




Crystal and electronic structure of GaTa₄Se₈ from first-principles calculations

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GaTa₄Se₈ belongs to the lacunar spinel family and there have been intensive studies on its novel properties, such as its possible Mott-insulator state and superconductivity under pressure. However, its crystal structure and phase transition are still not well known. In this work, we investigated three different crystal structures, proposed in experiments, using first-principles calculations. For the cubic phase with space group $F\bar{4}3m$, its phonon spectra have three soft modes in the whole Brillouin zone, indicating the strong dynamical instability. The second one is the trigonal phase with space group $R3m$, which has been proposed based on Raman spectra under high pressure. This phase can be deduced from the soft phonon modes at Γ of the cubic phase and it is dynamically stable according to its phonon spectra. The third one is the tetragonal phase with space group $P4_21m$, which is also stable according to its phonon spectra and may be the low-temperature phase from x-ray diffraction. Within local density approximation calculations, the cubic and trigonal phases are metals, while the tetragonal phase is a band insulator consistent with the insulating feature in experiments. Our results suggest the possibility of the non-Mott state of GaTa₄Se₈ at low temperature and ambient pressure as a result of lattice distortion. On the other hand, the electronic structure of the trigonal phase can be viewed as a single-band Hubbard model. The Mott-insulator state has been obtained within dynamical mean-field theory calculation when the interaction parameter U is larger than 0.40 eV vs a bandwidth of 0.25 eV. We hope these findings would be helpful in solving the long-standing problem of the ambiguity in the structural phase of GaTa₄Se₈.

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I. INTRODUCTION

GaTa₄Se₈ belongs to the lacunar spinel compounds family with AM_4X_8 as their chemical formula unit [1], where $A = \text{Ga}$ or Ge , $M = \text{V}$, Mo , Nb , or Ta , and $X = \text{S}$ or Se . It usually takes the typical cubic structure with a space-group symmetry of $F\bar{4}3m$ [2]. The M atoms can be considered to form interconnected M_4 clusters and they are thought to be responsible for most intriguing properties of the family compounds. GaTa₄Se₈, as well as GaNb₄S₈ and GaNb₄Se₈, has been proposed to be a Mott insulator at room temperature and ambient pressure [3]. GaTa₄Se₈ has no long-range magnetic order when the temperature is down to 1.6 K [4]. Under pressure, it has an insulator/metal coexistent state and a hysteresis phenomenon in resistivity vs temperature [1]. It has also been reported to have pressure-induced superconductivity at low temperatures [4]. These have been ascribed to the electrons from the molecular orbitals of Ta₄ clusters since these electrons have strong spin-orbit coupling (SOC) and

they are localized on the clusters with reduced kinetic energy due to the long-distance separation of the clusters. These make GaTa₄Se₈ an ideal platform to explore the correlation physics among the electrons with non-negligible SOC forming j_{eff} molecular orbitals on the M_4 clusters [5–8].

In addition to the correlation effects among Ta₄ molecular orbitals, the changes in crystal structure can affect the electronic structures of these compounds substantially [9], and the above novel physical properties may also be related to the changes. The tetragonal $P4_21m$ structure was proposed as the low-temperature and ambient-pressure phase in 2007 [10], and the trigonal $R3m$ structure was proposed as a possible high-pressure phase in 2009 [11]. However, very recent experiments proposed that GaTa₄Se₈ may have a structural phase transition to another tetragonal phase of $P4m2$ according to the powder x-ray diffraction (XRD) pattern at low temperature [12] and a high-pressure monoclinic phase of space group $C2$ from XRD and Raman spectra [13]. These disputes motivate us to study the crystal structures of GaTa₄Se₈ in detail based on first-principles calculations. In fact, there have been several first-principles calculations on AM_4X_8 family compounds [5,6,9,14]. For GaTa₄Se₈ with the above cubic and trigonal phases, some of these calculations showed that a band gap at the Fermi level can be achieved when a kind

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of magnetic ordering is artificially assumed [14], which is inconsistent with its nonmagnetic ground-state feature in experiments [12].

