PHYSICAL REVIEW B **76**, 214106 (2007)

Importance of cluster distortions in the tetrahedral cluster compounds $\mathrm{Ga}M_4X_8$ (M=Mo,V,Nb,Ta; X=S,Se): *Ab initio* investigations

M. Sieberer, S. Turnovszky, J. Redinger, and P. Mohn
Center for Computational Materials Science, Vienna University of Technology, Getreidemarkt 9/134, A-1060 Vienna, Austria

(Received 20 August 2007; published 12 December 2007)

In this paper, we study the structural properties of selected representatives of the so-called molybdenum cluster compounds. Belonging to this family are the $\mathrm{Ga}M_4X_8$ compounds with M=Mo as a group VIB element and V, Nb, or Ta as a group VB element. X denotes either S or Se. These compounds are known to exhibit semiconducting behavior in the electrical resistivity, caused by hopping of electrons between well-separated metal clusters. The large separation of the tetrahedral metal (M_4) clusters is believed to be the origin of strong correlations. We show that recent calculations neglected an important type of structural distortion, namely, those happening only within the M_4 unit at a fixed angle $\alpha=60°$ of the trigonal (fcc-like) cell. These internal distortions gain a significant amount of energy compared to the cubic cell and they are—to our knowledge—almost undetectable with powder x-ray diffraction experiments. However, they strongly influence the bandstructure by opening up a gap at the Fermi-energy. This, however, puts into question whether all compounds of this family are really Mott insulators as stated elsewhere. In particular, ferromagnetic $\mathrm{GaMo_4S_8}$ and $\mathrm{GaV_4S_8}$ are well described within density functional theory. Only the Nb- and Ta-based representatives require a large effort due to the lack of magnetic long-range order caused by frustrated antiferromagnetic M-M interactions.

DOI: 10.1103/PhysRevB.76.214106 PACS number(s): 61.82.Fk, 71.30.+h

I. INTRODUCTION

The molybdenum cluster compounds $\mathrm{Ga}M_4X_8$ with M=Mo (group VIB), V, Nb, or Ta (group VB) and X=S and Se are known to exhibit semiconducting behavior in the electrical resistivity, caused by variable range hopping[1] of electrons between well-separated metal clusters. The large separation of the tetrahedral metal (M_4) clusters is believed to be the origin of strong correlations. Regarding the crystal structure, $\mathrm{GaMo_4}X_8$ with X=S,Se and $\mathrm{GaV_4S_8}$ show a structural phase transition from a cubic to a slightly distorted trigonal structure around $T_S \approx 50$ K.[2] Well below T_S, at temperatures $T_c \approx 20$ K, ferromagnetism sets in. In contrast, $\mathrm{GaNb_4Se_8}$ and $\mathrm{GaTa_4Se_8}$ are known to remain cubic and paramagnetic without magnetic long-range order down to the lowest temperatures. The latter compounds have been reported to be Mott insulators and to become superconducting under external pressure.[3] In this paper we show that recent calculations neglected an important structural degree of freedom.[2–6] Even though the change from cubic to trigonal structure has been correctly ascribed to a Peierls distortion originating from the M_4 clusters,[2,4] no notice has been taken of the fact that the M_4 clusters can also distort in a geometry with ideal, fcc-like axes spanning an angle of $\alpha=60.0°$. To our knowledge, small distortions of roughly 3% occurring only within the M_4 units are practically undetectable within powder x-ray diffraction, in contrast to the strong broadening of the peaks in the case when the angle α deviates from 60°. In our calculations, however, the energy gain of distorting the M_4 units while fixing $\alpha=60°$ in the cases of $\mathrm{GaMo_4S_8}$ and $\mathrm{GaV_4S_8}$ is significant, making it very likely that the M_4 tetrahedra also distort above the structural phase transition. This would be hardly detectable experimentally. Moreover, we believe that the neglect of these degrees of freedom in previous density functional theory (DFT) investigations[2–6] led to an overestimation of the importance of electron-electron correlations. We find that M_4 distortions alone are enough to open up a gap at E_F. This shows that not all representatives of this family, in particular ferromagnetic $\mathrm{GaMo_4S_8}$ and $\mathrm{GaV_4S_8}$, can be called Mott insulators. If relaxations are performed properly, all compounds investigated exhibit a vanishing density of states (DOS) at the Fermi energy, in agreement with experiment. Only the Nb- and Ta-based representatives have to be treated with care. Their strong antiferromagnetic (AF) M-M interactions prohibit long-range order, and the strong coupling between cluster geometry and magnetic configuration makes the investigation very difficult.

