelastic neutron scattering, the neutron weighted phonon DOS was calculated by neutron cross-section for each atom and the projected phonon density of states as follows

$$PDOS(E) = \sum_i \sigma_i g_i(E), \quad (7.1)$$

where σ_i and $g_i(E)$ are neutron cross-section and projected phonon density of states for each species of atom. To simulate the measured PDOS, we convolved the instrumental

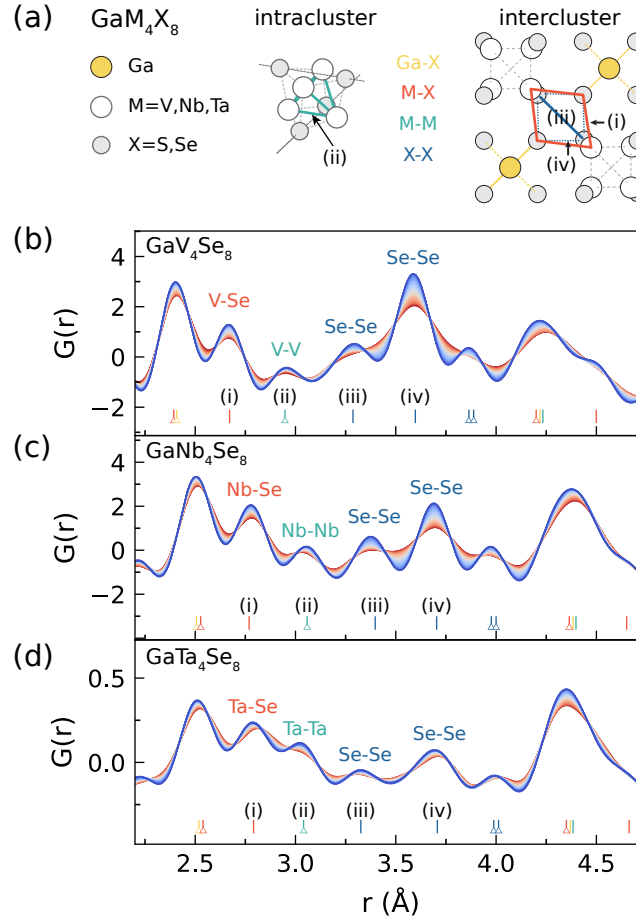


Figure 7.3: Temperature-dependent xPDFs. (a) Schematic illustration for interatomic distances. (b) GaV_4Se_8 . (c) GaNb_4Se_8 . (d) GaTa_4Se_8 .

resolution function at ARCS

$$f(E) = 6.2084 \times 10^{-7} \times E^3 + 1.9975 \times 10^{-4} \times E^2 - 4.7166 \times 10^{-2} \times E + 3.4035 \quad (7.2)$$

7.3 Local structure and preceding symmetry breaking

We start with investigating the local structure of GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}$; $\text{X}=\text{S}, \text{Se}$) across phase transitions. The pair distribution function (PDF) is sensitive to interatomic distances and local distortion across structural phase transitions.

It is informative to compare the experimental results of lacunar spinel selenide as

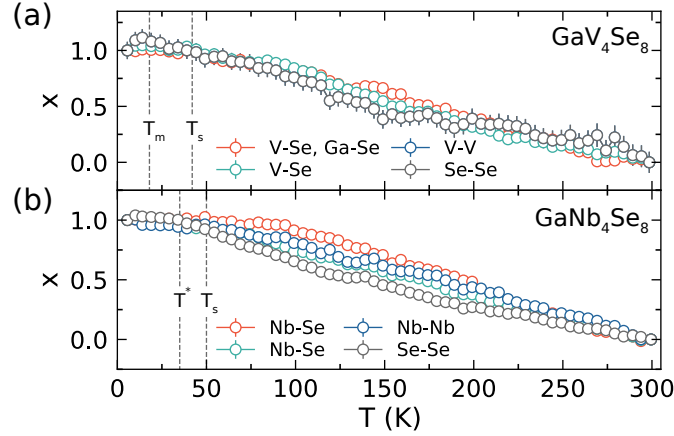


Figure 7.4: Normalized peak intensities (x-values) of GaV_4Se_8 and GaNb_4Se_8 .

their unit cell, and M_4 ($M=\text{V}, \text{Nb}, \text{Ta}$) cluster sizes are comparable. Fig. 7.3 shows the temperature-dependent PDFs for interatomic distances below 5 Å. In the strong spin-orbit coupling limit, GaTa_4Se_8 presents a disorder-order phase transition as no new length scales appear across the phase transition at $T^* = 50$ K. GaV_4Se_8 and GaNb_4Se_8 show similar results, in which no new length scales appear across structural phase transitions [Fig. 7.3 (a) and (b)]. The quantitative analysis is achieved by defining the normalized peak intensity

$$x(T) = \frac{I(T) - I(5K)}{I(300K) - I(5K)} \quad (7.3)$$

where $I(T)$ is the peak intensity at T . The temperature-dependent x-value allows us to monitor subtle differences across the phase transition.

Fig. 7.4 shows the temperature-dependent normalized peak intensities. The smooth change of the normalized peak intensities indicates that phase transitions in lacunar spinel selenides are of the disorder-order type. However, the driving mechanism is not necessarily spin-orbit coupling, as we discovered in GaTa_4Se_8 [16]. Instead, the Jahn-Teller effect introduced the lattice instability in GaV_4Se_8 as verified by dielectric constant measurements [24]. Therefore, we perform model-dependent PDF refinements for GaV_4Se_8 and GaNb_4Se_8 to obtain more insights. The symmetry of the lattice is associated with its space group. Hence, the refinement of the PDF data shows the symmetry of the

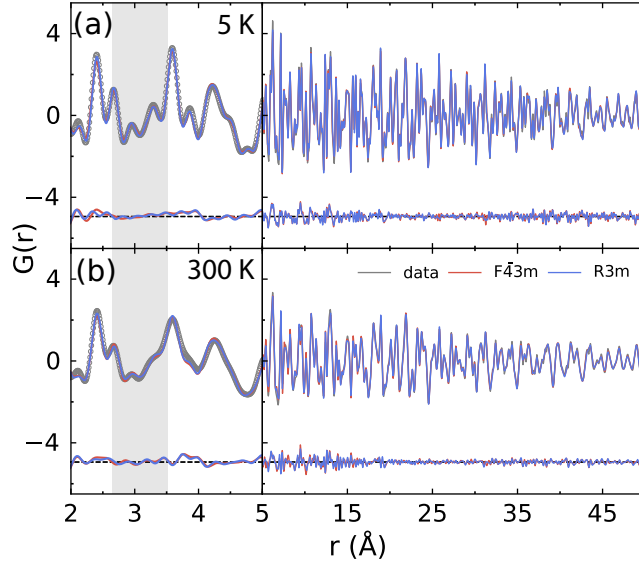


Figure 7.5: Model-dependent refinements for GaV_4Se_8 in $\text{F}\bar{4}3\text{m}$ and $\text{R}3\text{m}$ structures. (a) 5 K. (b) 300 K.

local structure, which is distinct from the average structure obtained from crystallography measurements.

The PDF refinements against high-temperature $\text{F}\bar{4}3\text{m}$ cubic structure and low-temperature $\text{R}3\text{m}$ rhombohedral cell of GaV_4Se_8 are shown in Fig. 7.5. For the local structure, we limit the interatomic distance to 2 to 10 Å for the refinements. The average structure refines to the range from 20 to 30 Å. The R_w values for refinements are listed in Tab. 7.2. At large interatomic distances, both high-temperature and low-temperature structures agree with the measured PDF [Fig. 7.5], while $\text{F}\bar{4}3\text{m}$ cubic structure has a slightly better fit than $\text{R}3\text{m}$ rhombohedral structure at 300 K, as expected that the crystal structure is still a cubic unit cell. At 5 K, $\text{R}3\text{m}$ rhombohedral structure has a better fit than the cubic cell as the consequence of a rhombohedral cell below the structural transition at $T_s = 42$ K.

Table 7.2: R_w values (%) for model-dependent refinements of GaV_4Se_8 .

	$\text{F}\bar{4}3\text{m}$		$\text{R}3\text{m}$	
	local	avg.	local	avg.
5 K	8.16	7.05	7.64	6.11
300 K	9.20	6.82	9.92	7.19

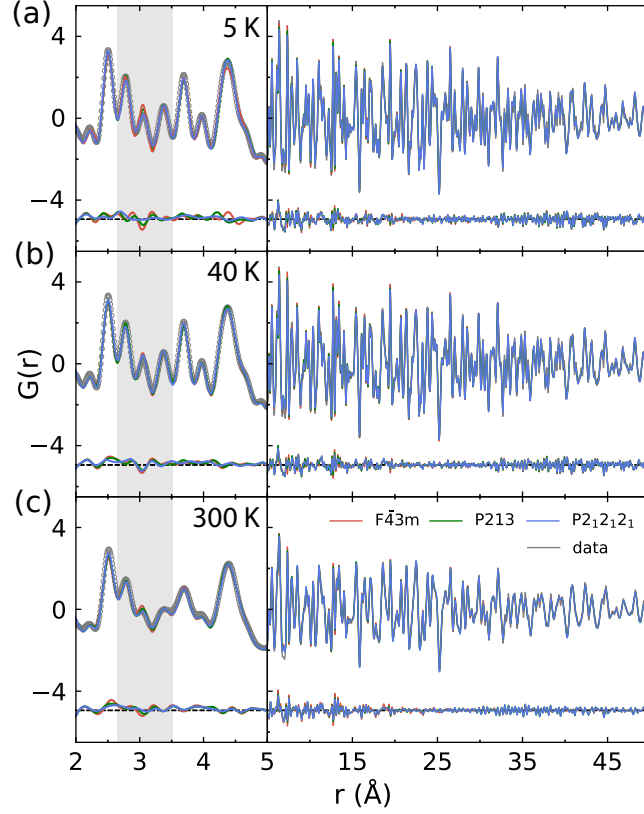


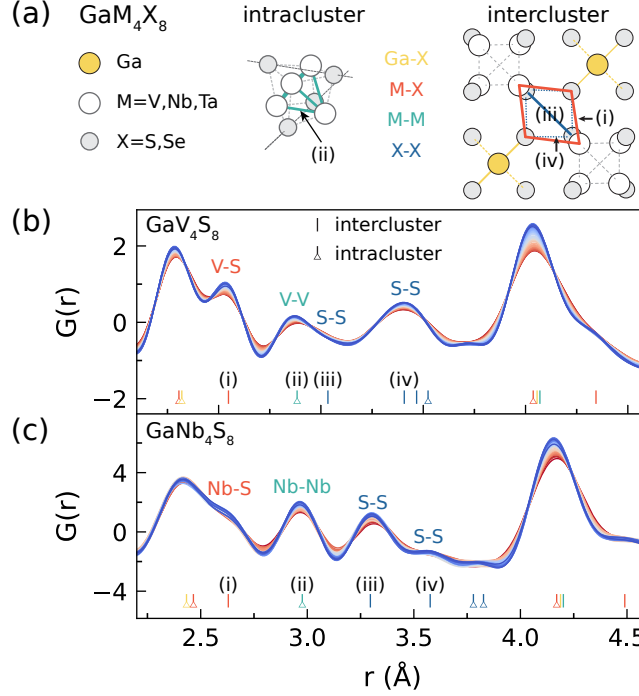
Figure 7.6: Model-dependent refinements for GaNb_4Se_8 in $\bar{F}43m$, $P213$, and $P2_12_12_1$ structures. (a) 5 K. (b) 40 K. (c) 300 K.