In this work, we performed first-principles calculations to study the phonon spectra and electronic structure of GaTa_4Se_8 for its three different crystal structures proposed in experiments, namely, the cubic ($F\bar{4}3m$), trigonal ($R3m$), and tetragonal ($P\bar{4}2_1m$) phases. The other tetragonal ($P\bar{4}m2$) and monoclinic ($C2$) phases were not studied since the complete crystal structural information is lacking. The soft modes at Γ in the $F\bar{4}3m$ phase can lead to the $R3m$ phase, of which the phonon spectra have no image frequency. The nonmagnetic first-principles calculations show these two phases are metallic, and the insulating state of these two phases can be obtained when correlation effects among the Ta_4 molecular orbitals are considered in Ref. [1] (for the $F\bar{4}3m$ phase) and this work (for the $R3m$ phase). For the $P\bar{4}2_1m$ phase, its phonon spectra also have no imaginary frequency. Our calculations show it can be an ordinary band insulator due to the tetramerization of Ta_4 clusters from the cubic phase.

This paper is organized as follows: We first introduce the calculation method and then discuss the three different crystal structures in the symmetry lowering order. In each case, the phonon spectra and electronic structure are shown and discussed. Finally, further discussions are made.

II. METHODOLOGY

We used the Vienna *Ab initio* Simulation package (VASP) [15,16] and the PHONOPY package [17] within the density-functional perturbation theory (DFPT) [18] scheme to perform the phonon spectra calculation. In the phonon spectra calculation of GaTa_4Se_8 , for both $F\bar{4}3m$ and $R3m$ space groups, we set the Monkhorst-Pack k -point mesh of $3 \times 3 \times 3$ and plane-wave cutoff energy of 420 eV. For the structure of $P\bar{4}2_1m$, we used the k -point mesh of $2 \times 2 \times 2$ and the same plane-wave energy cutoff. We used a $2 \times 2 \times 2$ supercell of the primitive cell in the phonon spectra calculation for all structures. In all calculations, the projector-augmented-wave (PAW) method [19,20] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [16] was used. For electronic structure calculation, the plane-wave energy cutoff was also set as 420 eV with a $7 \times 7 \times 7$ Monkhorst-Pack k -point mesh in the self-consistent-field calculation. Phonon spectra calculations were performed without considering the SOC, and all calculations were performed with the nonmagnetic state because of the absence of long-range magnetic order.

III. RESULTS AND DISCUSSIONS

A. $F\bar{4}3m$ structure

The lacunar spinel AM_4X_8 family has a fcc Bravais lattice with space group $F\bar{4}3m$ (No. 216). The conventional unit cell of GaTa_4Se_8 and its first Brillouin zone are shown in Figs. 1(a) and 1(b), respectively. It can be derived from the spinel structure AM_2X_4 of space group $Fd\bar{3}m$ [3,21]. Ga (atom A) occupies one-half of the tetrahedral sites in the cubic close packing of Se (atom X) atoms in an ordered way. Ta (atom M) shifts along the C_{3v} axis (u, u, u) from $u = 0.625$ to $u \approx$

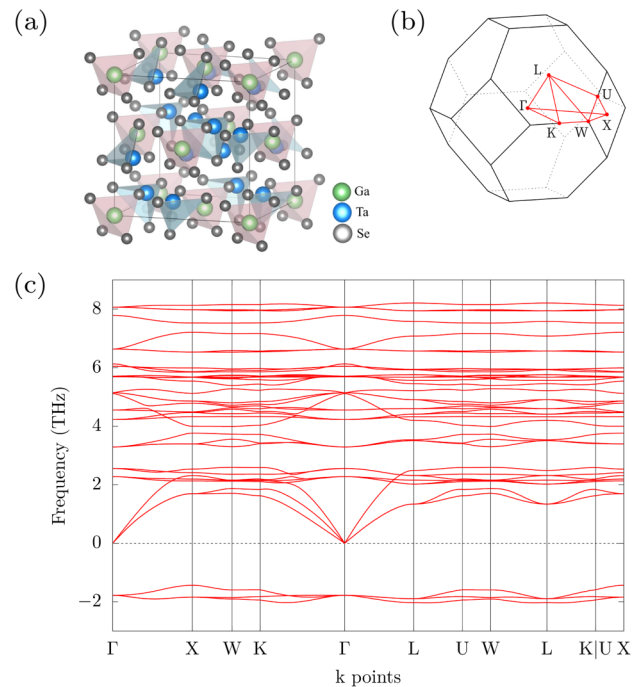


FIG. 1. (a) Crystal structure of $F\bar{4}3m$ GaTa_4Se_8 , (b) its Brillouin zone, and (c) the phonon spectra.

