Molecular Mott state in the deficient spinel GaV$_4$S$_8$

Heung-Sik Kim, Kristjan Haule, and David Vanderbilt

1Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA
2Department of Physics, Kangwon National University, Chuncheon 24341, Korea

(Received 22 October 2018; revised 24 February 2020; accepted 24 July 2020; published 6 August 2020)

In this study, we investigated theoretically the Mott-insulating phase of a deficient spinel chalcogenide GaV$_4$S$_8$, which is known to form a tetrahedral V$_4$S$_4$ cluster unit that results in molecular orbitals (MOs) with a narrow bandwidth in the noninteracting limit. We used a cluster extension of charge self-consistent embedded dynamical mean-field theory to study the impact of strong intracluster correlations on the spectral properties as well as the structural degrees of freedom of the system. We found that the strong tetrahedral clustering renders the atomic Mott picture ineffective, and that the resulting MO picture is essential to describe the Mott phase. It was also found that, while the spectral properties can be qualitatively described by the truncation of the Hilbert space down to the lowest-energy MO, a proper description of the structural degrees of freedom requires the inclusion of multi-MO correlations that span a larger energy window. Specifically, we found that the lowest-energy MO description overemphasizes the clustering tendency, while the inclusion of the Hund’s coupling between the lower- and higher-energy MOs corrects this tendency, bringing the theoretically predicted crystal structure into good agreement with the experiment.

DOI: 10.1103/PhysRevB.102.081105
parameter reported in Ref. [12] was employed, and optimizations of internal atomic coordinates were done using DMFT forces [36,37]. The hybridization-expansion continuous-time quantum Monte Carlo method [27,28] was employed as the impurity solver. The atomic on-site Coulomb interactions were unitarily transformed and projected onto the MO basis, where the impurity hybridization function has a more appropriate form for the impurity solver [38].

**Crystal structure and MO formation.** Figure 1(a) shows the crystal structure of cubic GaV$_4$S$_8$. Compared to the fictitious nondeficient spinel Ga$_2$V$_2$S$_5$ shown in Fig. 1(b), half of the Ga sites (white Ga$_2$ sites in the figure) are missing in GaV$_4$S$_8$, which breaks the inversion symmetry (space group $F43m$) and allows the clustering of V and half of S (S$_1$ sites in the figure). This gives rise to MOs formed out of the 12 atomic $t_{2g}$ orbitals in the V$_4$ cluster, as depicted in Fig. 1(c), where the 12 orbitals are split into five irreducible representations of the cubic $T_d$ point group, specifically $A^1 \oplus E \oplus T^2 \oplus 2T^1$ (two $2T^1$ denoted as $T^1_{1g}$ in the diagram). Note that the charge configuration is $(V_4)^{13+}$, so there are seven electrons left in the cluster, fully occupying the singlet $A^1$ and doublet $E$ and filling one electron in the $T^2$ triplet, as shown in Fig. 1(c). The result of a DFT calculation (without including $U$) is shown in Fig. 1(d), showing MO-projected fat bands and partial density of states (PDOS) where blue, green, and red colors depict the MO-$A^1$, $E$, and $T^2$ orbital characters, respectively. The MOs can be seen to be well separated in energy and show a narrow bandwidth because of the strong clustering; compared to the size of MO splitting, which is on the order of $\sim 1$ eV, the magnitude of the intercluster electron hopping is at most $\sim 0.02$ eV [39]. This implies that the MO orbitals can be a reasonable basis set for the following MO-DMFT calculations.

Single-site vs cluster MO DMFT. Figure 2 shows the comparison between the results from the conventional single-site DMFT and the simplest $T^2$-MO-DMFT calculations ($T = 232$ K) [40]. In the latter scheme, one treats the partially filled $T^2$ triplet MO as the correlated subspace. Note that choosing the $T^2$ only as the correlated subspace is the simplest cluster-type approximation, but it already yields a completely different result compared to the single-site DMFT. Figure 2(a) shows the $k$-dependent spectral function from the single-site DMFT calculation, employing the atomic V $t_{2g}$ orbitals as the correlated subspace with an on-site Coulomb repulsion of $U = 6$ eV, appropriate for the V $t_{2g}$ set of quasi-atomic orbitals. A metallic band structure is clearly visible around the Fermi level, similar to the DFT result [Fig. 1(d)], due to the strong hybridization between the intracluster V sites and the mixed valence occupancy ($d^{1.75}$ per V). Increasing the $U$ value within the single-site DMFT did not induce a qualitative change.