Now we shift our focus to GaNb_4Se_8 , which has a stronger spin-orbit coupling. The same model-dependent analysis is applied to the small- and large- r range refinements. As discussed in the previous chapter, GaNb_4Se_8 is the only lacunar spinel studied in this thesis with two structural phase transitions, $\bar{F}43m \rightarrow P213$ and $P213 \rightarrow P2_12_12_1$. Fig. 7.6 shows the PDF refinements at 5 K, 40 K, and 300 K corresponding to the $P2_12_12_1$, $P213$ and $\bar{F}43m$ phases. Table 7.3 lists the corresponding R_w values for refinements. The refinement of GaNb_4Se_8 is distinct from GaV_4S_8 , in which the crystallographic structure always has better refinements locally and globally. The unit cell doubled $P2_12_12_1$ constantly obtains better refinement results throughout all measured temperatures, indicating the symmetry of the local structure at high temperature is already broken.

The temperature-dependent interatomic distances of GaV_4S_8 and GaNb_4S_8 are shown

Table 7.3: Rw values (%) for model-dependent refinements of GaNb_4Se_8 .

	$F\bar{4}3m$		$P2_13$		$P2_12_12_1$	
	local	avg.	local	avg.	local	avg.
5 K	10.28	6.31	10.57	6.25	6.31	6.23
40 K	7.93	5.81	6.66	5.72	6.56	5.41
300 K	9.62	6.76	7.28	5.87	6.37	5.94

Figure 7.7: Temperature-dependent xPDFs for sulfides. (a) Schematic illustration for interatomic distances. (b) GaV_4S_8 . (c) GaNb_4S_8 .

in Fig. 7.7. Similar to lacunar spinel selenides, the x-ray PDFs do not show any apparent new length scales appearing below the transition temperature. The temperature-dependent normalized peak intensities of GaV_4S_8 have smooth change across $T_s = 40$ K and $T_m = 10$ K [Fig. 7.8 (a)], indicating the nature of disorder-order transitions. In contrast, GaNb_4S_8 shows a small peak intensities drop near the phase transition at $T^* = 32$ K [Fig. 7.8 (b)].

Fig. 7.9 shows the PDF refinements at 5 K and 300 K. At 300 K, the $F\bar{4}3m$ cubic structure has a better fit with the $R_1 = 9.52$ % for large- r range, while the rhombohedral $R\bar{3}m$ structure obtains $R_1 = 12.08$ %. For local structure, $F\bar{4}3m$ space group also reproduces

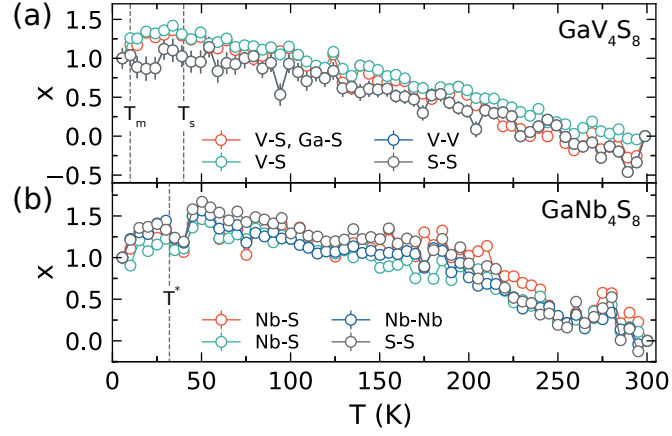


Figure 7.8: Normalized peak intensities (x-values) of GaV_4S_8 and GaNb_4S_8 .

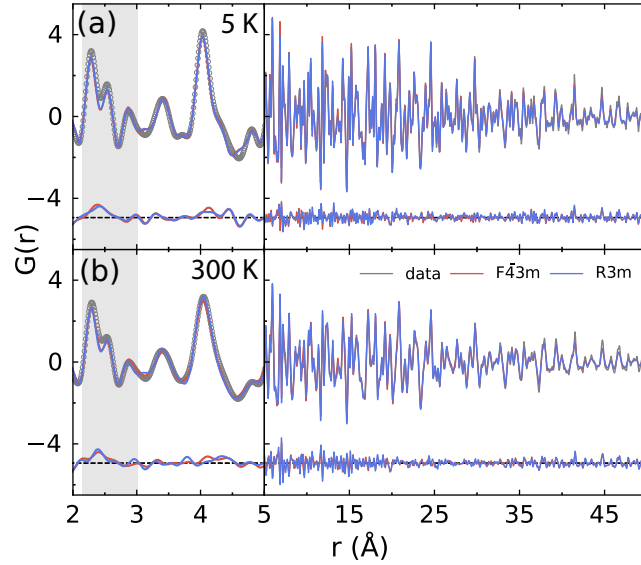


Figure 7.9: Model-dependent refinement for GaV_4S_8 in $\bar{F}43m$ and $P2_12_12_1$ structures. (a) 5 K. (b) 300 K.

a better result than R3m structure [Table 7.4]. This result indicates that the local and global symmetries of GaV_4S_8 remain cubic even though the phase transition is reported as a disorder-order type [43, 108]. On the other hand, the PDF refinement of GaNb_4S_8 shows a similar trend in GaNb_4Se_8 and GaTa_4Se_8 , in which the high-temperature PDF has a better fit to the low-temperature structure [Table 7.5]. However, the data quality of GaNb_4S_8 is not as good as GaNb_4Se_8 and GaTa_4Se_8 , probably due to impurities in the

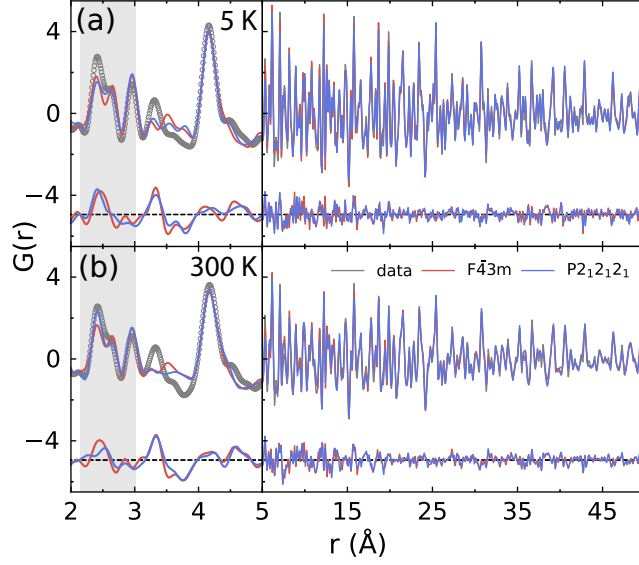


Figure 7.10: Model-dependent refinements for GaNb_4S_8 in $\text{F}\bar{4}3\text{m}$ and $\text{P}2_12_12_1$ structures. (a) 5 K. (b) 300 K.

powder sample [Fig. 7.10].

Table 7.4: Rw values (%) for model-dependent refinements of GaV_4S_8 .

	$\text{F}\bar{4}3\text{m}$		$\text{R}\bar{3}\text{m}$	
	local	avg.	local	avg.
5 K	12.84	10.18	12.09	10.48
300 K	13.74	9.52	17.99	12.08

Table 7.5: Rw values (%) for model-dependent refinements of GaNb_4S_8 .

	$\text{F}\bar{4}3\text{m}$		$\text{P}2_12_12_1$	
	local	avg.	local	avg.
5 K	27.47	13.52	25.49	12.89
300 K	33.48	16.60	29.53	14.93

7.4 Anomalous phonon mode and spin-orbital fluctuations

Having established the local structural distortion and preceding global symmetry breaking. We now are focusing on the evolution of the lattice dynamics as the function of the strength of SOC. We carried out a series of inelastic neutron scattering measurements at Spallation

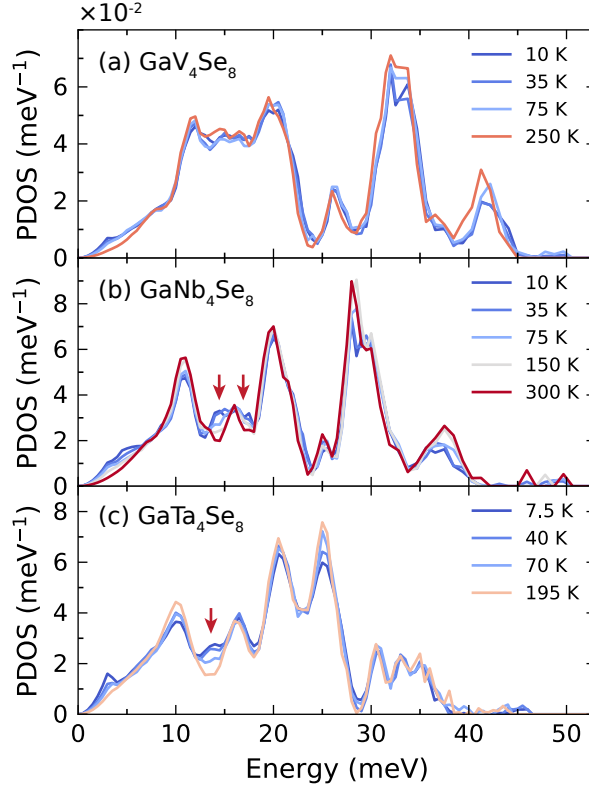


Figure 7.11: Measured phonon density of states. (a) GaV_4Se_8 . (b) GaNb_4Se_8 . (c) GaTa_4Se_8 .

Neutron Source, Oak Ridge national laboratory, to investigate the lattice dynamics in the temperature range of $5 \text{ K} \leq T \leq 300 \text{ K}$.

The most striking result is the anomalous temperature dependence of the phonon mode in strong SOC cases ($M=\text{Nb, Ta}$) [Fig. 7.11 and Fig. 7.12]. In lacunar spinel selenides, our inelastic neutron scattering shows that the phonon anomalies appear at 13 meV in GaNb_4Se_8 and GaTa_4Se_8 but no detectable change in GaV_4Se_8 [Fig. 7.11]. Further, Fig. 7.12 for lacunar spinel sulfides present the same trend of the phonon anomaly, but the energy is slightly higher at 17 meV, indicating the ligand sites (S, Se) contribute to the anomalous phonon mode.

