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

Heung-Sik Kim,$^1$ Kristjan Haule,$^1$ and David Vanderbilt$^1$

$^1$Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA

In this Letter, 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$_8$ 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 intra-cluster 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.

Intermetallic covalency in transition-metal chalcogenides or oxides often leads to the formation of density waves or cluster DMFT, 

\[ \text{DMFT, } \text{CDMFT} \]

employed a state-of-the-art DFT+embedded DMFT code [33, 34], which allows relaxation of internal atomic coordinates. In CDMFT the experimental lattice parameter reported in Ref. 12 was employed, and optimizations of internal atomic coordinates were done using DMFT forces [35]. The hybridization-expansion continuous-time quantum Monte
FIG. 1. (a) Crystal structure of the deficient spinel GaV$_4$S$_8$ in the cubic phase, in comparison with a fictitious perfect spinel Ga$_2$V$_4$S$_8$ illustrated in (b). Note the inter-cluster V-V bonds depicted in red dashed lines in (a), and white Ga sites in (b) which are absent in deficient spinel structure (a). (c) Splitting of 12 atomic $d$-orbitals as the correlated subspace (a), doublet $E$, and triplet $T^2$, as shown the diagram. (d) MO-projected fat-band representation and density of state (PDOS) plots of GaV$_4$S$_8$ from the DFT results (without $U$).

Carlo method [26, 27] 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. Details of this transformation and its implementation in the DFT+embedded DMFT code are discussed in the Supplementary Information (SI). The Vienna *ab-initio* Simulation Package (VASP) [36, 37] was used for independent structural optimizations at the DFT level.

**Crystal structure and MO formation.** Fig. 1(a) shows the crystal structure of cubic GaV$_4$S$_8$. Compared to the fictitious non-deficient spinel Ga$_2$V$_4$S$_8$ 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 $Fd3m$) 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 5 irreducible representations of the cubic $T_d$ point group, specifically $A^1$ + $E$ + $T^2$ + $2T^1$ (two $2T^1$ denoted as $T^1_{a,b}$ in the diagram). Note that the charge configuration is $(V_{4})^{3+}$, so there are 7 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) with 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 because of the strong clustering, implying that the MO orbitals can be a reasonable basis set for the following CDMFT calculations.

**Single-site vs. CDMFT.** Fig. 2 shows the comparison between the results from the conventional single-site DMFT and the simplest $T^2$-CDMFT calculations ($T = 232$ K) [38]. 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. Fig. 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 intra-cluster 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 CDMFT 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 [32], 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 [39]. 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.

**T² ⊕ E subspace and Hund’s coupling.** Despite the appearance of the Mott phase within the simplest T²-CDMFT 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 [40–43]. 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 ⊕ E MOs as our correlated subset. Fig. 3(a-c) shows 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_z = 1/2 and 5/2 states, plotted in Fig. 3(d), shows the same tendency that the S_z = 1/2 probability decreases and collapses almost to zero around J_H ~ 1 eV. Note that we report S_z values rather than S values, because of our choice of an Ising-type approximation of the Coulomb interaction in the CDMFT impurity solver [44]. For J_H > 1 eV, it can be seen that the E doublet becomes half-filled (see Fig. 3(c) and (e)), showing that the crossover to the high-spin state is almost complete. Note that even a moderate J_H < 1 eV, appropriate for 3d transition-metal compounds [45], 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 V₄S₈ clustering, in contrast with the Coulomb repulsion U which enhances the clustering, as shown in the following.

**V₄S₈ clustering from DFT.** A parameter quantifying the size of the V₄S₈ clustering is the ratio between the nearest-neighbor V-V distances, d_{ic}^{V}/d_{ic}^{N}, where d_{ic}^{V} and d_{ic}^{N} denote the inter- and intra-cluster V-V distances respectively as shown in Fig. 4(a). d_{int}^{N}/d_{ic}^{N} 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)) [50].

Fig. 4(c) shows the ratios obtained from DFT calculations with different choices of exchange-correlation functionals [29–31, 46–49], 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 \(d_{\text{int}}^N/d_{\text{ic}}^N\) 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 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 \(d_{\text{int}}^N/d_{\text{ic}}^N\) values results from the small admixture of the high-spin configurations to the dominant low-spin configuration in the electronic states of GaV\(_4\)S\(_8\), 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 \(d_{\text{int}}^N/d_{\text{ic}}^N\) 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.