While the single-site DMFT cannot open the Mott gap for any physical value of $U$, the MO-DMFT yields a qualitatively correct result even when applied to the simplest $T^2$-triplet MO as shown in Fig. 2(b). Therein the splitting of the $T^2$ states into the lower and upper Hubbard bands can be seen, depicted in red hue in the spectral function plot (and the red curve in the PDOS), which leads to the opening of a charge gap. Note that since the $T^2$ triplet is 1/6 filled, it is not possible to obtain an insulating phase in the band picture.
without breaking both the cubic and time-reversal symmetries [33], while in the Mott phase both symmetries can be kept. Hence we conclude that the cluster-MO description is indeed crucial in describing the Mott physics of GaV4S8, at least in its cubic and paramagnetic phase. Note that a similar result was previously reported on GaTa4Se8 by employing maximally localized Wannier functions for the T2 triplet and solving the Hubbard model via DMFT [41]. However, as we will show below, this approach overestimates the tendency toward V4 clustering since it ignores the important effect of the Hund’s coupling between the T2 and other MOs on the structural degrees of freedom.

\[ T^2 \oplus E \text{ subspace and Hund’s coupling.} \]

Despite the appearance of the Mott phase within the simplest T2-MO-DMFT calculation, this is a crude approximation because other MO states are separated from the T2 manifold by less than a fraction of an eV, and the Coulomb repulsion as well as the Hund’s coupling are larger or comparable to this separation. Therefore it is important to check what is the effect of including the next set of orbitals into the correlated space. Recently it was shown that the Hund’s coupling can have a very strong effect on the strength of correlations by promoting the local high-spin state and consequently allowing spins to decouple from the orbitals, thus allowing strong orbital differentiation [42–45]. Such physics is completely absent in the T2 model, as we assumed that the E MOs are completely filled and inert, leaving a single electron in the T2 MO set.

We next treat the combination of T2 \( \oplus E \) MOs as our correlated subset. Figures 3(a)–3(c) show the orbital-projected spectral functions from calculations with \( J_H = 0.5, 1.0, \) and 1.5 eV, respectively (\( T = 232 \) K, \( U = 8 \) eV). The red and green colors represent the T2 and E characters, respectively. The signature of a low-to-high spin crossover, from the \( S = 1/2 \) to 5/2 configuration, can be noticed in the plots where the fully occupied E doublet (at \( J_H = 0.5 \) eV) begins to lose spectral weight as \( J_H \) is enhanced. Tracking the Monte Carlo probabilities for the \( S_c = 1/2 \) and 5/2 states, plotted in Fig. 3(d), shows the same tendency that the \( S_c = 1/2 \) probability decreases and collapses almost to zero around \( J_H \sim 1 \) eV. Note that we report \( S_c \) values rather than \( S \) values, because of our choice of an Ising-type approximation of the Coulomb interaction in the MO-DMFT impurity solver [46]. For \( J_H \geq 1 \) eV, it can be seen that the E doublet becomes half-filled [see Figs. 3(c) and 3(e)], showing that the crossover to the high-spin state is almost complete. Note that even a moderate \( J_H \ll 1 \) eV, appropriate for 3d transition-metal compounds [47], induces substantial mixing between the low-spin and high-spin states. Therefore one may suspect a potential role of the Hund’s coupling physics in the high-temperature cubic phase of GaV4S8. Unexpectedly, it turns out that the Hund’s coupling significantly weakens the degree of the V4S4 clustering, in contrast with the Coulomb repulsion \( U \) which enhances the clustering, as shown in the following.

\[ \text{V}4\text{S}4 \text{ clustering from DFT.} \]

A parameter quantifying the size of the V4S4 clustering is the ratio between the nearest-neighbor V-V distances, \( d_{\text{NN}}^{\text{V}}/d_{\text{ic}}^{\text{V}} \), where \( d_{\text{NN}}^{\text{V}} \) and \( d_{\text{ic}}^{\text{V}} \) denote the inter- and intracluster V-V distances, respectively, as shown in Fig. 4(a). \( d_{\text{NN}}^{\text{V}}/d_{\text{ic}}^{\text{V}} \) is unity in the ideal spinel structure, while in GaV4S8 the value was reported to be 1.35 at \( T = 295 \) K and 1.37 at 20 K, respectively [see the horizontal dashed/dotted lines in Fig. 4(c)] [52].