The temperature-dependent mode intensities extracted from inelastic neutron scattering are shown in Fig. 7.13. The anomalous phonon modes extend to at least 120 K, much higher than the transition temperatures ranging from 30 to 50 K. As we mentioned in

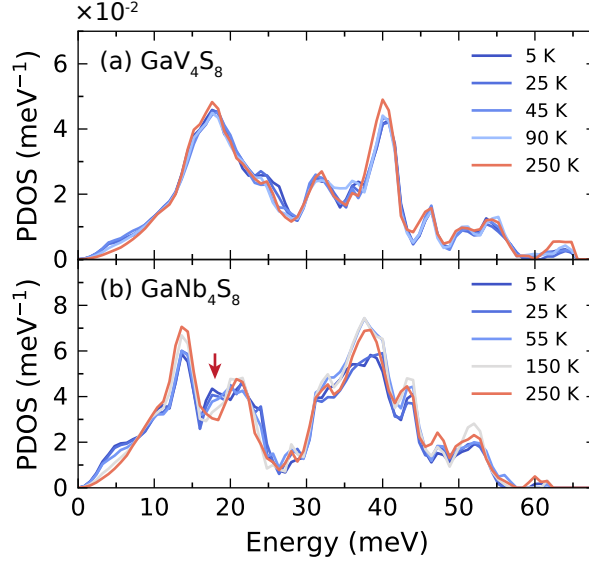


Figure 7.12: Measured phonon density of states. (a) GaV_4S_8 . (b) GaNb_4S_8 .

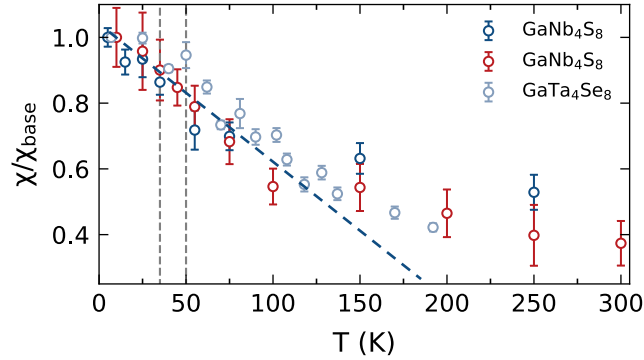


Figure 7.13: Temperature-dependent anomalous phonon mode intensity.

chapter 5, in GaTa_4Se_8 , this phonon mode originates from the low-temperature tetragonal structure, which indicates fluctuations of spin-orbital dimers above the transition temperature $T^* = 50$ K. Here, we performed the first principle phonon calculations for GaV_4Se_8 , GaNb_4Se_8 , GaV_4S_8 , and GaNb_4S_8 . The comparison between those compounds is informative in understanding the nature of anomalous phonon mode in lacunar spinels with stronger spin-orbit coupling.

The first principle phonon calculations of GaV_4Se_8 and GaNb_4Se_8 are shown in Fig. 7.14. In both compounds, the low-energy phonon modes are mainly from the vibration modes

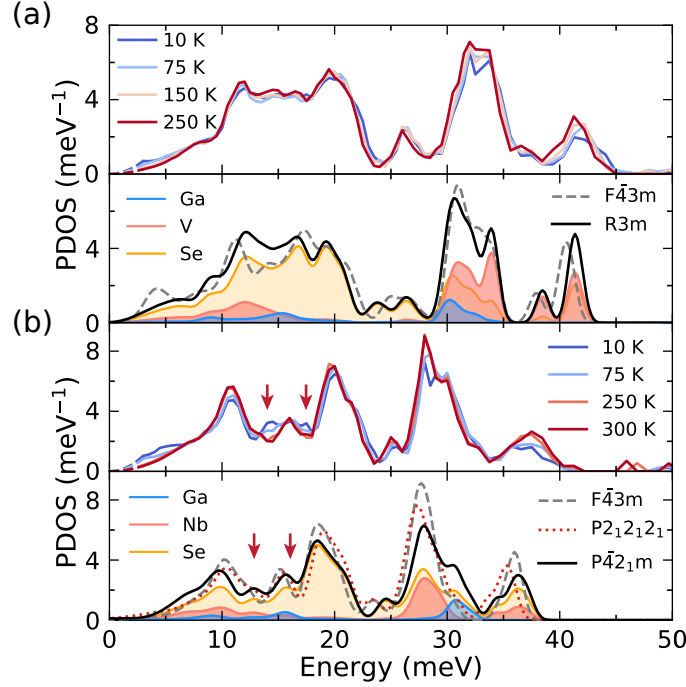


Figure 7.14: Measured and calculated phonon density of states for (a) GaV_4Se_8 and (b) GaNb_4Se_8 .

of seleniums, as indicated by the projected phonon density of states. In GaV_4Se_8 , the low-temperature rhombohedral structure with $R\bar{3}m$ space group does not introduce new phonon modes, but phonon mode intensities change between two structures [Fig. 7.14 (a)]. Experimentally, GaNb_4Se_8 shows a pronounced change in the energy range from 12 to 14 meV [Fig. 7.14 (b)]. However, the phonon calculations for the cubic and orthorhombic structures are almost identical. Surprisingly, the phonon modes obey the symmetry of $P\bar{4}2_1m$ in excellent agreement with the experimental result. This observation implies that the phonon anomaly in GaNb_4Se_8 is driven by spin-orbit coupling as what we observed in GaTa_4Se_8 [16].

Fig. 7.15 shows phonon density of states for GaV_4S_8 and GaNb_4S_8 . Similar to selenides, GaV_4S_8 and GaNb_4S_8 demonstrate the same trend of the anomalous phonon mode. The first principle phonon calculations on $F\bar{4}3m$ and $P2_12_12_1$ are almost identical. However, the phonon calculation based on the symmetry of the tetragonal $P\bar{4}2_1m$ well reproduces

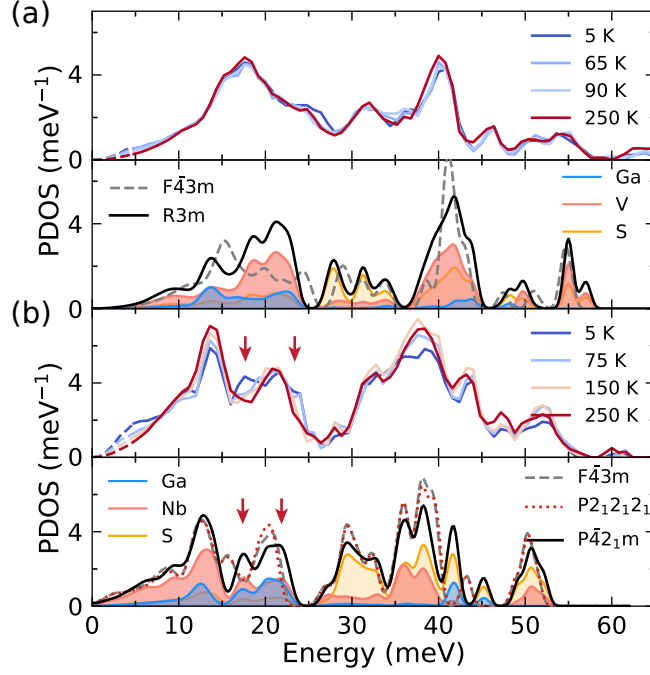


Figure 7.15: Measured and calculated phonon density of states for (a) GaV_4S_8 and (b) GaNb_4S_8 .

the phonon anomalies at 17 and 22 meV.

7.5 Discussion

We find that the structural phase transitions in lacunar spinels, GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$), are the disorder-order type. Our PDF measurements indicate that phase transitions do not create new interatomic distances but change and freeze the bond orientations. The lattice dynamics of lacunar spinels are studied by inelastic neutron scattering, showing the phonon anomaly in stronger spin-orbit coupling lacunar spinels ($\text{M}=\text{Nb}$ and Ta). The systematic comparison, $\text{V} \rightarrow \text{Nb} \rightarrow \text{Ta}$, provides a remarkable opportunity to study the interplay between the Jahn-Teller effect, spin-orbit coupling, and lattice dynamics. In addition, the substitution of ligand site atoms ($\text{S} \leftrightarrow \text{Se}$) changes the lattice size, directly affecting the exchange coupling between correlation units. The competing energy scales give rise to the vast phase space of lacunar spinels, including Néel-type

skyrmion, cooperative Jahn-Teller effect, antipolar ordering, and spin-orbital fluctuations [15, 16, 18, 24, 87].

Interestingly, our PDF measurements do not observe any new length scales appearing across phase transitions in d^1 lacunar spinels. The missing feature of the phase transition in PDF implies a disorder-order type structural phase transition. However, the model-dependent PDF refinements indicate that the transition of GaV_4S_8 and GaV_4Se_8 is distinct from that in GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 . GaV_4S_8 and GaV_4Se_8 have Jahn-Teller-driven phase transitions. Above the structural phase transition, both local and average structures have better fits to $F\bar{4}3m$ cubic structure, and $R\bar{3}m$ rhombohedral structure constantly obtains better results below the transition temperature. On the other hand, the local structure of GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 can not be captured by the high-temperature cubic structure, and the low-temperature structure obtains a better fit through the entire measured temperature range from 5 K to 310 K. This result indicates that the local symmetry is already broken before phase transitions.

Our inelastic neutron scattering measurements directly observe the phonon anomaly associated with the spin-orbital dimer phase in GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 . In the strong SOC limit, GaTa_4Se_8 , the phonon density of states and the local structure agree with the low-temperature $P\bar{4}2_1m$ structure. With a weaker spin-orbit coupling in GaNb_4S_8 and GaNb_4Se_8 , the anomalous phonon mode from the symmetry of $P\bar{4}2_1m$ space group survives, but the crystal structure turns into a unit cell doubled orthorhombic $P2_12_12_1$ cell. This observation reinforces that the phonon anomaly is induced by spin-orbit coupling.