0.602. This shift of Ta leads to the formation of Ta_4 tetrahedral clusters with intracluster $M-M$ distance of 3.001 Å and intercluster distance of 4.339 Å (the experimental structure at room temperature [22]). Thus, the structure can be appropriately considered as a rocksaltlike arrangement of Ta_4Se_4 cubes and GaSe_4 tetrahedrons [3]. However, as shown in Fig. 1(c), the phonon spectra of this $F\bar{4}3m$ structure have large imaginary frequencies in the whole Brillouin zone, indicating the dynamical instability of this structure. At Γ , the three soft modes are degenerate, which is consistent with the cubic symmetry that the possible spontaneous symmetry breaking is equivalent in three directions.

The electronic band structures in Fig. 2 show no gap at the Fermi level in calculations with and without spin-orbit coupling. This indicates that $F\bar{4}3m$ GaTa_4Se_8 is a metal in our single-particle approximation calculation. The narrow bands around the Fermi level are composed of molecular orbitals from Ta_4 clusters. Based on this, the Mott-insulator state for $F\bar{4}3m$ GaTa_4Se_8 has been obtained in dynamical mean-field theory (DMFT) calculation [1] when the correlation effects among these molecular orbitals are considered. As it was mentioned before, there is evidence showing that GaTa_4Se_8 may have structural phase transitions while the temperature decreases, and the structural distortion may change the electronic states dramatically. Therefore, it is necessary to investigate the possibility of the ordinary band-insulator state resulting from the lattice distortion, instead of taking it as a Mott insulator directly at low temperatures.

The soft-mode analysis is a common method to capture possible phase transitions within first-principles calculations. It is known that a complete investigation of all the linear combinations of soft modes is infeasible. Herein, we take one of the three degenerate soft modes at Γ for the analysis to explore

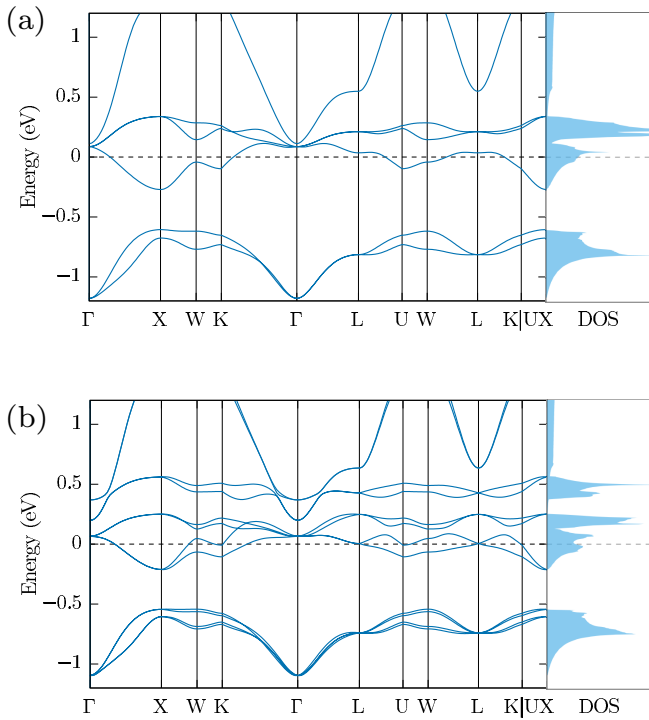


FIG. 2. The band structure and density of states (DOS) for non-magnetic GaTa_4Se_8 of $F\bar{4}3m$ structure (a) without and (b) with SOC.

how and what structural phase transition will happen if it is frozen. We multiply the mode with a dimensionless scaling factor varying from -2 to 3 in 250 steps to obtain various atomic displacements away from the original primitive cell of the $F\bar{4}3m$ structure. After the total energy self-consistent calculations for each crystal structure with the above structural distortions, we get an asymmetric double well of total energy vs distortion, as shown in Fig. 3. It is noted that the original cubic structure is noncentrosymmetric and the distortions with the above positive scaling factor are not symmetric with that