Figure 4(c) shows the ratios obtained from DFT calculations with different choices of exchange-correlation functionals [30–32,48–51], which have been reported to yield different values of lattice parameters. Three distinct magnetic configurations were considered: a nonmagnetic configuration (NM), a low-spin ferromagnetic configuration (L-FM) with \( S = 1/2 \), and high-spin ferromagnetic configurations (H-FM) with \( S = 5/2 \) or 7/2. These are schematically illustrated in Fig. 4(b). Note that because the V4 cluster is believed to host a cluster spin moment, FM configurations were considered in our DFT calculations as appropriate for systems with local moments.

Remarkably, the values of \( d_{\text{NN}}^{\text{V}}/d_{\text{ic}}^{\text{V}} \) shown in Fig. 4(c) are almost identical, at about 1.4, for all the results on the NM or L-FM configurations, despite different optimized lattice parameters (except HSE; see below). Thus, the degree of clustering is consistently overestimated compared to...
H-FM configurations are obtained by employing hybrid functional \[31,32\]. In the DFT MO bonding states (We notice that in H-FM solutions the lowest occupied \(d\) lengths horizontal gray dashed and black dotted lines show the values of \(d\) solutions with the DFT experimental values. On the other hand, the H-FM so-

experimental values. On the other hand, the H-FM solutions with the DFT+U or HSE06 hybrid functionals severely underestimate the clustering, as shown in Fig. 4(c). We notice that in H-FM solutions the lowest occupied MO bonding states \((E, A^1)\) have been emptied at the expense of occupying higher nonbonding- or antibonding-like states. Therefore it is natural that H-FM solutions show a reduced tendency to clustering. Hence it appears that the small but significant discrepancy between the theoretical (in NM or L-FM) and experimental \(d^V_{\text{int}}/d^V_{\text{ic}}\) values results from the small admixture of the high-spin configurations to the dominant low-spin configuration in the electronic states of GaV4S8, which cannot be captured in the framework of conventional DFT. Note that even though the HSE06 results with NM or L-FM configurations seem to reproduce reasonable \(d^V_{\text{int}}/d^V_{\text{ic}}\) values, those states are much higher in energy by 1.5 eV / f.u. compared to the \(S=7/2\) H-FM phase. Also, all of the DFT results (NM, L-FM, and H-FM) fail to reproduce the insulating phase, signifying the failure of the DFT methods in this system.

\(V_{4}\) \(S_4\) \text{clustering from MO-DMFT}. Figure 5 shows the evolution of the \(d^V_{\text{int}}/d^V_{\text{ic}}\) values from the DMFT results. As explained above, within the single-site DMFT the correlations appear to be weak, so that the predicted structure is very close to the DFT prediction. As the intracluster correlations are considered via the \(T^2\) MO, the local Hubbard \(U\) enhances the clustering tendency, which is clear from the predicted values at \(J_H=0\). It can be seen that the clustering tendency is substantially overemphasized when the \(T^2 \oplus E\) are considered as correlated, due to the bonding nature of the \(E\) MO. When the antibonding \(J_H^F\) MO is also included, the degree of clustering reverts back to similar value as for the \(T^2\)-only calculation. Still, the value of \(d^V_{\text{int}}/d^V_{\text{ic}}\) is larger than the DFT-optimized one at \(J_H=0\), showing the role of \(U\) in enhancing the clustering.

Once the Hund’s coupling is turned on, the degree of clustering is quickly reduced (except for the \(T^2\)-only case where there is only one electron) as shown in Fig. 5. We then obtain the experimental \(d^V_{\text{int}}/d^V_{\text{ic}}\) values around \(J_H=0.5\) eV, which is a reasonable value for our model, in which \(e_g\) states (as well as \(A^1\) and \(T^1\)) are screening the interaction. This observation is consistent with the spectroscopic tendency mentioned above, where \(J_H\) promotes the high-spin state so that spin moments can be more localized on each \(V\) site. We thus find, quite surprisingly, that in cases with strong clustering the Coulomb \(U\) and Hund’s \(J_H\) can play opposite roles: the former promotes nonlocal correlations and formation of the bonding molecular orbital state, while the latter promotes local atom-centered high-spin states. This Janus-faced effect of \(U\) and \(J_H\) is a central result of this study. Note also that the reduction of \(d^V_{\text{int}}/d^V_{\text{ic}}\) is significant already at \(J_H=0.5\) eV, where the mixture of the high-spin configurations is quite small as shown in Fig. 3(d). This implies an unusual strong coupling between the electronic configuration and the \(V_{4}\) clustering, which may be exploited to tune the spin configuration by employing optical pumping techniques as done in VO2 \[53\].