In a system with octahedral coordination and d^1 configuration, a single electron occupies a t_{2g} level. Two distortion modes, Q_2 and Q_3 [Fig. 7.2 (b) and (c)], are available to stabilize the lattice by lowering the total energy. In a system with dominating Jahn-Teller effect, there are four energetic minimums in the distortion mode coordinates, resulting in the system staying at one of four distortions [14]. As the spin-orbit coupling increases, the energy barriers between minimums decrease, which activates the quantum tunneling between minimums. Due to the strong spin-orbit coupling, the system stabilizes the

complex wavefunction, in which spin, orbital, and lattice are entangled. This quantum tunneling is represented by the anomalous phonon mode. It becomes clear with the wavefunctions of $j_{eff}=3/2$

$$\begin{aligned} |j_{3/2}, j_{3/2}^z\rangle &= |l_1^z, \uparrow\rangle = -\frac{1}{\sqrt{2}}(i|xz, \uparrow\rangle + |yz, \uparrow\rangle) \\ |j_{3/2}, j_{-3/2}^z\rangle &= |l_{-1}^z, \downarrow\rangle = -\frac{1}{\sqrt{2}}(i|xz, \downarrow\rangle - |yz, \downarrow\rangle) \end{aligned} \quad (7.4)$$

$$\begin{aligned} |j_{3/2}, j_{1/2}^z\rangle &= \sqrt{\frac{2}{3}}|l_0^z, \uparrow\rangle + \frac{1}{\sqrt{3}}|l_1^z, \downarrow\rangle = \sqrt{\frac{2}{3}}|xy, \uparrow\rangle - \frac{1}{\sqrt{6}}|ixz + yz, \downarrow\rangle \\ |j_{3/2}, j_{-1/2}^z\rangle &= \sqrt{\frac{2}{3}}|l_0^z, \downarrow\rangle + \frac{1}{\sqrt{3}}|l_{-1}^z, \uparrow\rangle = \sqrt{\frac{2}{3}}|xy, \downarrow\rangle - \frac{1}{\sqrt{6}}|ixz - yz, \uparrow\rangle \end{aligned} \quad (7.5)$$

The orbital part of $j_{\pm 3/2}^z$ only contains $|xz\rangle$ and $|yz\rangle$, therefore, the wavefunction is stabilized with elongated octahedral. On the other hand, the $|xy\rangle$ orbital dominates the $j_{\pm 1/2}^z$ wavefunctions, preferring a compressed octahedral.

7.6 Conclusion

In conclusion, combining a series of x-ray pair distribution function measurements, inelastic neutron scattering, and first principle phonon calculation, we provide promising evidence for spin-orbital fluctuations in lacunar spinels with strong spin-orbit coupling. The systematic comparison of GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$) provides an unprecedented opportunity to investigate the novel quantum phase induced by the competing Jahn-Teller effect and spin-orbit coupling. In stronger spin-orbit coupling lacunar spinels, GaNb_4S_8 , GNSe , and GaTa_4Se_8 , the local structure is already distorted up to 310 K, indicating a disorder-order phase transition. The lattice dynamics are studied by inelastic neutron scattering and first principle phonon calculation, showing that the local distortion is dynamic and induced by spin-orbit coupling. The spin-orbital fluctuation corresponds to the quantum tunneling between potential minimums of lattice distortions. Our comprehensive studies shed light on understanding the novel quantum phases in unconventional molecular $j_{eff}=3/2$ systems.

Chapter 8

Pressure-dependent Phase Transitions of GaTa₄Se₈

This chapter contains the high-pressure diamond anvil cell measurements for GaTa₄Se₈. The high-pressure phases of GaTa₄Se₈ are interesting because the unconventional $j_{eff}=3/2$ feature survives at high pressure in the metallic and superconducting phases. Here we carried out high-pressure x-ray diffraction measurements to investigate the structural transition in GaTa₄Se₈ across insulator-metal and metal-superconductor phase transitions. This work provides preliminary results and could guide future studies for the unconventional phases of GaTa₄Se₈ at high-pressure.

8.1 Introduction

The ability to tune the material property is crucial for understanding phase transitions and material applications. For example, in Mott insulators, the electronic gap is produced by strong Coulomb repulsion, which is sensitive to the distances between electrons. A hydrostatic pressure environment reduces the volume of material and directly alters the electron Coulomb interaction.

GaTa₄Se₈ has a insulator-metal transition at 5 GPa, and becomes superconducting at

10 GPa [54, 80, 100, 102]. Recently, resonant inelastic x-ray scattering (RIXS) measurements confirmed that the $j_{eff}=3/2$ state survives at high pressure up to 12 GPa, indicating that the metallic and superconducting phases are unconventional [107]. Interestingly, recent research found that the strong spin-orbit coupling can play a crucial role in GaTa_4Se_8 and creates the topological superconducting phase at high pressure [100]. However, the investigation of structures in high-pressure phases is missing, which is crucial in understanding the unconventional quantum phases in GaTa_4Se_8 .

In this work, we study pressure-dependent structural phase transitions in GaTa_4Se_8 using a high-pressure diamond anvil cell and x-ray diffraction. At low pressure, a small strain on the single crystal of GaTa_4Se_8 breaks the domain structure, and the superlattice peaks are along a single axis. As the pressure increases, we observe the redistribution of the intensities of weak reflections, indicating that the crystal structure is distorted. Above the pressure of the superconducting phase, our diffraction data shows that the unit cell changes to an I-centered tetragonal cell due to the absence of $h+k+l = 2n+1$ peaks. This preliminary result is crucial for the proposed unconventional topological superconducting phase of GaTa_4Se_8 at high-pressure.

8.2 Methods

High-pressure diamond anvil cell

We used a diamond anvil cell (DAC) for the high-pressure sample environment. The Diacell Bragg-LT(G) Plus DAC system from Almax-easyLab and two diamonds with 800 μm culet size were used to achieve the pressure range from ambient to 14 GPa. The gaskets were made with a pre-indented 150 μm thick stainless steel 301 sheet, and an electrical discharge machining drill made the hole. The sample and a piece of Ag foil were mounted on the diamond using silicon grease. We used an ethanol-methanol mixture for the pressure medium within our measured pressure range. Then entire DAC was mounted on the closed-cycle helium cryostat for low-temperature experiments.

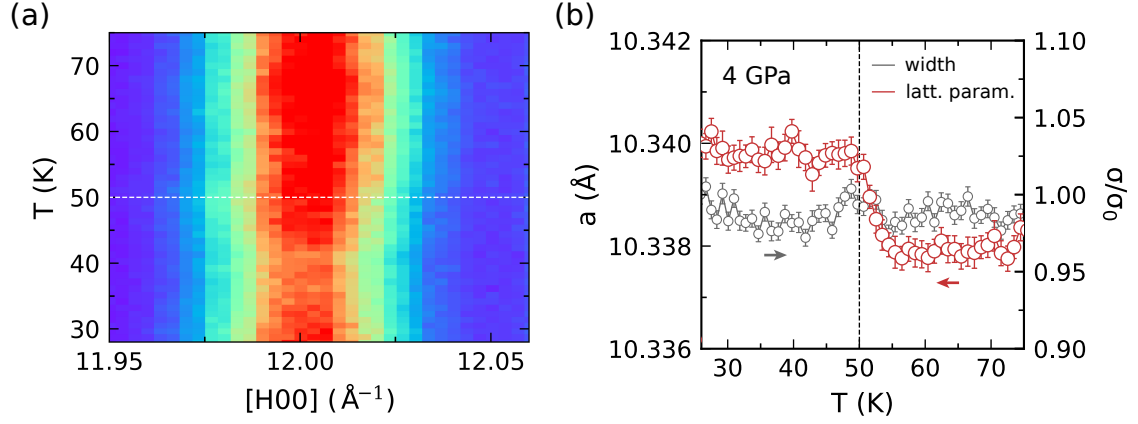


Figure 8.1: Temperature-dependent $[12,0,0]$ peak and lattice parameter at 4 GPa. (a) Longitudinal cut through $[12,0,0]$ peak. (b) Temperature-dependent lattice parameter and normalized peak width extracted from $[12,0,0]$ peak in (a). The peak width is normalized to the width at 25 K.

8.3 Preliminary Results

At ambient pressure, the broadening of the $[H00]$ type peak due to the domain structure allows us to determine the unit cell of GaTa_4Se_8 below the transition temperature [16]. However, the domain structure can be broken by a small strain from the inhomogeneity of the pressure distribution of the sample environment. Resulting in the separation of structural Bragg's reflections, which allows us to disentangle two different lattice parameters, a and c , in a tetragonal unit cell.

Fig. 8.1 shows the results from temperature-dependent diffraction measurements on the cubic $[12,0,0]$ reflection at 4 GPa. There are two major observations. First, the width of $[12,0,0]$ peak remains the same across the phase transition at 50 K [Fig. 8.1]. This is because the domains at ambient pressure align in the same direction under pressure. Second, the lattice parameter extracted from $[12,0,0]$ increases below the transition temperature [Fig. 8.1 (b)]. Since the insulator-metal phase transition occurs at 5 GPa, the lattice parameter extracted from $[12,0,0]$ must be along a or b -axis, and the lattice parameter along the c -axis should be able to check with the other measurement on any $[1,1,1]$ type reflection.

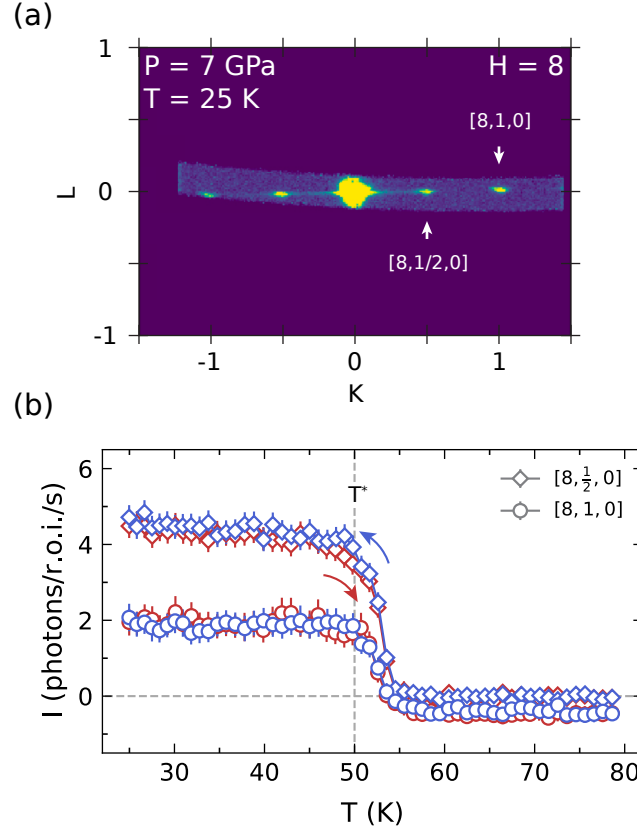


Figure 8.2: Temperature-dependent peak intensities at 7 GPa. (a) The reciprocal space reconstruction from a series of x-ray diffraction scans. (b) Temperature-dependent peak intensity for $[8, \frac{1}{2}, 0]$ and $[8, 1, 0]$ reflections.