\(V_4S_4\) clustering from CDMFT. Figure 5 shows the evolution of the \(d_{\text{int}}^N/d_{\text{ic}}^N\) 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 intra-cluster 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 \(T^2 + E\) are considered as correlated, due to the bonding nature of the \(E\) MO. When the antibonding \(T^3\) MO is also included, the degree of clustering reverts back to similar value as for the \(T^2\)-only calculation. Still, the value of \(d_{\text{int}}^N/d_{\text{ic}}^N\) 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 \(d_{\text{int}}^N/d_{\text{ic}}^N\) values around \(J_H = 0.5\) eV, which is a reasonable value for our model, in which \(\epsilon_g\) states (as well as \(A^1\) and \(T^2\)) 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 non-local 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 \(d_{\text{int}}^N/d_{\text{ic}}^N\) is significant already at \(J_H = 0.5\) eV, where the mixture of the high-spin configurations is quite small as shown in Fig. 5(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 VO\(_2\) [51].

Discussion and Summary. Our results demonstrate the promise of the MO-CDMFT approach employed in this work. With a careful choice of the MO correlated subspace, this approach can tackle systems with large-sized clusters that are not amenable to solution using conventional cluster DMFT.
approaches, also yielding much improved results compared to conventional DFT or single-site DMFT. Hence, with proper caution, it should be capable of treating other systems in which large clusters appear, such as $1\times1\times1$. Overall, in this work we have clarified the significance of electron correlations in describing the MO Mott physics and structural properties of $\text{GaV}_4\text{S}_8$, especially the Janus-faced role of $U$ and $J_{\text{H}}$ in its crystal structure. It should be emphasized that this is the first ab-initio study on the Mott phase of this compound, which can be extended to investigate the low-temperature ferroelectric and multiferroic phases [19–21] and possible unconventional electron-lattice couplings therein.

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SUPPLEMENTARY INFORMATION

Density functional theory calculations

For unit cell optimizations (cell volume and shape) and relaxations of initial internal coordinates, the Vienna ab-initio Simulation Package (VASP), which employs the projector-augmented wave (PAW) basis set [36, 37], was used for density functional theory (DFT) calculations in this work. 330 eV of plane-wave energy cutoff (PREC=high) and 15×15×15 Γ-centered k-grid sampling were employed. For the treatment of electron correlations within DFT, several exchange-correlation functionals were employed, including Ceperley-Alder (CA) parametrization of local density approximation [46], Perdew-Burke-Ernzerhof generalized gradient approximation (PBE) [47] and its revision for crystalline solids (PBEsol) [48], SCAN meta-GGA functional [29], DFT+U [49] on top of LDA, PBE, and PBEsol, and HSE06 hybrid functional [30, 31]. 10⁻⁴ eV/Å of force criterion was employed for structural optimizations.

Cluster dynamical mean-field theory calculations

A fully charge-self-consistent dynamical mean-field method[33], implemented in DFT + Embedded DMFT (eDMFT) Functional code (http://haulewweb.rutgers.edu/tutorials/) which is combined with wienn2k code[52], is employed for computations of electronic properties and optimizations of internal coordinates[35]. At the DFT level the Perdew-Wang (PW) local density approximation is employed, which was argued to yield the best agreement of lattice properties when combined with DMFT[53]. 15×15×15 Γ-centered k-grid was used to sample the first Brillouin zone with RK_{max} = 7.0. A force criterion of 10⁻⁴ Ry/Bohr was adopted for optimizations of internal coordinates. The cubic lattice parameter was fixed to be the experimental value reported in Ref. 12. A continuous-time quantum Monte Carlo method in the hybridization-expansion limit (CT-HYB) was used to solve the auxiliary quantum impurity problem[54]. For the CT-HYB calculations, up to 3 × 10¹⁰ Monte Carlo steps were employed for each Monte Carlo run. In most runs temperature was set to be 232K, but in calculations with 8 molecular orbitals (MOs) the temperature was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs) (ture was set to be 232K, but in calculations with 8 molecular orbitals (MOs). Up to 1160K because of the increased computational cost. -10 to +10 eV of hybridization window (with respect to the Fermi level) was chosen, and the on-site Coulomb interaction parameters U and Jₜ for Vₜ₂₆ orbitals were varied within the range of 6 ~ 8 eV and 0 ~ 1.5 eV, respectively. A simplified Ising-type (density-density terms only) Coulomb interaction was employed in this work, and it was tested that the use of full Coulomb interaction yields only quantitative difference in results with MO-T² and T² ⊕ E (not tested for MO-T² ⊕ E ⊕ T₁ case due to the high cost). A nominal double counting scheme was used, with the MO occupations for double counting corrections for for the Vₜ cluster were chosen to be 1 or 5, depending on the choice of correlated subspace; 1 for MO-T² and T² ⊕ T₁, and 5 for other cases with including E in the correlated subspace.