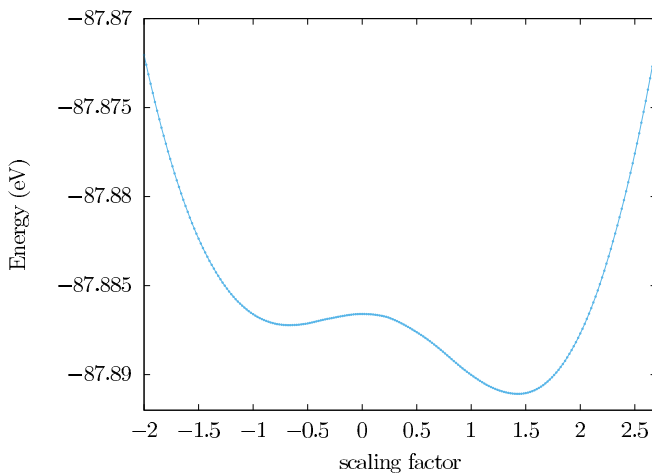


FIG. 3. The asymmetric “double” well of the $F\bar{4}3m$ structure in plot of total energy vs distortion originated from the absence of inversion symmetry. The scaling factor is a dimensionless number to indicate the size of distortion away from the $F\bar{4}3m$ structure.

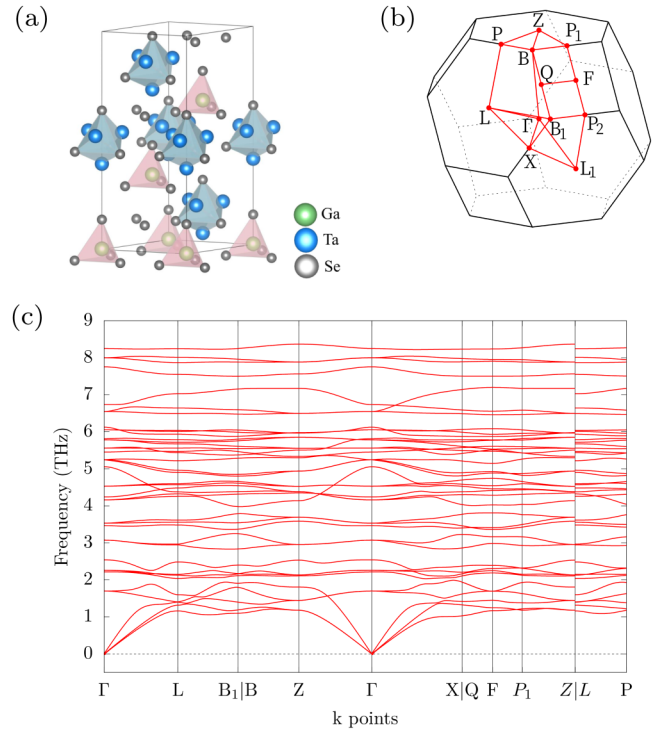


FIG. 4. (a) Crystal structure, (b) Brillouin zone, and (c) the phonon spectra of $R3m$ GaTa_4Se_8 .

of the opposite sign. This is different from the symmetric double well in the transition from paraelectric to ferroelectric phase. The structure with the scaling factor around 1.5 has the lowest total energy. We found that this distorted structure has a space group $R3m$ (No. 160). In fact, the $R3m$ phase is commonly seen in lacunar spinel materials, such as GaV_4S_8 [23], GaV_4S_8 [21], and GaMo_4S_8 [24]. There was already a proposal that the $R3m$ structure may be a high-pressure phase of GaTa_4Se_8 according to the Raman spectra [11]. We further investigate this phase in the next section.

B. $R3m$ structure

The conventional unit cell of $R3m$ GaTa_4Se_8 is shown in Fig. 4(a), which is obtained through the full structural optimization of the distorted crystal structure at the bottom of the lower potential well in Fig. 3. In the $R3m$ phase, the Ta_4 clusters are elongated along the C_{3v} axis. As a result, the original regular tetrahedron Ta_4 clusters are transformed into regular triangular pyramids, with two different bond lengths: 2.950 Å (base face bond length) and 3.119 Å (lateral edge bond length). There is one chemical formula unit in the primitive cell and the volume of the primitive cell is slightly larger than that of the $F\bar{4}3m$ structure. The calculated total energy per chemical formula for the fully optimized trigonal $R3m$ phase is lower than that of $F\bar{4}3m$ by 0.01 eV. The phonon spectra in Fig. 4(c) show no imaginary frequency in the whole Brillouin zone, indicating that $R3m$ GaTa_4Se_8 is dynamically stable.