Considering the sibling compound, GaNb_4Se_8 , in which we found that the cubic $[8, 1/2, 0]$ and $[8, 1, 0]$ contribute to different distortion modes and are separated. Therefore, we check the temperature-dependence of $[8, 1/2, 0]$ and $[8, 1, 0]$ in the metallic phase at 7 GPa [Fig. 8.2]. Fig. 8.2 (a) shows the reconstruction of the reciprocal space at 25 K. The intensity is calculated by the integration of the counts around the peak. The integrated peak intensities are shown in Fig. 8.2 (b). Our result at 7 GPa indicates that both $[8, 1/2, 0]$ and $[8, 1, 0]$ appear at 53 K, and the intensity saturates at 50 K upon cooling. The structure of the superconducting phase has a different low-temperature space group to the Mott insulator and metallic phases. A series of pressure-dependent measurements of a wide range of momentum space is shown in Fig. 8.3. At ambient pressure, GaTa_4Se_8 has

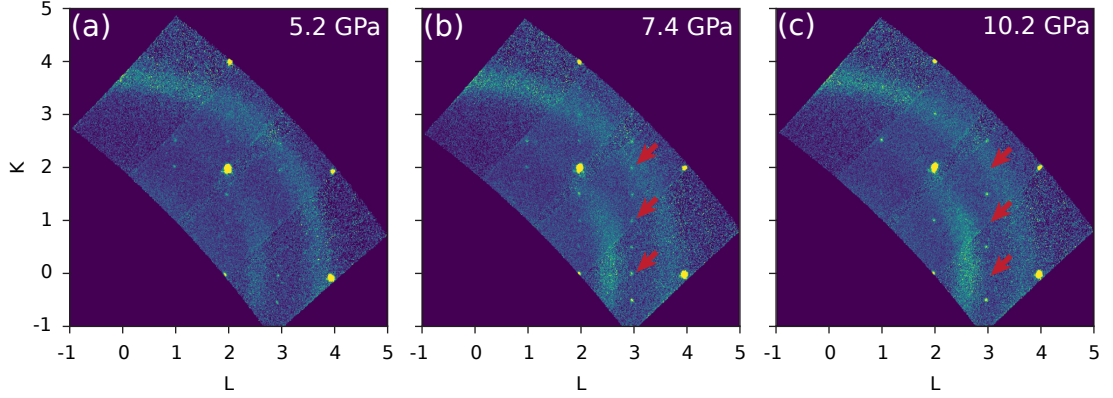


Figure 8.3: Pressure-dependent reconstructions of reciprocal space from a series of x-ray diffraction measurements. (a) 5.2 GPa. (b) 7.4 GPa. (c) 10.2 GPa. Red arrows indicate reflections that satisfy the reflection condition: $h + k + l = 2n + 1$.

a unit cell doubled tetragonal $P\bar{4}2_1m$ structure. As the pressure approaches the insulator-metal transition at 5 GPa, the intensity drops for peaks do not satisfy the condition h, k, l (all h, k, l are even or odd) [Fig. 8.3 (a)]. In the metallic phase, reflections still satisfy the extinction rule for the tetragonal $P\bar{4}2_1m$ space group, indicating that the unit cell and crystal symmetry remain the same [Fig. 8.3 (b)]. However, the superconducting phase, above 10 GPa, shows different reflection conditions, where the $h + k + l = 2n + 1$ reflections are missing, indicating an I-centered tetragonal space group for the superconducting phase.

The reflections of the superconducting phase satisfy the reflection condition: $h + k + l = 2n$, and the superlattice reflections only appear along one reciprocal axis [Fig. 8.3 (c)]. Those two observations already indicate that the structure is a unit cell doubled I-centered tetragonal cell, and there are only three possible space groups, $I\bar{4}$, $I\bar{4}2m$, and $I\bar{4}2d$.

8.4 Summary and Future work

The preliminary results for the crystal structure of GaTa_4Se_8 at high pressure indicate that the structure at the metallic phase has the symmetry of $P\bar{4}2_1m$ space group as in the ambient pressure. While in the superconducting phase, the structure has higher symmetry, and Bragg's reflections obey the extinction rule of an I-centered tetragonal

space group. Investigating the x-ray diffraction measure at 10.2 GPa and possible space groups, we conclude that only three space groups satisfy the conditions, $I\bar{4}$, $I\bar{4}2m$, and $I\bar{4}2d$. Therefore, more diffraction measurements are required to determine the actual structure for further theoretical investigations for the interesting topological superconducting phase in GaTa_4Se_8 .

Chapter 9

Inelastic Neutron Scattering of GaTa_4Se_8 single crystal arrays

9.1 Introduction

GaTa_4Se_8 is a Mott insulator with tetrahedral clusters on Ta_4 on which a single unpaired electron is localized. The molecular orbital wavefunctions maintain the character of the d-orbitals, and strong spin-orbit coupling results in the formation of highly quantum $j_{eff}=3/2$ molecular orbitals, as confirmed by resonant inelastic x-ray scattering [20]. Neutron diffraction, μSR , and NMR measurements find no evidence for magnetic order [26]. Detailed information about the momentum and energy structure of these excitations is required to elucidate the quantum state of this model material, and measurements on single crystals are required.

9.2 Methods

Single crystal arrays

We co-aligned more than six thousand GaTa_4Se_8 single crystals on our custom-designed metallic 3D-printed sample mount [Fig. 9.1 and 9.2]. The dimensions of the sample mount

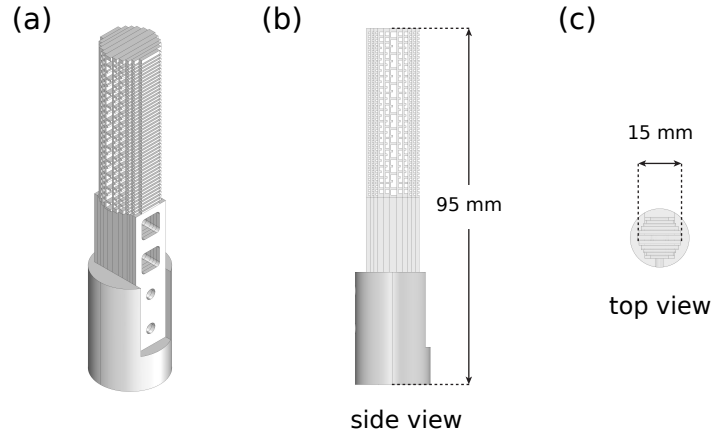


Figure 9.1: Design of the sample mount for neutron scattering. (a) The sample mount consists 11 thin plate to hold single crystals. The entire mount carries over 6000 single crystals of GaTa_4Se_8 . (b) The side view of the sample mount. The height is designed for the CCR helium cryostat at SNS at ORNL. (c) The top view of the sample mount. The diameter of the cylinder is designed as 15 mm for the scattering cross-section of GaTa_4Se_8 .

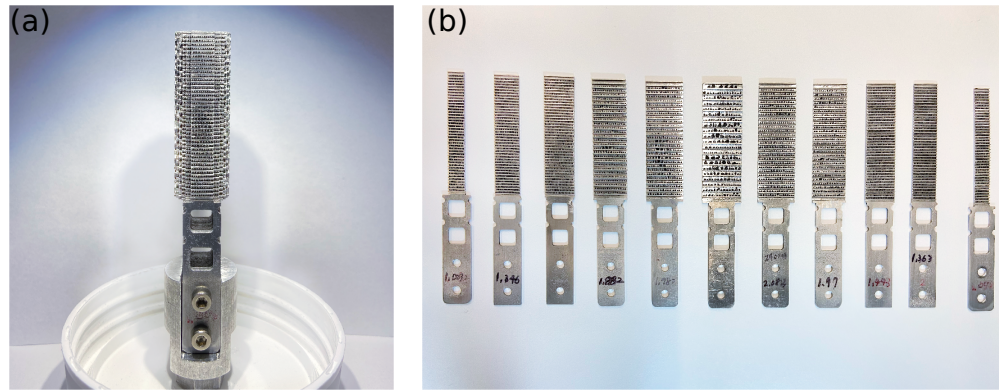


Figure 9.2: The finished GaTa_4Se_8 single crystal arrays and 11 plates holding various sizes of single crystals. (a) The assembled sample mount. (b) the front view of all plates and single crystals.

are designed to obtain the optimal coverage of the incident neutron beam at SEQUOIA spectrometer at Spallation Neutron Source (SNS). The sample mount consists of 11 thin aluminum plates, each with 20 to 40 rows of teeth to hold single crystals in position. We used hydrogen-free Fomblim grease as the adhesive to mount single crystals. The single crystal size ranges from $500 \mu\text{m}$ to 2 mm . The preparation of the single crystal GaTa_4Se_8 is shown in Chapter 4.

Inelastic neutron scattering

Inelastic neutron scattering measurements were carried out on the SEQUIOA spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. 1.8 g single crystal arrays were loaded into an Al sample can and mounted on the cold finger of a closed cycle cryostat to achieve a base temperature of 5 K. Measurements were conducted using a fixed incident energy $E_i = 25, 45$, and 80 meV, and the coarse Fermi chopper rotating at 300 Hz. We used the high-flux mode, which provides an energy resolution at the elastic line of 0.85, 1.265, and 4.24 meV for $E_i = 25, 45$, and 80 meV, respectively. All data were normalized and reduced using algorithms in the MANTID analysis software [58].

9.3 Results and future work

Fig. 9.3 shows $S(Q)$ at 5 K with $E_i = 80$ and 25 meV. The background is subtracted by measuring an empty sample mount for each experimental configuration. The $S(Q)$ demonstrates the high quality of the GaTa_4Se_8 single crystal array, where we can see clear Bragg reflections from the co-aligned single crystals [Fig. 9.3 (a) and (b)]. Unfortunately, we do not observe the superlattice reflections from our measurements, which could be the problem of strong neutron absorption cross-sections of Ta ($\sigma_{abs} = 20.6$ barn) and Se ($\sigma_{abs} = 11.7$ barn). We reduce the single crystal data as a powder sample for the inelastic neutron scattering to emphasize the weak signals. Fig. 9.4 shows the $S(\text{---}Q\text{---}, E)$ with the incident energy $E_i = 45$ meV.