II. RESULTS AND DISCUSSION

All calculations were performed using the projector augmented wave (PAW) technique[7] as implemented in the VASP package.[8] For Ga a PAW potential with s, p, and d electrons as valence states has been chosen; for X (S, Se) s and p electrons were treated as valence states. During all calculations a plane-wave expansion up to 400 eV was applied and at least 85 irreducible $\boldsymbol{k}$ points (for a trigonal setup) were used. In all cases the Wyckoff positions were relaxed at fixed volume and fixed cutoff. In the low-symmetry setup, the trigonal angle α was changed by hand and never relaxed automatically, avoiding too many degrees of freedom.

At high temperatures, all cluster compounds of the type $\mathrm{Ga}M_4X_8$ with M=Mo, V, Nb, and Ta and X=S,Se crystallize in a face-centered cubic (fcc) phase ($F\bar{4}3m$), which can be derived from the spinel structure ($Fd\bar{3}m$, hypothetical $\mathrm{Ga_2}M_4X_8$) by removing half of the Ga atoms. Complete ordering of the resulting vacancies finally results in the present structure having symmetry $F\bar{4}3m$. Some representatives, like Mo-based $\mathrm{GaMo_4}X_8$ with X=S,Se and V-based $\mathrm{GaV_4S_8}$, however, undergo a structural phase transition upon cooling into a slightly distorted, trigonal structure ($R3m$). While the

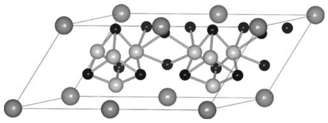

FIG. 1. Doubled fcc unit cell. The corner atoms are Ga, the small bright atoms form the tetrahedral M_4 clusters, and the small dark spheres are X. One can easily see the bridge between two M_4 clusters mediated by two X atoms and the M-X-M angle of $\approx 104.6°$.

Mo-based compounds distort toward a trigonal angle α larger than the ideal (fcc) one of 60.0° ($\alpha_{expt}=60.53°$ for $GaMo_4S_8$), the V-based compounds distort in the opposite direction ($\alpha_{expt}=59.6°$ for GaV_4S_8). Both types order ferromagnetically below a T_c of 19.5, 26.7, and 10 K for $GaMo_4S_8$, $GaMo_4Se_8$, and GaV_4S_8, respectively. For the Mo compounds, metamagnetism with rather low magnetic critical fields has been reported.[9] Unlike the above representatives, the Nb- and Ta-based cluster compounds not only remain cubic down to lowest temperatures, they also exhibit no magnetic long-range order even though from the Curie law a magnetic moment of roughly $1\mu_B$/f.u. has been extrapolated. A doubled unit cell containing two formula units is shown in Fig. 1. In the cubic geometry the M_4 units build a fcc lattice and one M atom is connected via two X atoms with the neighboring cluster. For the low-temperature phase $R3m$ trigonal axes were used. In the trigonal geometry all the axis lengths are equal ($a=b=c$) and only the angle $\alpha=\beta=\gamma$ can be changed. The basis vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ are related to the simple cubic axes $\vec{A}$, $\vec{B}$, and $\vec{C}$ via

$$\begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \\ \vec{b}_3 \end{pmatrix} = \frac{b}{\sqrt{1+2x+3x^2}} \begin{pmatrix} 1+x & x & x \\ x & 1+x & x \\ x & x & 1+x \end{pmatrix} \begin{pmatrix} \vec{A} \\ \vec{B} \\ \vec{C} \end{pmatrix}.$$