The electronic band structure and density of states (DOSs) of $R3m$ GaTa_4Se_8 are shown in Fig. 5. Both of them indicate $R3m$ GaTa_4Se_8 is metallic in our first-principles calculation, which conflicts with the experimentally observed insulating

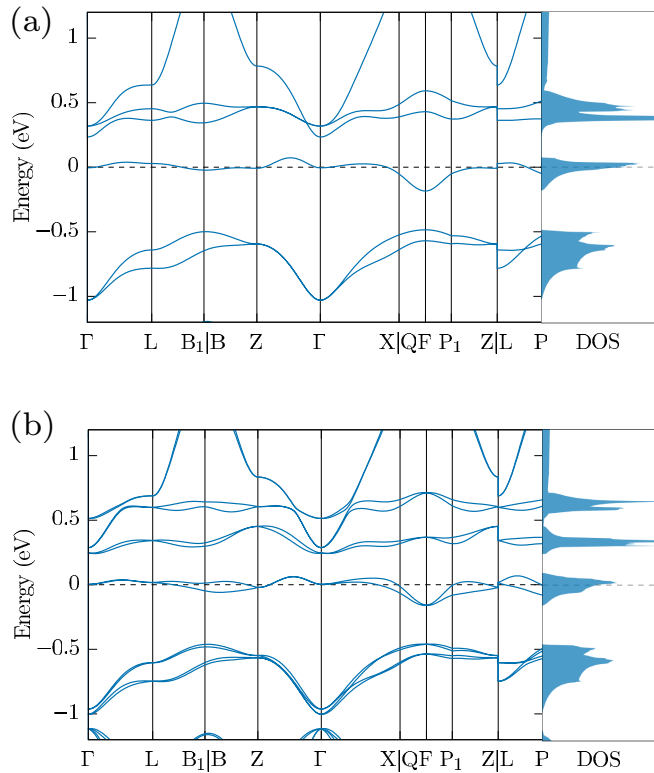


FIG. 5. The band structure and DOS of nonmagnetic $R3m$ GaTa_4Se_8 (a) without and (b) with SOC.

state. Because of the distortion of Ta_4 clusters, the T_2 representation breaks into a two-dimensional representation E in higher energy and a one-dimensional representation A_1 in lower energy, which coincides with the Jahn-Teller effect, as shown in the band structure. It is noted that the single band crossing the Fermi level is half filled and the bandwidth is about 0.25 eV, which is much narrower compared with that of 0.75 eV in $F\bar{4}3m$ GaTa_4Se_8 [5]. In the Hubbard model, a single band crossing the Fermi level with half filling usually implies a tendency toward an antiferromagnetic ordering state [25]. In experiments, GaTa_4Se_8 has no long-range magnetic order even when the temperature is down to 1.6 K. For the fcc structure, there is an antiferromagnetic frustration preventing the formation of antiferromagnetic order even at very low temperatures. This frustration originates from the fcc grids formed by Ta_4 clusters. For $R3m$ structure with an elongation distortion, Ta_4 clusters form a lattice of equilateral triangles respecting C_{3v} symmetry. There still exists geometrical frustration within the triangle plane to prevent the formation of long-range antiferromagnetic order, while the A -type interlayer antiferromagnetic coupling is possible.

On the other hand, $R3m$ GaTa_4Se_8 may be a Mott insulator due to the narrow band formed from the molecular orbitals of Ta_4 clusters. To investigate this, we performed DMFT [26] calculation on the single-band (or single-orbital) Hubbard model using the IQIST package [27], which employs the continuous-time quantum Monte Carlo (CTQMC) [28] impurity solver to solve the impurity imaginary time Green's function. Due to the absence of long-range magnetic order,