Although we successfully co-aligned more than 6000 single crystals on the custom-designed sample holder, the scattering from the sample is still too weak to map out the neutron dispersion relation due to the absorption of Ta and Se atoms. The future work to improve the experiment can be in two directions: First, the sample can be improved by overcoming the limit of single crystal size. The possible method is self-selecting vapor growth which can obtain large high-quality single crystals in a reasonable time [109]. Second, the lower incident neutron energy can be used to gain energy resolution and

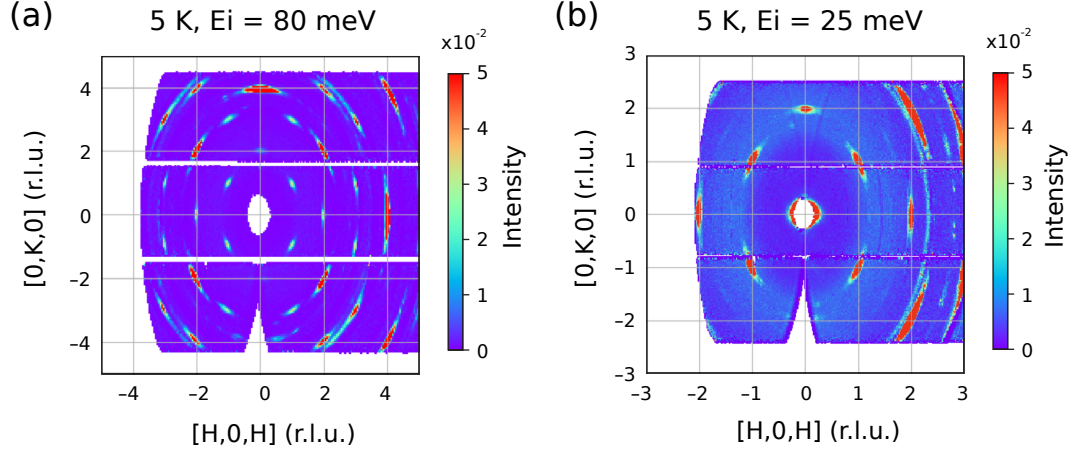


Figure 9.3: Measured structure factor $S(Q)$ at 5 K. The $S(Q)$ is obtained by integrating the energy of $S(Q,E)$ from $-\delta E$ to δE , where δE is the energy resolution. (a) $E_i = 80$ meV. (b) $E_i = 25$ meV.

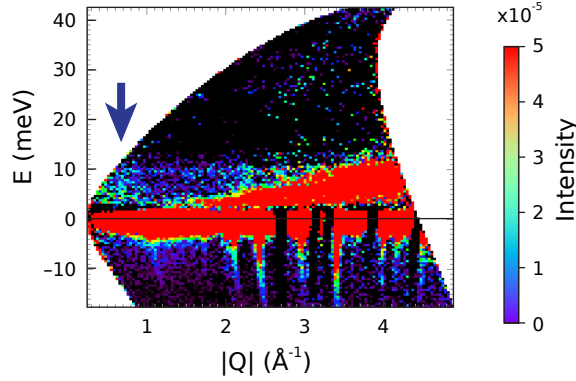


Figure 9.4: Inelastic neutron scattering with $E_i = 45$ meV and reduced as powder to emphasize the weak signals. The excitations at low $|Q|$ (indicated by the blue arrow) indicate the magnetic excitations at 5 K.

reduce the background. This can be achieved by using a cold neutron source facility like the CNCS beamline at Spallation Neutron Source at ORNL.

Chapter 10

Conclusion

This thesis presented comprehensive studies on the lattice structure, local distortion, lattice dynamics of d^1 lacunar spinels. The novel phase we observed in the strong spin-orbit coupling limit, GaTa_4Se_8 , demonstrates the spin-orbital fluctuations and bond ordering of molecular $J_{eff}=3/2$ states. The systematic investigation of d^1 lacunar spinels carried out in this thesis provides an unprecedented opportunity to explore the interaction between the Jahn-Teller effect, spin-orbit coupling, electronic correlation, and exchange in $J_{eff}=3/2$ cluster Mott insulators, and revealing the roles of these energy scales for stabilizing quantum phases of matter. Finally, the high-pressure x-ray diffraction measurements uncovered the structural phase transition in the putative topological superconducting phase in GaTa_4Se_8 . The results presented in this thesis can guide future research on the unconventional quantum phases in lacunar spinels.

In Chapter 5, we have used a combination of single crystal diffraction, total scattering, and inelastic neutron scattering measurements to show that Ta_4 tetrahedral clusters in GaTa_4Se_8 are locally and dynamically distorted up to at least 300 K. We resolve the optical phonon modes associated with lattice fluctuations between degenerate orbital configurations on the FCC lattice. We propose that the degeneracy of these configurations is broken through inter-cluster spin-orbit exchange interactions. A collective order-disorder spin-orbital transition in GaTa_4Se_8 is characterized by the long-range orientational ordering

of distorted Ta_4 clusters to form weak structural dimers aligned along $\langle 110 \rangle$ directions. This suggests that a spin-orbital valence bond solid ground state may be realized in GaTa_4Se_8 .

In Chapter 6, we have used a series of single crystal diffraction, crystallography and space group analysis to show that two phase transitions are related to the competition between the Jahn-Teller effect and spin-orbit coupling. We resolved the detailed structures in the low-temperature phases and used group theory analysis to decouple the contributions from two effects. At the quadrupolar order temperature, $T_Q = 50$ K, we found the phase transition is continuous and can be described by the irreducible representation X_5 mode, which is Jahn-Teller active. The structure of the spin-orbital ordered phase at $T^* = 29$ K is also provided, showing the unit cell doubles due to the canted order of spin-orbital dimers. The phase transitions in GaNb_4Se_8 is distinct from other sibling compounds and allows the investigation of the interaction between multiple energy scales. Further theoretical studies are required to understand the unexplored new type molecular $J_{eff} = 3/2$ Mott insulators.

In Chapter 7, we combined a series of x-ray pair distribution function measurements, inelastic neutron scattering, and first principle phonon calculation, which provide promising evidence for spin-orbital fluctuations in lacunar spinels with strong spin-orbit coupling. The systematic comparison of GaM_4X_8 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$) provides an unprecedented opportunity to investigate the novel quantum phase induced by the competing Jahn-Teller effect and spin-orbit coupling. In stronger spin-orbit coupling lacunar spinels, GaNb_4S_8 , GaNb_4Se_8 , and GaTa_4Se_8 , the local structure is already distorted up to 310 K, indicating a disorder-order phase transition. The lattice dynamics are studied by inelastic neutron scattering and first principle phonon calculation, showing that the local distortion is dynamic and induced by spin-orbit coupling. The spin-orbital fluctuation corresponds to the transitions between potential minimums of lattice distortions. Our comprehensive studies shed light on understanding the novel quantum phases in unconventional molecular $j_{eff}=3/2$ systems.

In Chapter 8, the preliminary results for the crystal structure of GaTa_4Se_8 at high pressure indicate that the structure at the metallic phase has the symmetry of $\text{P}\bar{4}2_1\text{m}$ space group as in the ambient pressure. While in the superconducting phase, the structure has higher symmetry, and Bragg's reflections obey the extinction rule of an I-centered tetragonal space group. Investigating the x-ray diffraction measured at 10.2 GPa and possible space groups, we conclude that only three space groups satisfy the conditions, $\text{I}\bar{4}$, $\text{I}\bar{4}2\text{m}$, and $\text{I}\bar{4}2\text{d}$. However, more diffraction measurements are required to determine the detailed atomic positions for further theoretical investigations for the interesting topological superconducting phase in GaTa_4Se_8 .

To conclude, the studies presented in this thesis demonstrate the novel quantum phases in strong spin-orbit coupling lacunar spinels. In these model materials, the Jahn-Teller effect is suppressed by the Jahn-Teller effect suppressed by spin-orbit coupling promotes quantum fluctuations in spin and orbital degrees of freedom. On the other hand, the enlarged spin space of $j_{\text{eff}}=3/2$ introduces more fluctuations in the material, opening up to possibility to realize long-sought spin-orbital liquid phases of matter. Therefore, the novel fluctuating phase we observed is not limited for lacunar spinels. This phenomenon can be generalized to other crystal structures and materials with $j=3/2$ ground state.

Appendix A

Irreducible representation modes for lattice distortions

This appendix contains the information of the atomic distortions for GaNb_4Se_8 and GaTa_4Se_8 from space group theory analysis using Bilbao crystallography server [104–106].

A.1 GaNb_4Se_8

Table A.1 and A.2 are refined crystal structure and atomic displacements at 40 K. Table A.3 and A.4 are Γ and X_5 distortion modes in $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_13$ phase transition. Table A.5 shows the atomic distortion related to the high temperature $\text{F}\bar{4}3\text{m}$ structure. Table A.6 to A.13 list distortion normal modes for $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$ phase transition.

Table A.1: GaNb_4Se_8 : Fractional atomic positions at 40 K for $\text{P}2_13$ space group.

Atom	WP	x	y	z	U
Ga1	4a	0.49948(8)	0.50052(8)	0.00052(8)	0.003870
Nb1	12b	0.60424(4)	0.60347(4)	0.39955(4)	0.004973
Nb2	4a	0.39542(4)	0.39542(4)	0.39542(4)	0.003990
Se1	4a	0.63364(6)	0.36636(6)	0.86636(6)	0.003470
Se2	12b	0.63454(6)	0.63342(7)	0.13584(6)	0.004070
Se3	4a	0.63761(8)	0.63761(8)	0.63761(8)	0.006660
Se4	12b	0.63413(7)	0.36412(6)	0.36489(6)	0.004167

Table A.2: GaNb₄Se₈: Atomic displacements at 40 K.

Atom	WP	δ_x/a	δ_y/b	δ_z/c	$ u $ (Å)
Ga1	4a	0.0005	-0.0005	0.0005	0.0094
Nb1	12b	0.0011	0.0003	0.0027	0.0304
Nb2	4a	-0.0015	-0.0015	-0.0015	0.0263
Se1	4a	0.0007	-0.0007	0.0007	0.0124
Se2	12b	-0.0009	-0.0015	-0.0002	0.0185
Se3	4a	0.0020	0.0020	0.0020	0.0361
Se4	12b	-0.0003	0.0005	-0.0015	0.0165

Table A.3: F $\bar{4}3m \rightarrow P2_13$: Γ_1 mode

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0000
Nb1	12b	0.0088	0.0088	-0.0088
Nb2	4a	-0.0088	-0.0088	-0.0088
Se1	4a	-0.0041	0.0041	-0.0041
Se2	12b	0.0041	-0.0041	-0.0041
Se3	4a	0.0099	0.0099	0.0099
Se4	12b	-0.0099	-0.0099	0.0099

Table A.4: F $\bar{4}3m \rightarrow P2_13$: X_5 mode

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0031	-0.0031	0.0031
Nb1	12b	0.0064	0.0017	0.0165
Nb2	4a	-0.0084	-0.0084	-0.0084
Se1	4a	0.0044	-0.0044	0.0044
Se2	12b	-0.0057	-0.0090	-0.0011
Se3	4a	0.0117	0.0117	0.0117
Se4	12b	-0.0012	0.0035	-0.0094

Table A.5: GaNb_4Se_8 : Atomic displacements at 20 K.