The length of all basis vectors is b. These vectors span the volume of the trigonal unit cell, V_T, given by

$$V_T = b^3 \frac{(1+3x)}{(1+2x+3x^2)^{3/2}}. \tag{1}$$

The quantity x is related to the angle α via the equation

$$x = -\frac{1}{3} + \sqrt{\frac{1}{9} - \frac{u}{3(u-1)}}, \tag{2}$$

where u denotes the cosine of α. An angle of $\alpha=60°$ ($u=0.5$, equivalent to fcc axes) results in $x=1/3$. For simplicity, only α and the corresponding simple cubic lattice constant a_0 will be used. The quantity a_0 is related to the cell volume V_T via $a_0=(4V_T)^{1/3}$. The results for the cubic geometry are listed in Table I. The optimized values for a_0 are in good agreement with experiment (in parentheses); due to the generalized gradient approximation (GGA) they slightly overestimate the true volume. The DOSs for the cubic compounds of interest are compared in Fig. 2. It confirms that for all compounds only M states are situated at E_F. While the cluster orbitals are almost filled for $GaMo_4X_8$, they are almost empty in the cases M=V, Nb, and Ta. Recently, it has been pointed out that the cluster orbitals at E_F stem from bonding combinations of atomic, M-like t_{2g} orbitals.[10] For example, in $GaMo_4X_8$, six electrons per Mo ($6\times 4=24$ per cluster) and three electrons per Ga yielding a total number of 27 valence electrons, are available. From those $8\times 2=16$ can be attributed to X, since it is most electronegative. The remaining 11 electrons per cluster almost completely fill the (4×3) Mo t_{2g} cluster orbitals.

TABLE I. Tabulated are the sc lattice constants a_0 (bohr), the intra-(d_{intra}) and inter-(d_{inter}) cluster M-M distances, the density of states at E_F [$N(E_F)$] [states/(eV f.u.)], the bandwidths W in the ferromagnetic (FM) state (eV), and the dimensionless ratio I/W relating the Stoner I (eV) and bandwidth W (eV). In all cases the cubic phase was assumed; values in parentheses refer to experiment.

Compound	a_0	d_{intra}/d_{inter}	$N(E_F)$	W	I/W
$GaMo_4S_8$	9.84 (9.73)	2.85/4.10	45	0.570	1.09
$GaMo_4Se_8$	10.30	2.91/4.37	59	0.426	1.46
GaV_4S_8	9.68 (9.66)	2.84/4.00	10.3	0.401	1.76
GaV_4Se_8	10.19	2.93/4.27	12.4	0.296	2.39
$GaNb_4S_8$	10.06 (10.02)	2.99/4.12	7.1	0.689	0.87
$GaNb_4Se_8$	10.53 (10.42)	3.06/4.39	8.9	0.500	1.20
$GaTa_4S_8$	10.04	2.98/4.12	6.3	0.827	0.6
$GaTa_4Se_8$	10.51 (10.37)	3.04/4.39	8.9	0.604	0.8

III. RESULTS FOR $GaMo_4S_8$, GaV_4S_8, $GaNb_4Se_8$, AND $GaTa_4Se_8$

In the following section the magnetic properties of the compounds $GaMo_4S_8$, GaV_4S_8, $GaNb_4Se_8$, and $GaTa_4Se_8$ will be compared. In order to describe the low-temperature phase ($R3m$) two types of distortion were taken into account. On the one hand, the M_4 tetrahedra were allowed to distort, and on the other hand, the angles α spanned by the trigonal axes were modified by hand.