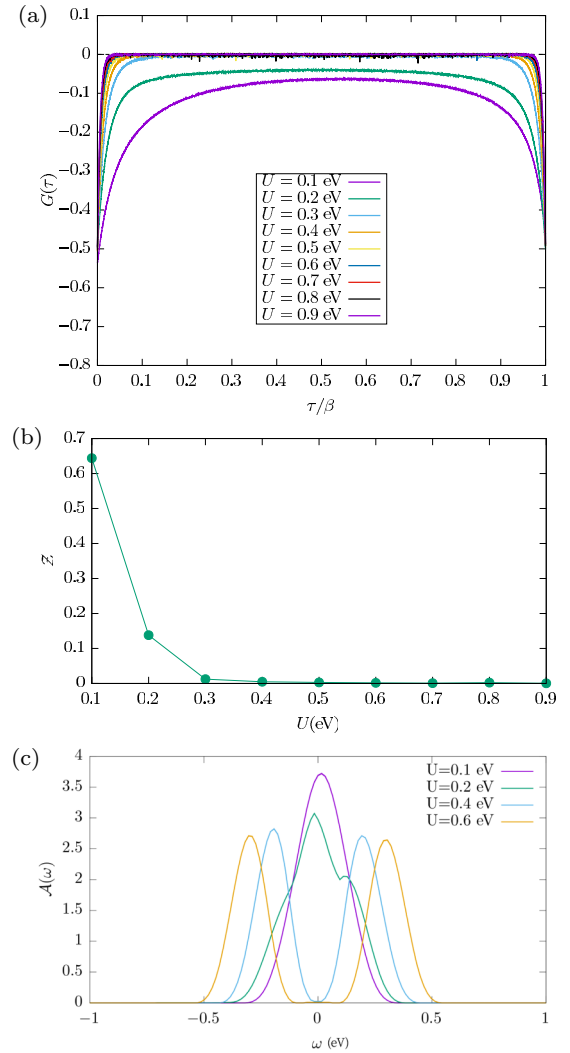


FIG. 6. DMFT result of $R3m$ GaTa_4Se_8 . (a) The impurity local image time Green's function, $G(\tau)$. (b) The quasiparticle weight \mathcal{Z} . (c) The spectrum function, $\mathcal{A}(\omega)$, of different Hubbard U .

we imposed the nonmagnetic phase in DMFT calculation and ignored SOC for simplicity. We used the DOS calculated from DFT to initialize the local Green's function. The DMFT calculation was performed at temperature controlled by the parameter β of 400 corresponding to about 29.01 K. The local imaginary time Green's function $G(\tau)$ [Fig. 6(a)], the quasiparticle weight \mathcal{Z} [Fig. 6(b)], and the spectrum function $\mathcal{A}(\omega)$ [Fig. 6(c)] were calculated. The spectrum function is obtained from the analytic continuation using the maximal entropy method [29].

From \mathcal{Z} and the spectrum function shown in Fig. 6, we conclude that the metal-insulator transition (MIT) occurs when we increase the on-site Coulomb interaction U to about 0.3–0.4 eV, which equals $1.60W$ with W being the bandwidth of 0.25 eV. The on-site interaction of about 0.40 eV is still smaller than the band gap between the $n+1$ band and the $n-1$ band, where n is the index of the single band crossing the Fermi level. At the qualitative level, the single-band scheme is sufficient. All the results show that the single flat band comes from the unpaired d electron, which is extremely localized on

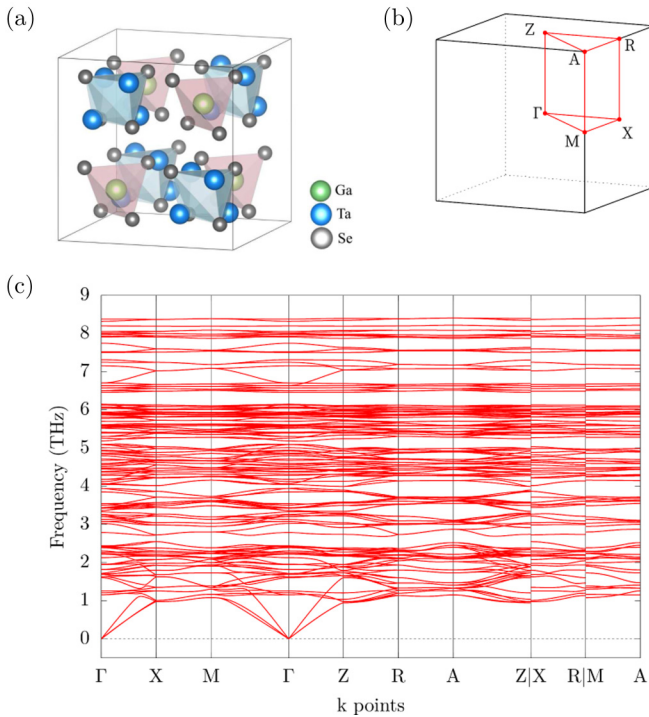


FIG. 7. (a) Crystal structure, (b) Brillouin zone, and (c) the phonon spectra of $P\bar{4}2_1m$ GaTa_4Se_8 .

the Ta_4 cluster, indicating the possible Mott-insulator state of GaTa_4Se_8 in the trigonal $R\bar{3}m$ structure.