In the CT-HYB calculations of the T² ⊕ E ⊕ T₁ MO subspace, MO multiplet states with the occupancy n ≤ 7 were kept (26,333 states out of 4⁰ = 65,536 states in the 8 orbital Fock space) to reduce the computational cost, where the average impurity occupancy was ~ 5. It was checked that the sum of probabilities for n ≥ 8 configurations are less than 1 percent. The high-frequency tail of the Green’s function was calculated via the Hubbard-I approximation.

Projecting the on-site Coulomb interactions onto the MO subspace

Note that the U and Jₜ are parameters defined for the atomic orbitals, which should be unitary transformed and projected onto the MOs for the impurity solver. More generally, the Coulomb repulsion matrix elements Uₘ₁ₐₜₚₐₘ₂ₐₜ₂ₖₚ₂ are nonzero only for k = 0, 2, 4 for d-orbitals (l = 2) and Y₁ₐₜₚₐₘ₁ₐₜ₁ are Clebsch-Gordan coefficients. We introduce the MO states

\[ D_α = \sum_{i m} (Q^i)^{im} |Y^i_{lm}\rangle, \]

(2)

where \(Q\) is the unitary transform between the MO and the atomic orbitals, and \(i = 1, \ldots , 4\) are the MO orbital and atomic site indices respectively. Then the Coulomb repulsion matrix elements for the MO states \(U_{α₁,α₂,α'ₗ₂,α'ₗ₂'}\) can be written as

\[ U_{α₁,α₂,α'_₁,α'_₂} = \sum_{i m k} \frac{4}{2π + 1} (D_{α₁} |Y^{i}_{km}\rangle |D_{α₂} |Y^{i'}_{km}\rangle |D_{α'_₁} |Y^{i'}_{km}\rangle |D_{α'_₂} |Y^{i'}_{km}\rangle F^{k}_{α₁,α₂,α'_₁,α'_₂}) \]

(3)

\[ ∼ (QQQ^T)^{-1}_{α₁} U^T_{i m}. \]

(4)

Note that the inter-site Coulomb interactions were ignored here, which can be considered insignificant in 3d transition metal compounds.

Below we show explicitly how the on-site Coulomb interactions projected onto the T² triplet subspace should look like. As shown in Fig. 1 in the main text, electronic structure near the Fermi level ([-1eV, 1eV] window with respect to the Fermi level) is dominated by the atomic t₂₆ orbitals of V due to the distorted but prevalent cubic VS₆ octahedral environment. Therefore choosing 12 t₂₆ orbitals as our main interest is a reasonable choice. For simplicity we chose the
Cartesian
In the above expression, product of \( \sum \) different kinds; i) \( \sum \) are free of spin components and can be classified into four (ces does not have spin indices, all full 12-dimensional molecular orbital space.

Kanamori form of the Coulomb interaction, which is written in a normal-ordered form as follows;

\[
\hat{H}_K = -\sum_i [(U - 2J) \sum_{mm'} \hat{d}_{im\uparrow}^\dagger \hat{d}_{im'\uparrow}^{ \dagger} \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im'\downarrow}^{ \dagger} + 2J \sum_m \hat{d}_{im\uparrow}^\dagger \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im\uparrow}^{ \dagger}]
+ \frac{U - 3J}{2} \sum_{m\neq m',\sigma} \hat{d}_{im\sigma}^\dagger \hat{d}_{im'\sigma}^{ \dagger} \hat{d}_{im\sigma}^{ \dagger} \hat{d}_{im'\sigma}^{ \dagger} - J \sum_{m\neq m'} \hat{d}_{im\uparrow}^\dagger \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im\uparrow}^{ \dagger} - J \sum_{m\neq m'} \hat{d}_{im\uparrow}^\dagger \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im\downarrow}^{ \dagger} \hat{d}_{im\uparrow}^{ \dagger}].
\]

Here \( i, \sigma, \) and \( m, m' \) are site, spin, and orbital indices for Cartesian \( t_{2g} \) orbitals \( d_{xz,yz,xy} \) respectively.