In the cubic structure only $GaMo_4S_8$ and GaV_4S_8 develop an integer magnetic moment of $1\mu_B$ per cluster. This is in agreement with experiments yielding FM states below T_c for the Mo- and V-based compounds. The Nb- and Ta-based representatives end up nonmagnetic in our calculations; only in an AF (1,0,0) setup (the only one tested) do small magnetic moments on Nb or Ta arise. This is an indication of strong but frustrated AF interactions present in the cubic compounds $GaNb_4X_8$ and $GaTa_4X_8$. Plots of the energy versus the angle α for the compounds of interest are shown in Fig. 3. Easiest to understand is $GaMo_4S_8$. In the cubic geometry the compound is clearly FM with an integer moment of $1\mu_B$. This is because there is one hole in the almost filled cluster orbital complex. Energetically, the nonmagnetic state is roughly 30 meV above the cubic FM state. The compound is a half metal because of its vanishing DOS at E_F in the majority spin channel. When the Mo_4 tetrahedra are allowed to distort (transition from $F\bar{4}3m$ to $R3m$) upon fixed unit cell axes ($\alpha=60.0°$), the total energy can already be lowered by

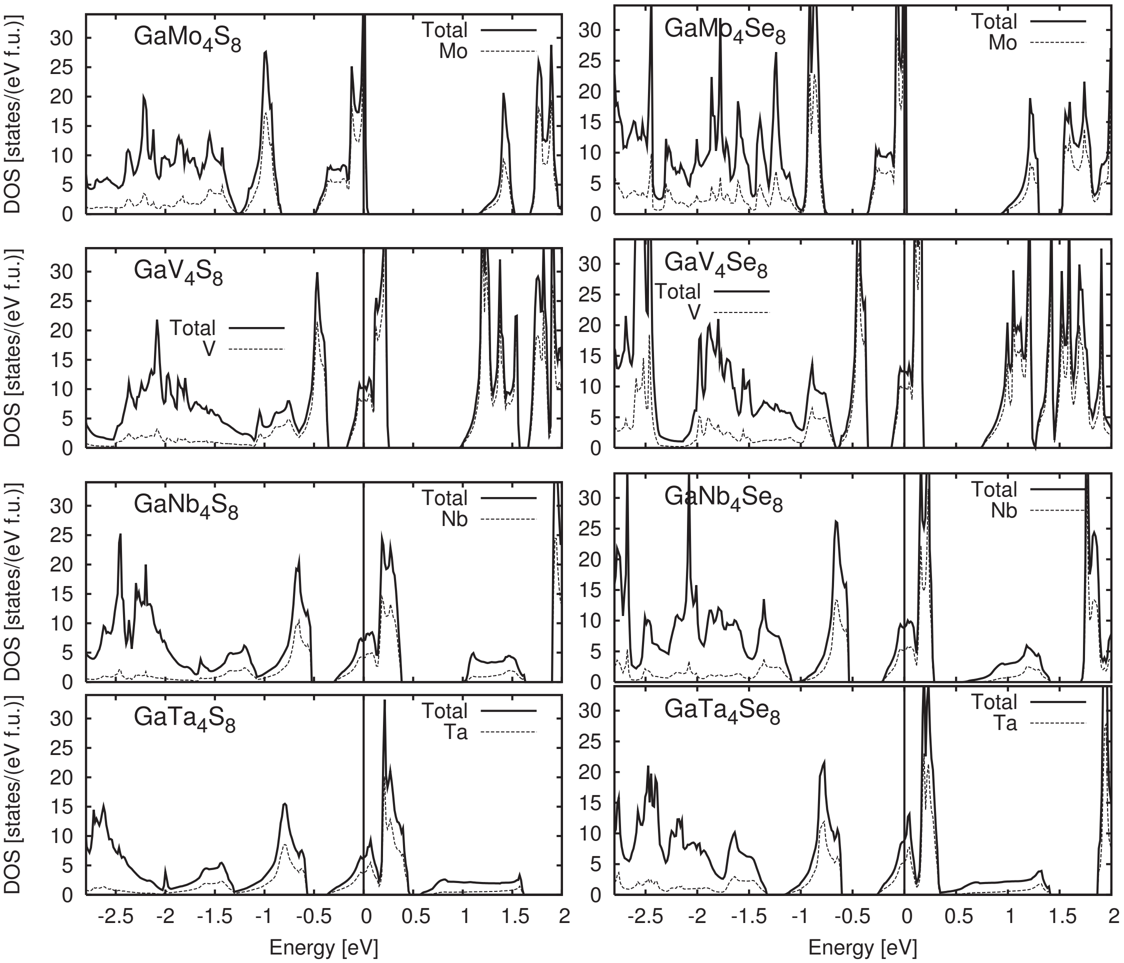

FIG. 2. Total and M-projected density of states for the cubic compounds GaM_4X_8 with X=S (left panel) and Se (right panel) and M=Mo, V, Nb, and Ta.