Atom	WP	δ_x/a	δ_y/b	δ_z/c	$ u $ (Å)
Ga1	4a	-0.0025	0.0011	0.0000	0.0286
Ga2	4a	-0.0002	0.0014	-0.0000	0.0143
Nb1	4a	0.0011	0.0024	-0.0030	0.0680
Nb2	4a	-0.0003	0.0016	0.0018	0.0421
Nb3	4a	-0.0002	-0.0027	-0.0004	0.0296
Nb4	4a	-0.0010	-0.0024	-0.0005	0.0287
Nb5	4a	-0.0053	-0.0033	0.0003	0.0655
Nb6	4a	0.0007	-0.0014	0.0015	0.0351
Nb7	4a	-0.0048	-0.0035	0.0003	0.0623
Nb8	4a	-0.0001	-0.0013	-0.0011	0.0272
Se1	4a	0.0007	0.0015	-0.0001	0.0173
Se2	4a	-0.0007	0.0014	0.0015	0.0346
Se3	4a	0.0005	0.0001	0.0011	0.0229
Se4	4a	0.0003	0.0030	0.0012	0.0394
Se5	4a	-0.0006	0.0007	0.0012	0.0277
Se6	4a	0.0010	0.0018	-0.0017	0.0419
Se7	4a	0.0023	-0.0006	-0.0001	0.0247
Se8	4a	0.0033	-0.0015	0.0000	0.0377
Se9	4a	-0.0024	-0.0014	-0.0025	0.0591
Se10	4a	-0.0046	-0.0026	0.0020	0.0681
Se11	4a	0.0004	-0.0012	-0.0001	0.0137
Se12	4a	0.0009	-0.0008	-0.0003	0.0139
Se13	4a	-0.0003	-0.0013	-0.0019	0.0415
Se14	4a	0.0010	0.0025	-0.0007	0.0321
Se15	4a	0.0007	0.0023	-0.0006	0.0284
Se16	4a	0.0012	-0.0014	0.0008	0.0250

Table A.6: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: Γ_1 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0000
Ga2	4a	0.0000	0.0000	0.0000
Nb1	4a	0.0059	0.0059	-0.0030
Nb2	4a	-0.0059	-0.0059	-0.0030
Nb3	4a	-0.0059	0.0059	0.0030
Nb4	4a	0.0059	-0.0059	0.0030
Nb5	4a	-0.0059	0.0059	0.0030
Nb6	4a	-0.0059	-0.0059	-0.0030
Nb7	4a	0.0059	-0.0059	0.0030
Nb8	4a	0.0059	0.0059	-0.0030
Se1	4a	0.0018	-0.0018	0.0009
Se2	4a	-0.0018	0.0018	0.0009
Se3	4a	-0.0018	-0.0018	-0.0009
Se4	4a	0.0018	0.0018	-0.0009
Se5	4a	0.0018	0.0018	-0.0009
Se6	4a	-0.0018	-0.0018	-0.0009
Se7	4a	-0.0018	-0.0018	-0.0009
Se8	4a	0.0018	0.0018	-0.0009
Se9	4a	0.0076	0.0076	0.0038
Se10	4a	-0.0076	-0.0076	0.0038
Se11	4a	-0.0076	0.0076	-0.0038
Se12	4a	0.0076	-0.0076	-0.0038
Se13	4a	0.0076	0.0076	0.0038
Se14	4a	-0.0076	0.0076	-0.0038
Se15	4a	0.0076	-0.0076	-0.0038
Se16	4a	-0.0076	-0.0076	0.0038

Table A.7: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: Γ_3 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0000
Ga2	4a	0.0000	0.0000	0.0000
Nb1	4a	-0.0047	0.0005	-0.0021
Nb2	4a	0.0047	-0.0005	-0.0021
Nb3	4a	0.0047	0.0005	0.0021
Nb4	4a	-0.0047	-0.0005	0.0021
Nb5	4a	0.0047	0.0005	0.0021
Nb6	4a	0.0047	-0.0005	-0.0021
Nb7	4a	-0.0047	-0.0005	0.0021
Nb8	4a	-0.0047	0.0005	-0.0021
Se1	4a	0.0043	-0.0070	-0.0056
Se2	4a	-0.0043	0.0070	-0.0056
Se3	4a	-0.0043	-0.0070	0.0056
Se4	4a	0.0043	0.0070	0.0056
Se5	4a	0.0043	0.0070	0.0056
Se6	4a	-0.0043	-0.0070	0.0056
Se7	4a	-0.0043	-0.0070	0.0056
Se8	4a	0.0043	0.0070	0.0056
Se9	4a	0.0008	0.0048	-0.0028
Se10	4a	-0.0008	-0.0048	-0.0028
Se11	4a	-0.0008	0.0048	0.0028
Se12	4a	0.0008	-0.0048	0.0028
Se13	4a	0.0008	0.0048	-0.0028
Se14	4a	-0.0008	0.0048	0.0028
Se15	4a	0.0008	-0.0048	0.0028
Se16	4a	-0.0008	-0.0048	-0.0028

Table A.8: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: $\Delta_3\Delta_4$ mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	-0.0058	-0.0007	0.0000
Ga2	4a	0.0058	0.0007	0.0000
Nb1	4a	0.0003	0.0085	-0.0028
Nb2	4a	0.0003	0.0085	0.0028
Nb3	4a	0.0113	0.0022	0.0002
Nb4	4a	0.0113	0.0022	-0.0002
Nb5	4a	-0.0113	-0.0022	-0.0002
Nb6	4a	-0.0003	-0.0085	-0.0028
Nb7	4a	-0.0113	-0.0022	0.0002
Nb8	4a	-0.0003	-0.0085	0.0028
Se1	4a	-0.0005	0.0067	0.0017
Se2	4a	-0.0005	0.0067	-0.0017
Se3	4a	0.0081	0.0013	-0.0002
Se4	4a	0.0081	0.0013	0.0002
Se5	4a	0.0005	0.0067	0.0017
Se6	4a	0.0005	0.0067	-0.0017
Se7	4a	0.0081	0.0013	-0.0002
Se8	4a	0.0081	0.0013	0.0002
Se9	4a	-0.0099	-0.0016	-0.0023
Se10	4a	-0.0099	-0.0016	0.0023
Se11	4a	-0.0006	-0.0087	0.0003
Se12	4a	-0.0006	-0.0087	-0.0003
Se13	4a	0.0099	0.0016	0.0023
Se14	4a	0.0006	0.0087	-0.0003
Se15	4a	0.0006	0.0087	0.0003
Se16	4a	0.0099	0.0016	-0.0023

Table A.9: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: X_3 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0002
Ga2	4a	0.0000	0.0000	0.0002
Nb1	4a	0.0015	0.0015	-0.0017
Nb2	4a	-0.0015	-0.0015	-0.0017
Nb3	4a	0.0015	-0.0015	-0.0017
Nb4	4a	-0.0015	0.0015	-0.0017
Nb5	4a	0.0015	-0.0015	-0.0017
Nb6	4a	-0.0015	-0.0015	-0.0017
Nb7	4a	-0.0015	0.0015	-0.0017
Nb8	4a	0.0015	0.0015	-0.0017
Se1	4a	-0.0030	0.0030	0.0060
Se2	4a	0.0030	-0.0030	0.0060
Se3	4a	-0.0030	-0.0030	0.0060
Se4	4a	0.0030	0.0030	0.0060
Se5	4a	-0.0030	-0.0030	-0.0060
Se6	4a	0.0030	0.0030	-0.0060
Se7	4a	-0.0030	-0.0030	0.0060
Se8	4a	0.0030	0.0030	0.0060
Se9	4a	0.0015	0.0015	-0.0051
Se10	4a	-0.0015	-0.0015	-0.0051
Se11	4a	0.0015	-0.0015	-0.0051
Se12	4a	-0.0015	0.0015	-0.0051
Se13	4a	0.0015	0.0015	-0.0051
Se14	4a	0.0015	-0.0015	-0.0051
Se15	4a	-0.0015	0.0015	-0.0051
Se16	4a	-0.0015	-0.0015	-0.0051

Table A.10: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: X_4 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0000
Ga2	4a	0.0000	0.0000	0.0000
Nb1	4a	-0.0004	0.0004	0.0000
Nb2	4a	0.0004	-0.0004	0.0000
Nb3	4a	-0.0004	-0.0004	0.0000
Nb4	4a	0.0004	0.0004	0.0000
Nb5	4a	-0.0004	-0.0004	0.0000
Nb6	4a	0.0004	-0.0004	0.0000
Nb7	4a	0.0004	0.0004	0.0000
Nb8	4a	-0.0004	0.0004	0.0000
Se1	4a	0.0105	0.0105	0.0000
Se2	4a	-0.0105	-0.0105	0.0000
Se3	4a	0.0105	-0.0105	0.0000
Se4	4a	-0.0105	0.0105	0.0000
Se5	4a	0.0105	-0.0105	0.0000
Se6	4a	-0.0105	0.0105	0.0000
Se7	4a	0.0105	-0.0105	0.0000
Se8	4a	-0.0105	0.0105	0.0000
Se9	4a	-0.0058	0.0058	0.0000
Se10	4a	0.0058	-0.0058	0.0000
Se11	4a	-0.0058	-0.0058	0.0000
Se12	4a	0.0058	0.0058	0.0000
Se13	4a	-0.0058	0.0058	0.0000
Se14	4a	-0.0058	-0.0058	0.0000
Se15	4a	0.0058	0.0058	0.0000
Se16	4a	0.0058	-0.0058	0.0000

Table A.11: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: X_5 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	-0.0042	0.0038	0.0000
Ga2	4a	-0.0042	0.0038	0.0000
Nb1	4a	0.0010	0.0011	-0.0058
Nb2	4a	0.0010	0.0011	0.0058
Nb3	4a	-0.0088	-0.0092	-0.0000
Nb4	4a	-0.0088	-0.0092	0.0000
Nb5	4a	-0.0088	-0.0092	-0.0000
Nb6	4a	0.0010	0.0011	0.0058
Nb7	4a	-0.0088	-0.0092	0.0000
Nb8	4a	0.0010	0.0011	-0.0058
Se1	4a	0.0004	0.0003	-0.0036
Se2	4a	0.0004	0.0003	0.0036
Se3	4a	-0.0037	0.0041	-0.0000
Se4	4a	-0.0037	0.0041	0.0000
Se5	4a	0.0004	-0.0003	0.0036
Se6	4a	0.0004	-0.0003	-0.0036
Se7	4a	0.0037	-0.0041	0.0000
Se8	4a	0.0037	-0.0041	-0.0000
Se9	4a	-0.0047	-0.0051	-0.0055
Se10	4a	-0.0047	-0.0051	0.0055
Se11	4a	0.0024	0.0022	0.0000
Se12	4a	0.0024	0.0022	-0.0000
Se13	4a	-0.0047	-0.0051	-0.0055
Se14	4a	0.0024	0.0022	0.0000
Se15	4a	0.0024	0.0022	-0.0000
Se16	4a	-0.0047	-0.0051	0.0055