Now we introduce the MO creation/annihilation operators;

\[
\hat{d}_{im\sigma} = \sum_{\alpha} Q_{im}^{\alpha} \hat{D}_{\alpha\sigma}
\]
\[
\hat{d}_{im\sigma}^{\dagger} = (Q_{im}^{\alpha})^\dagger \hat{D}_{\alpha\sigma}^{\dagger}
\]

where \( \alpha \) runs over the 12 molecular orbitals and we are ignoring spin-orbit coupling (SOC) at this stage. \( Q_{im}^{\alpha} \) is the 12 \( \times \) 12 transformation matrix from the atomic \( t_{2g} \) to the MO spaces.

In terms of \textit{global} coordinates (using the same cartesian coordinates for all V sites) it is tabulated in Table I. Note that in actual calculations, since the four V sites are equivalent to each other up to a symmetry operation, \( Q \) should be unitarily transformed to a local coordinate system at each V site.

Plugging them into \( \hat{H}_K \) yields,

\[
\hat{H}_K = -\sum_{\alpha\beta\gamma\delta} [(U - 2J) \sum_i \left\{ \sum_{mm'} (Q_{im}^{\alpha\beta})(Q_{im'}^{\alpha\beta})^\dagger \hat{D}_{\alpha\beta\gamma\delta}^{\dagger} \hat{D}_{\gamma\delta\alpha\beta} \right\} + 2J \sum_i \left\{ \sum_m (Q_{im}^{\alpha\beta})(Q_{im}^{\beta\gamma})^\dagger \hat{D}_{\alpha\beta\gamma\delta}^{\dagger} \hat{D}_{\gamma\delta\alpha\beta} \right\}]
+ \frac{U - 3J}{2} \sum_i \left\{ \sum_{m\neq m'} (Q_{im}^{\alpha\beta})(Q_{im'}^{\alpha\beta})^\dagger \hat{D}_{\alpha\beta\gamma\delta}^{\dagger} \hat{D}_{\gamma\delta\alpha\beta} \right\} - J \sum_i \left\{ \sum_{m\neq m'} (Q_{im}^{\alpha\beta})(Q_{im'}^{\alpha\beta})^\dagger \hat{D}_{\alpha\beta\gamma\delta}^{\dagger} \hat{D}_{\gamma\delta\alpha\beta} \right\}
- J \sum_i \left\{ \sum_{m\neq m'} (Q_{im}^{\alpha\beta})(Q_{im'}^{\alpha\beta})^\dagger \hat{D}_{\alpha\beta\gamma\delta}^{\dagger} \hat{D}_{\gamma\delta\alpha\beta} \right\].
\]

In the above expression, product of \( Q_8 \) can be rewritten as

\[
(Q_{im}^{\alpha\beta})(Q_{im'}^{\alpha\beta})^\dagger \equiv (Q_{im}\sigma)(Q_{im'}\sigma)^\dagger
\]
\[
(Q \otimes Q)_{im\gamma\delta}^\dagger \equiv Q_{im}\sigma_{\gamma\delta}
\]

and, since we are considering \textit{local} Coulomb interactions, we are taking direct products of \( i \)-subsections \( \{i=1, \cdots, 4\} \) of \( Q \) and \( Q^\dagger \) matrices, so that \( Q \otimes Q \) (and \( Q^\dagger \otimes Q^\dagger \)) has dimension of \( 9 \times 144 \) for each \( i \) when we are considering the full 12-dimensional molecular orbital space.