16 meV. Relaxing also the angle α further reduces the total energy by approximately 12 meV (see Fig. 3). The angle found in our calculations (α=60.6°) is in very good agreement with the experimental one (α_{expt}=60.53°). Most impressive is the effect of the distortions on the DOS. We found that the cluster distortions alone are enough to open up a gap at E_F. A comparison between cubic and trigonal DOSs is given in Fig. 4. The gap in trigonal GaMo$_4$S$_8$ has a width of roughly 0.08 eV. It changes only slightly when α is modified, but it is very sensitive to the degree of Mo$_4$ cluster distortion. Regarding the physical properties, the compound closest to GaMo$_4$S$_8$ is GaV$_4$S$_8$. However, in its cubic form the nonmagnetic state is situated energetically only 10 meV above the FM one. Hence its FM state is strongly destabilized compared to GaMo$_4$S$_8$ (30 meV). Our calculations yield $\alpha \approx 59.6°$, again in very good agreement with experiment. The $R3m$ configuration (distorted M_4 tetrahedron) with α=60.0 is more stable than the ideal, cubic (fcc) one by approximately 11 meV. Further relaxations of α yield only a lowering of the energy by 5 meV. This is again lower than the corresponding relaxation energy for GaMo$_4$S$_8$ (12 meV). The behavior of GaNb$_4$Se$_8$ and GaTa$_4$Se$_8$ is much more complex. In their cubic form they strongly disfavor the FM state. Their cubic, nonmagnetic state is lower in energy by 26 and 30 meV for Nb and Ta, respectively. The situation changes when cluster relaxations are taken into account. In that case the FM configuration can be stabilized without fixing the moment artificially. The internal Nb$_4$ and Ta$_4$ relaxations gain energy of about 40 and 50 meV with respect to the cubic FM state. This is large compared to the change in the total energy when the angle α is modified (3 and 11 meV for M=Nb and Ta, respectively). However, this huge energy gain related to internal distortions is expected to be an artifact of assuming a FM state, which is not the experimental ground state. A comparison of the DOSs between cubic and trigonal (α=60°) geometry for the compounds of interest is given in Fig. 4. In all cases M_4 distortions of about 3–4% significantly change the DOS. Thus also for M=Mo and V a strong pressure dependence of the electrical resistivity is expected.

In conclusion, there is a big difference between the Mo- and V-based and the Nb- Ta-based compounds. Within the series Mo-V-Nb-Ta, the DOS at E_F determined from the nonmagnetic state steadily decreases. This reduction in $N(E_F)$ weakens the tendencies of structural distortions. As a consequence only the Mo- and V-based representatives deviate from α=60°. However, it has to be checked whether M_4 distortions also occur at a fixed angle α=60° above the structural phase transition T_s. This is because powder x-ray dif-