C. $P\bar{4}2_1m$ structure

The third crystal structure of GaTa_4Se_8 studied in this work is the tetragonal lattice with space group $P\bar{4}2_1m$ (No. 113), of which the details of crystal structure were reported in Ref. [10] based on XRD experiments. This phase was also reported for GaNb_4S_8 , where an anomalous magnetic susceptibility behavior appears together with the phase transition from $F\bar{4}3m$ to $P\bar{4}2_1m$ [30]. Considering the similarity between GaTa_4Se_8 and GaNb_4S_8 in crystal structure and physical properties, such as the pressure-induced superconductivity [3,4] and the magnetic susceptibility anomaly [30,31], we believe that the $P\bar{4}2_1m$ structure of GaTa_4Se_8 may be plausible. The fully relaxed crystal structure and its phonon spectra are shown in Fig. 7(a). The symmetry of Ta_4 clusters is lowered to C_s . Each of them has different orientations and has four different bond lengths, as shown in Fig. 8. The alternative orientation with this ordering structure expands the primitive cell, which is a kind of cooperative Jahn-Teller distortion.

There are four chemical formula units in a primitive cell after the cooperative Jahn-Teller distortion of the Ta_4 clusters, which can be considered as a kind of tetramerization of the cubic phase. The total energy per formula unit for $P\bar{4}2_1m$ GaTa_4Se_8 is 0.03 eV lower than that of the $R\bar{3}m$ phase. The phonon spectra in Fig. 7(c) have no imaginary frequency, indicating the $P\bar{4}2_1m$ structure is also dynamically stable.

Comparing with the former two phases, the electronic structure of $P\bar{4}2_1m$ GaTa_4Se_8 changes qualitatively with a band gap appearing at the Fermi level as shown in Fig. 9(a).

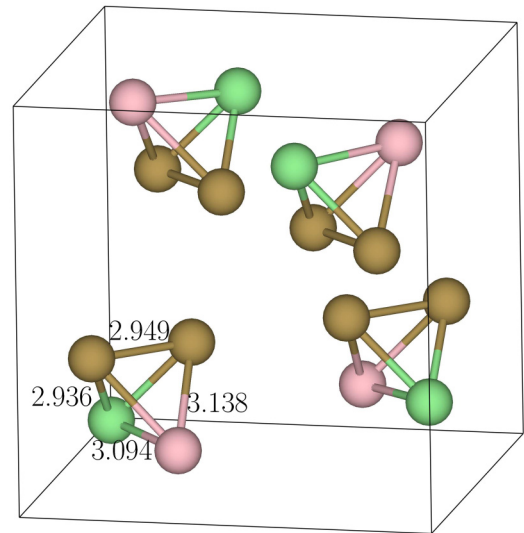


FIG. 8. Ta_4 clusters in $P\bar{4}2_1m$ GaTa_4Se_8 after tetramerization. Different colors correspond to different Wyckoff positions of Ta atoms (brown, 8f; pink, 4e; green, 4e). The numbers label the bond lengths (in units Å). Each Ta_4 cluster has a C_s symmetry, but their “orientation” is different.

The new primitive cell of $P\bar{4}2_1m$ GaTa_4Se_8 has four chemical formula units and contains an even number of valence electrons, which is different from the $F\bar{4}3m$ and $R\bar{3}m$ phases with an odd number of valence electrons. Furthermore, SOC brings spin splitting in the bands due to the absence of inversion symmetry as shown in Fig. 9(b), which keeps the band gap. It is noted that the band-insulator state of GaTa_4Se_8 has been ruled out based on experimental optical conductivity analysis [32]. This may be true for the $F\bar{4}3m$ structure at room temperature