\textbf{Discussion and summary}. In summary, in this work we have clarified the significance of electron correlations in describing the MO Mott physics and structural properties of GaV4S8, especially the Janus-faced role of \(U\) and \(J_H\) in its crystal structure, which can be extended to study the low-temperature ferroelectric and multiferroic phases \[20-22\] of the same compound and possible unconventional electron-lattice couplings therein. With a careful choice of the MO correlated subspace, our MO-based DMFT approach can tackle systems with large-sized clusters that are not amenable to solution using conventional cluster DMFT approaches, such as \(1T^2\) Ta[S, Se]2 and other cluster Mott-insulating systems \[54,55\].

\textbf{Acknowledgments}. This work was supported by NSF DMR-1629059. H.-S.K. was funded by the National Research Foundation of Korea (Basic Science Research

FIG. 4. (a) Definitions of the intra- and intercluster V-V bond lengths \(d^V_{\text{int}}\) and \(d^V_{\text{ic}}\), respectively. (b) Schematic representations of the nonmagnetic (NM), low-spin (L-FM, \(S=1/2\)), and high-spin ferromagnetic (H-FM, \(S=5/2\) or \(7/2\)) configurations, where the dots and arrows depict nonmagnetic and magnetic electrons, respectively. (c) \(d^V_{\text{int}}/d^V_{\text{ic}}\) from DFT results with different choices of exchange-correlation potentials: LDA \[48\], PBE \[49\], PBEsol \[50\], SCAN meta-GGA functional \[30\], DFT+U \[51\], and HSE06 hybrid functional \[31,32\]. In the DFT+U results, the L-FM and H-FM configurations are obtained by employing \(U_{\text{eff}}=2\) and 4 eV in the simplified rotationally invariant DFT+U scheme \[51\]. Horizontal gray dashed and black dotted lines show the values of \(d^V_{\text{int}}/d^V_{\text{ic}}\) from experimental structures measured at \(T=295\) and 20 K, respectively \[12\].

FIG. 5. \(d^V_{\text{int}}/d^V_{\text{ic}}\) from DFT results as a function of \(J_H\). Note that MO-\(T^2\) and MO-\(\{T^2 \oplus T^1\}\) configurations are not affected by \(J_H\) because of the single occupancy, and that the MO-\(\{T^2 \oplus E \oplus T^1\}\) reaches the experimental \(d^V_{\text{int}}/d^V_{\text{ic}}\) near \(J_H=0.5\) eV.
Program, Grant No. 2020R1C1C1005900), and also thanks the National Supercomputing Center of Korea for the support of supercomputing resources including technical assistance (Grant No. KSC-2019-CRE-0036).


[34] K. Haule, C.-H. Yee, and K. Kim, Dynamical mean-field theory within the full-potential methods: Electronic structure of CeIrIn_5, CeCoIn_5, and CeRhIn_5, Phys. Rev. B 81, 195107 (2010).


[38] Details of this transformation and its implementation in the DFT+embedded DMFT code are discussed in the Supplemental Material. Therein it is argued that intracluster Coulomb repulsions in this system should be insignificant and can be ignored [56]. Note that the DFT+embedded DMFT code runs based on the WIEN2k package [57]. Choices of U and J values in this DMFT implementation was discussed in Ref. [58]. The Vienna Ab initio Simulation Package (VASP) [59, 60] was used for independent structural optimizations at the DFT level.


[42] This approximation leads to some mixing between half-integer spin states, but is not expected to change qualitative aspects of the results.


[48] Note that at T = 20K, the compound has a rhombohedral distortion. The value 1.37 is obtained by averaging d_u^4 and d_u^6 separately and taking the ratio between them.