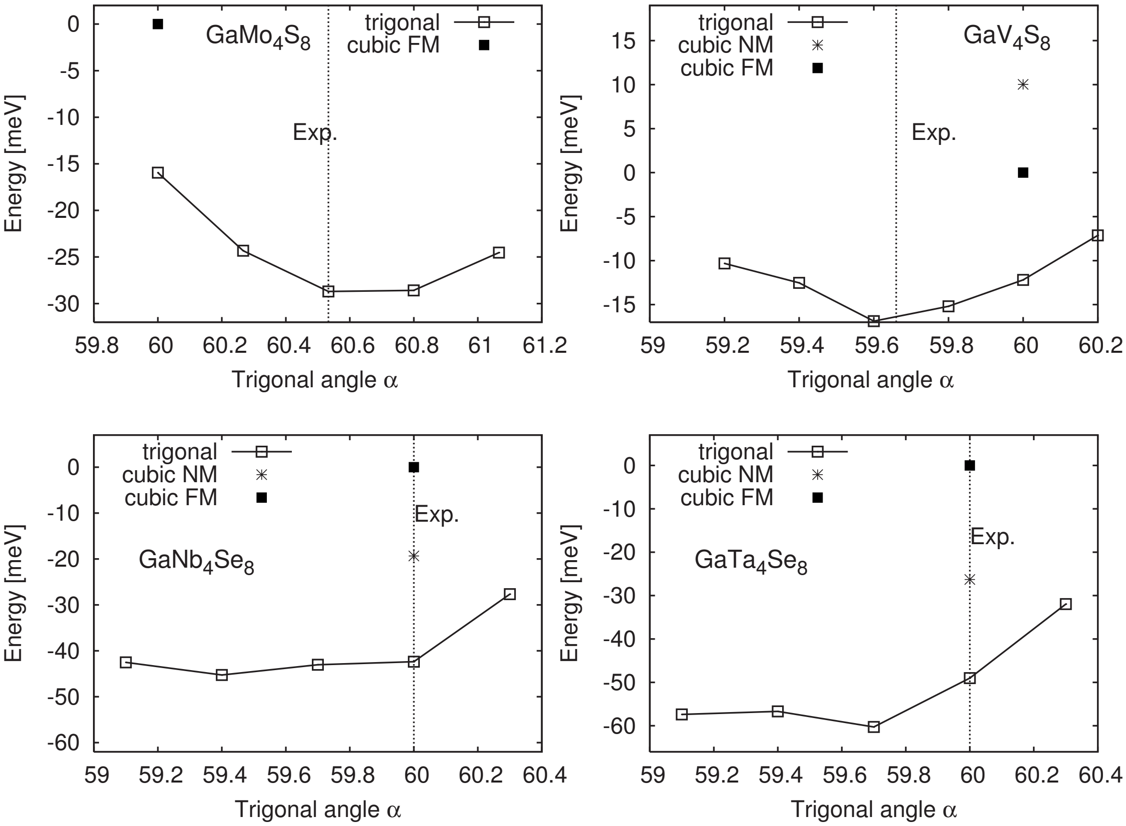

FIG. 3. Energy versus trigonal angle α for selected compounds. Except for GaMo$_4$S$_8$, in addition to the cubic FM states also the cubic nonmagnetic (NM) configurations are plotted.