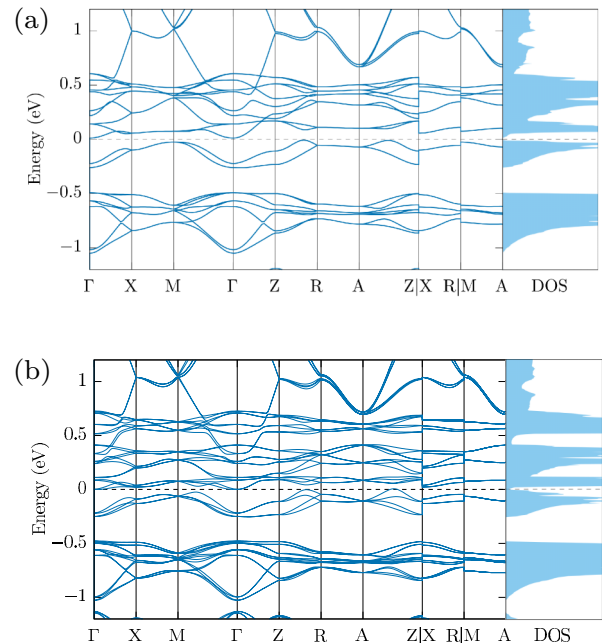


FIG. 9. Band structure and DOS of nonmagnetic $P\bar{4}2_1m$ GaTa_4Se_8 (a) without and (b) with SOC.

TABLE I. Crystal and electronic structures for different phases of GaTa_4Se_8 . The DFT results do not include SOC. The lattice constants in parentheses are from experiments [10,22]. There is no detailed structure of the $R3m$ phase reported in experiments.

	$F\bar{4}3m$	$R3m$	$P\bar{4}2_1m$
a (Å)	10.51 (10.38)	7.40	10.50 (10.38)
b (Å)	10.51 (10.38)	7.40	10.50 (10.38)
c (Å)	10.51 (10.38)	18.39	10.53 (10.37)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	120	90
Total energy (eV)/(f.u.)	-87.88	-87.89	-87.92
Volume (Å ³)/(f.u.)	289.90	290.42	290.48
DFT band gap (eV)	0	0	0.02
Insulator type	Mott	Mott	Band insulator

or high pressure, but the low-temperature condition was not considered. Our calculation results indicate that the $P\bar{4}2_1m$ GaTa_4Se_8 is the most likely low-temperature phase and it is a band insulator instead of a Mott insulator.

IV. DISCUSSION AND CONCLUSION

In Table I, we summarized the crystal structures and the corresponding electronic structures for $F\bar{4}3m$, $R3m$, and $P\bar{4}2_1m$ phases studied in this work. The presence of soft modes with imaginary frequency in the phonon spectra of the $F\bar{4}3m$ phase suggests that this phase is not dynamically stable at low temperatures and ambient pressure.

The trigonal $R3m$ phase can be deduced from the $F\bar{4}3m$ phase when the soft modes at Γ are frozen as experimental condition changes. In fact, the $R3m$ phase was proposed as a possible high-pressure phase based on the Raman spectra in 2009 [11]. The high-pressure structural phase transition of GaTa_4Se_8 should be noticed, especially in the research of the pressure-induced superconductivity, which has drawn much attention recently [7,8]. As we have seen in the electronic structure of the $R3m$ phase, the slight elongation of Ta_4 regular tetrahedron clusters along the $\langle 111 \rangle$ direction breaks the original T_d point symmetry and affects the electronic structure near the Fermi level profoundly. The triple-degenerate molecular orbitals split into a double-degenerate and a nondegenerate orbital. In the DFT level, $R3m$ GaTa_4Se_8 is metallic with only one flat band crossing the Fermi level. This is nearly a Hubbard model with half occupation and our DMFT results indicate that the correlation can lead to a Mott-insulator state when the on-site interaction is larger than 0.4 eV, being enough to destroy the Fermi liquid picture and open a spectral gap at the Fermi level.

The $P\bar{4}2_1m$ phase proposed in Ref. [10] may be the most possible low-temperature structure at ambient pressure. Recently, it was considered in the studies of lattice dynamics and electronic excitation of lacunar spinel materials [33]. The electronic structure of $P\bar{4}2_1m$ shows a band gap at the Fermi level with no need of Hubbard U or magnetic order as the subsequence of the tetramerization of the Ta_4 clusters shown in Fig. 8. This coincides with the nonmagnetic ground state of GaTa_4Se_8 from experiments [12], indicating that the low-temperature phase of GaTa_4Se_8 is not a Mott insulator, but a band insulator.

We hope this work can shed light on the long-standing problem of the ambiguity in the structural phase of GaTa_4Se_8 , and can provide more theoretical hints for further research in the related field.

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