Since we don’t include SOC and the transformation matrices does not have spin indices, all \( (Q^\dagger \otimes Q^\dagger) \cdot (Q \otimes Q) \) terms are free of spin components and can be classified into four different kinds; i) \( \sum_{mm'} (Q^\dagger_{im} \otimes Q^\dagger_{im'})_{\alpha\beta} \sigma (Q \otimes Q)_{im}\gamma\delta, \)  

ii) \( \sum_m (Q^\dagger_{im} \otimes Q^\dagger_{im})_{\alpha\beta} \sigma (Q \otimes Q)_{im}\gamma\delta, \)  

iii) \( \sum_{mm'} (Q^\dagger_{im} \otimes Q^\dagger_{im'})_{\alpha\beta} \sigma (Q \otimes Q)_{im}\gamma\delta, \)  

iv) \( \sum_{mm'} (Q^\dagger_{im} \otimes Q^\dagger_{im'})_{\alpha\beta} \sigma (Q \otimes Q)_{im}\gamma\delta, \)  

Here case iii) is just the subtraction of ii) from i).

Computation of the transformation matrix is straightforward, but now all different molecular orbitals can mix even in a simple density-density interaction form (the first three terms in \( \hat{H}_K \)). However, things become much simpler in the most basic case of considering only the \( T^2 \) irrep as the correlated subspace. In that case, all \( Q_i \) and \( Q_i^\dagger\) become \( 3 \times 3 \) identity matrix (with normalization factor 1/2), so that all \( Q \otimes Q \) and \( Q^\dagger \otimes Q^\dagger \) become \( 9 \times 9 \) identity matrix with a prefactor 1/4, so
TABLE I. Transformation matrix $Q'_{im}$ from atomic $t_{2g}$ to molecular orbital basis before normalization, where $w = e^{2\pi i/3}$.

| Irreps No. Coeff. | $V_1$ (0.4,0.4,0.4) | $V_2$ (0.4,0.6,0.6) | $V_3$ (0.6,0.6,0.4) | $V_4$ (0.6,0.6,0.6) |
|-------------------|-------------------|-------------------|-------------------|-------------------|
|                   | $d_{xy}$ | $d_{yz}$ | $d_{xz}$ | $d_{xy}$ | $d_{yz}$ | $d_{xz}$ | $d_{xy}$ | $d_{yz}$ | $d_{xz}$ |
| $A$               | +1     | +1     | +1     | -1     | -1     | -1     | +1     | +1     | +1     | +1     | +1     |
| $E$               | +1     | $w^1$  | $w^2$  | +1     | $w^1$  | $w^2$  | +1     | $w^1$  | $w^2$  | +1     | $w^1$  |
| $T^2$             | +1     | 0     | 0     | +1     | 0     | 0     | +1     | 0     | 0     | +1     | 0     |
|                  | 0     | 0     | +1     | 0     | 0     | +1     | 0     | 0     | +1     | 0     |
| $T^3$             | +1     | 0     | -1     | 0     | -1     | -1     | 0     | -1     | +1     | 0     |
|                  | 0     | 0     | -1     | 0     | -1     | -1     | 0     | -1     | +1     | 0     |
| $T^4$             | +1     | 0     | +1     | 0     | -1     | -1     | 0     | -1     | +1     | -1    |
|                  | +1     | 0     | +1     | 0     | -1     | -1     | 0     | -1     | +1     | -1    |

Hence $\hat{H}_K$, projected onto the MO-$T^2$ subspace, becomes

$$\hat{H}^{\text{MO}}_K = \frac{1}{4} \left[ (U - 2J) \sum_{nm'} (\hat{D}_{m\uparrow}^\dagger \hat{D}_{n\downarrow}^\dagger \hat{D}_{m\downarrow}^\dagger \hat{D}_{n\uparrow}^\dagger) + 2J \sum_m (\hat{D}_{m\uparrow}^\dagger \hat{D}_{m\downarrow}^\dagger \hat{D}_{m\downarrow}^\dagger \hat{D}_{m\uparrow}^\dagger) + U - \frac{3J}{2} \sum_{m \neq m', \sigma} \hat{D}_{m\sigma}^\dagger \hat{D}_{m\sigma}^\dagger \hat{D}_{m\sigma} \hat{D}_{m'\sigma} - J \sum_{m \neq m'} (\hat{D}_{m\uparrow}^\dagger \hat{D}_{m\downarrow}^\dagger \hat{D}_{m\downarrow} \hat{D}_{m\uparrow}^\dagger) - J \sum_{m \neq m'} (\hat{D}_{m\uparrow}^\dagger \hat{D}_{m\downarrow}^\dagger \hat{D}_{m\downarrow}^\dagger \hat{D}_{m\uparrow}) \right]. \tag{15}$$

Note that $\hat{H}^{\text{MO}}_K$ has the exactly same form with the atomic $\hat{H}_K$, except the prefactor $1/4$ because of the equidistribution of the MO-$T^2$ wavefunctions all over the four $V$ sites.