Table A.12: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: W_1 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0000
Ga2	4a	0.0000	0.0000	0.0000
Nb1	4a	0.0039	-0.0016	-0.0001
Nb2	4a	-0.0039	0.0016	-0.0001
Nb3	4a	0.0016	0.0039	0.0001
Nb4	4a	-0.0016	-0.0039	0.0001
Nb5	4a	-0.0016	-0.0039	-0.0001
Nb6	4a	0.0039	-0.0016	0.0001
Nb7	4a	0.0016	0.0039	-0.0001
Nb8	4a	-0.0039	0.0016	0.0001
Se1	4a	-0.0017	-0.0046	0.0068
Se2	4a	0.0017	0.0046	0.0068
Se3	4a	0.0046	-0.0017	0.0068
Se4	4a	-0.0046	0.0017	0.0068
Se5	4a	0.0017	-0.0046	0.0068
Se6	4a	-0.0017	0.0046	0.0068
Se7	4a	-0.0046	0.0017	-0.0068
Se8	4a	0.0046	-0.0017	-0.0068
Se9	4a	0.0066	0.0041	-0.0007
Se10	4a	-0.0066	-0.0041	-0.0007
Se11	4a	-0.0041	0.0066	0.0007
Se12	4a	0.0041	-0.0066	0.0007
Se13	4a	-0.0066	-0.0041	0.0007
Se14	4a	0.0041	-0.0066	-0.0007
Se15	4a	-0.0041	0.0066	-0.0007
Se16	4a	0.0066	0.0041	0.0007

Table A.13: $\text{F}\bar{4}3\text{m} \rightarrow \text{P}2_12_12_1$: W_2 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Ga1	4a	0.0000	0.0000	0.0003
Ga2	4a	0.0000	0.0000	-0.0003
Nb1	4a	0.0041	0.0029	-0.0044
Nb2	4a	-0.0041	-0.0029	-0.0044
Nb3	4a	0.0029	-0.0041	-0.0044
Nb4	4a	-0.0029	0.0041	-0.0044
Nb5	4a	-0.0029	0.0041	0.0044
Nb6	4a	0.0041	0.0029	0.0044
Nb7	4a	0.0029	-0.0041	0.0044
Nb8	4a	-0.0041	-0.0029	0.0044
Se1	4a	0.0102	0.0004	-0.0021
Se2	4a	-0.0102	-0.0004	-0.0021
Se3	4a	0.0004	-0.0102	0.0021
Se4	4a	-0.0004	0.0102	0.0021
Se5	4a	-0.0102	0.0004	-0.0021
Se6	4a	0.0102	-0.0004	-0.0021
Se7	4a	-0.0004	0.0102	-0.0021
Se8	4a	0.0004	-0.0102	-0.0021
Se9	4a	0.0064	0.0005	0.0023
Se10	4a	-0.0064	-0.0005	0.0023
Se11	4a	0.0005	-0.0064	0.0023
Se12	4a	-0.0005	0.0064	0.0023
Se13	4a	-0.0064	-0.0005	-0.0023
Se14	4a	-0.0005	0.0064	-0.0023
Se15	4a	0.0005	-0.0064	-0.0023
Se16	4a	0.0064	0.0005	-0.0023

A.2 GaTa₄Se₈

This section shows the distortion normal modes for GaTa₄Se₈ in $F\bar{4}3m \rightarrow P\bar{4}2_1m$ phase transition.

Table A.14: $F\bar{4}3m \rightarrow P\bar{4}2_1m$: Γ_1 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Se1	4e	-0.0091	0.0091	-0.0046
Se2	4e	0.0091	-0.0091	-0.0046
Se3	8f	0.0091	0.0091	0.0046
Se4	4e	-0.0091	-0.0091	0.0046
Se5	4e	0.0091	0.0091	0.0046
Se6	8f	0.0091	0.0091	0.0046
Ta1	8f	0.0025	0.0025	0.0012
Ta2	4e	-0.0025	0.0025	0.0012
Ta3	4e	0.0025	-0.0025	0.0012
Ta4	8f	-0.0025	0.0025	0.0012
Ta5	4e	-0.0025	0.0025	0.0012
Ta6	4e	0.0025	-0.0025	0.0012
Ga1	4e	0.0000	0.0000	0.0000
Ga2	4e	0.0000	0.0000	0.0000
Se7	8f	-0.0030	-0.0030	-0.0015
Se8	4e	0.0030	-0.0030	0.0015
Se9	4e	-0.0030	0.0030	0.0015
Se10	8f	-0.0030	-0.0030	-0.0015
Se11	4e	-0.0030	0.0030	0.0015
Se12	4e	0.0030	-0.0030	0.0015

Table A.15: $F\bar{4}3m \rightarrow P\bar{4}2_1m$: Γ_3 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Se1	4e	0.0029	-0.0029	-0.0029
Se2	4e	-0.0029	0.0029	-0.0029
Se3	8f	-0.0029	-0.0029	0.0029
Se4	4e	0.0029	0.0029	0.0029
Se5	4e	-0.0029	-0.0029	0.0029
Se6	8f	-0.0029	-0.0029	0.0029
Ta1	8f	-0.0059	-0.0059	-0.0059
Ta2	4e	0.0059	-0.0059	0.0059
Ta3	4e	-0.0059	0.0059	0.0059
Ta4	8f	0.0059	-0.0059	0.0059
Ta5	4e	0.0059	-0.0059	0.0059
Ta6	4e	-0.0059	0.0059	0.0059
Ga1	4e	0.0000	0.0000	0.0000
Ga2	4e	0.0000	0.0000	0.0000
Se7	8f	0.0026	0.0026	-0.0026
Se8	4e	-0.0026	0.0026	0.0026
Se9	4e	0.0026	-0.0026	0.0026
Se10	8f	0.0026	0.0026	-0.0026
Se11	4e	0.0026	-0.0026	0.0026
Se12	4e	-0.0026	0.0026	0.0026

Table A.16: $F\bar{4}3m \rightarrow P\bar{4}2_1m$: Δ_3 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Se1	4e	-0.0125	0.0125	-0.0028
Se2	4e	0.0125	-0.0125	-0.0028
Se3	8f	-0.0042	-0.0042	-0.0013
Se4	4e	0.0125	0.0125	-0.0028
Se5	4e	-0.0125	-0.0125	-0.0028
Se6	8f	0.0042	0.0042	0.0013
Ta1	8f	-0.0009	-0.0009	-0.0017
Ta2	4e	0.0013	-0.0013	-0.0010
Ta3	4e	-0.0013	0.0013	-0.0010
Ta4	8f	-0.0009	0.0009	-0.0017
Ta5	4e	-0.0013	0.0013	0.0010
Ta6	4e	0.0013	-0.0013	0.0010
Ga1	4e	0.0000	0.0000	-0.0025
Ga2	4e	0.0000	0.0000	0.0025
Se7	8f	-0.0021	-0.0021	0.0008
Se8	4e	0.0083	-0.0083	0.0023
Se9	4e	-0.0083	0.0083	0.0023
Se10	8f	0.0021	0.0021	-0.0008
Se11	4e	0.0083	-0.0083	-0.0023
Se12	4e	-0.0083	0.0083	-0.0023

Table A.17: $F\bar{4}3m \rightarrow P\bar{4}2_1m$: X_3 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Se1	4e	0.0027	-0.0027	-0.0053
Se2	4e	-0.0027	0.0027	-0.0053
Se3	8f	0.0027	0.0027	-0.0053
Se4	4e	0.0027	0.0027	0.0053
Se5	4e	-0.0027	-0.0027	0.0053
Se6	8f	0.0027	0.0027	-0.0053
Ta1	8f	-0.0049	-0.0049	-0.0006
Ta2	4e	-0.0049	0.0049	-0.0006
Ta3	4e	0.0049	-0.0049	-0.0006
Ta4	8f	0.0049	-0.0049	0.0006
Ta5	4e	-0.0049	0.0049	-0.0006
Ta6	4e	0.0049	-0.0049	-0.0006
Ga1	4e	0.0000	0.0000	0.0007
Ga2	4e	0.0000	0.0000	0.0007
Se7	8f	-0.0019	-0.0019	-0.0053
Se8	4e	-0.0019	0.0019	-0.0053
Se9	4e	0.0019	-0.0019	-0.0053
Se10	8f	-0.0019	-0.0019	-0.0053
Se11	4e	0.0019	-0.0019	-0.0053
Se12	4e	-0.0019	0.0019	-0.0053

Table A.18: F $\bar{4}3m \rightarrow P\bar{4}2_1m$: X_5 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Se1	4e	-0.0074	0.0074	-0.0051
Se2	4e	-0.0074	0.0074	0.0051
Se3	8f	0.0034	-0.0034	0.0000
Se4	4e	-0.0074	-0.0074	0.0051
Se5	4e	-0.0074	-0.0074	-0.0051
Se6	8f	0.0034	-0.0034	0.0000
Ta1	8f	-0.0077	0.0077	0.0000
Ta2	4e	0.001	-0.001	-0.0055
Ta3	4e	0.001	-0.001	0.0055
Ta4	8f	-0.0077	-0.0077	0.0000
Ta5	4e	0.001	-0.001	-0.0055
Ta6	4e	0.001	-0.001	0.0055
Ga1	4e	-0.0033	0.0033	0.0000
Ga2	4e	-0.0033	0.0033	0.0000
Se7	8f	-0.0052	0.0052	0.0000
Se8	4e	0.0006	-0.0006	-0.0033
Se9	4e	0.0006	-0.0006	0.0033
Se10	8f	-0.0052	0.0052	0.0000
Se11	4e	0.0006	-0.0006	0.0033
Se12	4e	0.0006	-0.0006	-0.0033

Table A.19: F $\bar{4}3m \rightarrow P\bar{4}2_1m$: W_4 mode.

Atom	WP	δ_x/a	δ_y/b	δ_z/c
Se1	4e	-0.0061	0.0061	0.0064
Se2	4e	-0.0061	0.0061	-0.0064
Se3	8f	0.0041	-0.0041	0.0000
Se4	4e	0.0061	0.0061	0.0064
Se5	4e	0.0061	0.0061	-0.0064
Se6	8f	-0.0041	0.0041	0.0000
Ta1	8f	-0.0033	0.0033	0.0000
Ta2	4e	0.0006	-0.0006	0.0015
Ta3	4e	0.0006	-0.0006	-0.0015
Ta4	8f	0.0033	0.0033	0.0000
Ta5	4e	-0.0006	0.0006	-0.0015
Ta6	4e	-0.0006	0.0006	0.0015
Ga1	4e	-0.0014	0.0014	0.0000
Ga2	4e	0.0014	-0.0014	0.0000
Se7	8f	0.0119	-0.0119	0.0000
Se8	4e	0.0000	0.0000	-0.0009
Se9	4e	0.0000	0.0000	0.0009
Se10	8f	-0.0119	0.0119	0.0000
Se11	4e	0.0000	0.0000	-0.0009
Se12	4e	0.0000	0.0000	0.0009

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