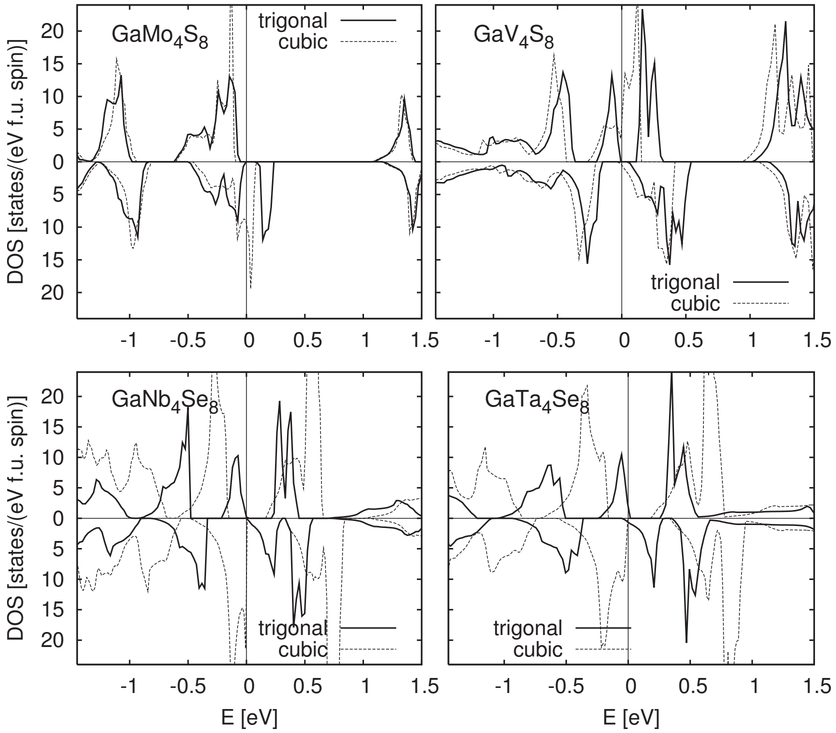

FIG. 4. Comparison between total DOS for trigonal (always α=60°) and cubic GaMo$_4$S$_8$ (upper left panel), GaV$_4$S$_8$ (upper right panel), GaNb$_4$Se$_8$ (lower left panel), and GaTa$_4$Se$_8$ (lower right panel). Only ferromagnetic configurations are compared; for M=Nb and Ta this is not the experimental ground state.

fraction is very insensitive to these types of structural change, in contrast to change in α, which are easy to identify. All compounds require a proper treatment of the internal degrees of freedom. This has not been taken into account up to now, but it must be included in all future DFT calculations. Moreover, our (plane-wave) GGA calculations clearly yield a gap at E_F for trigonal $GaMo_4S_8$, indicating that this compound is not a Mott insulator as stated elsewhere.[2] This is because in the trigonal structure not correlations but cluster distortions create the gap at E_F. Hence, correlation corrections like local density approximation LDA+U are not necessary for trigonal $GaMo_4S_8$ to reproduce the gap. A similar situation is found for GaV_4S_8, even though its tendency to FM order is reduced compared to the Mo-based compound. The situation changes strongly for $GaNb_4Se_8$ and $GaTa_4Se_8$. Their (nonmagnetic) DOSs at E_F are of intermediate height. On the one hand, they are not high enough to distort the lattice and to stabilize FM order in the cubic state; on the other hand the ratio of I/W for the cubic state is 1.2 and 0.8 for $GaNb_4Se_8$ and $GaTa_4Se_8$, placing them in the moderately correlated regime. While $GaMo_4S_8$ and GaV_4S_8 can be treated reasonably well within the GGA, assuming a FM ground state, the Nb- and Ta-related compounds can only be treated reasonably if their magnetic configuration is accounted for correctly. Since these compounds show no long-range order and seem to have an extremely strong interplay between cluster distortions and magnetism, their description is difficult and would require a disordered local moment picture.

ACKNOWLEDGMENTS

The authors thank K. Mereiter and S. Khmelevskyi for valuable discussions. M.S. is grateful for financial support from the Austrian Science Fund (FWF) in terms of the Science College Computational Materials Science, Project No. W004.

---

[1] Y. Sahoo and A. K. Rastogi, J. Phys.: Condens. Matter **5**, 5953 (1993).

[2] R. Pocha, D. Johrendt, and R. Pöttgen, Chem. Mater. **12**, 2882 (2000).

[3] M. M. Abd-Elmeguid, B. Ni, D. I. Khomskii, R. Pocha, D. Johrendt, X. Wang, and K. Syassen, Phys. Rev. Lett. **93**, 126403 (2004).

[4] H. Müller, W. Kockelmann, and D. Johrendt, Chem. Mater. **18**, 2174 (2006).

[5] R. Pocha, D. Johrendt, Bingfang Ni, and M. Abd-Elmeguid, J. Am. Chem. Soc. **127**, 8732 (2005).

[6] N. Shanthi and D. D. Sarma, J. Solid State Chem. **148**, 143 (1999).

[7] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[8] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[9] A. K. Rastogi and E. P. Wohlfarth, Phys. Status Solidi B **142**, 569 (1987).

[10] H. Nakamura, H. Chudo, and M. Shiga, J. Phys.: Condens. Matter **17**, 6015 (2005).