On-site and inter-site self-energies

In this section the role of the Hund’s coupling is discussed in terms of the real space representation of the self-energy. Here we focus on the $T^2 \oplus E$ subspaces and their self-energies. Similar analysis can be done with other MO subspaces, however, for the purpose of discussing the role of $J_H$ it seems that $T^2 \oplus E$ should suffice.

In our calculations the cluster self-energies are diagonalized within the MO representation. When back-transformed into the atomic orbital basis representation, on-site (local) and inter-site (non-local) self-energies within the $V_4$ tetrahedron can be obtained. In the simplest case with the correlated MO-$T^2$ triplet only, the form of the self-energy in the atomic representation becomes simple; Namely, in the four-site real-space representation (four sites $\otimes$ atomic $t_{2g}$), all the on-site and inter-site blocks are enforced to be identical due to the choice of the $T^2$ correlated orbitals when the cubic and time-reversal symmetries are present, so that

$$\Sigma [T^2](\omega) = \frac{1}{4} \Sigma^{T^2} \omega \left( \begin{array}{cccc} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{array} \right), \tag{16}$$

where each $3 \times 3$ block $\Sigma^{T^2} = \Sigma^{T^2} \times \hat{I}_{3 \times 3}$ in the atomic $t_{2g}$ space ($d_{xy}$, $d_{yz}$, and $d_{xz}$). $\hat{I}_{3 \times 3}$ is an identity matrix of dimension 3, and the frequency $\omega$ can be either real or imaginary. Note that $\Sigma^{T^2}$ is the diagonal self-energy in the $T^2$-MO representation, and that the prefactor $\frac{1}{4}$ in Eq. (16) is the one appearing in Eq. (15). Here we choose the same global coordinate in defining the $t_{2g}$ orbitals at all sites, and proper coordinate transforms should be applied to each block when represented in local coordinates ($\Sigma^{T^2}_{ij} \rightarrow (Q^\dagger)_{ij} \Sigma^{T^2}_{ij} Q_{ij}$, where the transformation $Q_{ij}$ is made from the global to the site-$i$ local coordinates). Fig. S6 plots the real and imaginary parts of...
\[ \Sigma_{T^2} \] in the real frequency space, showing a pole in the imaginary part inside the Mott gap.

From this real-space representation of the self-energy, the implication of choosing only the \( T^2 \) MO as correlated orbitals becomes clearer; i) it introduces the inter-site self-energy in addition to the on-site counterpart, and ii) it prevents the correlations from becoming more local by enforcing the on-site and inter-site self-energies to be identical. The latter, especially, can be a serious issue when the size of the correlations favor the formation of the local moments, e.g. the Hund’s coupling, becomes comparable to that of inter-site hopping.

Next, the form of self-energy in the \( T^2 \oplus E \) is as presented below:

\[ \Sigma \left[ T^2 \oplus E \right] (\omega) = \Sigma \left[ T^2 \right] (\omega) + \Sigma \left[ E \right] (\omega), \quad (17) \]

Other \( \hat{\Delta}_{ii} \), for a coordinate choice, should be as follows,

\[ \hat{\Delta}_{22} = \begin{pmatrix} 0 & +1 & -1 \\ +1 & 0 & +1 \\ -1 & +1 & 0 \end{pmatrix}, \quad \hat{\Delta}_{33} = \begin{pmatrix} 0 & +1 & +1 \\ +1 & 0 & -1 \\ +1 & -1 & 0 \end{pmatrix}, \quad \hat{\Delta}_{44} = \begin{pmatrix} 0 & -1 & +1 \\ -1 & 0 & +1 \\ +1 & +1 & 0 \end{pmatrix}. \quad (21) \]

Note that this is the coordinate choice that was adopted in this work.

The inter-site component \( \hat{\Sigma}_{ij} \) has a similar form; \( \hat{\Sigma}_{ij} \equiv \frac{1}{t_{2g}} \Sigma^E (\omega) \hat{O}_{ij} \), where

\[ \hat{O}_{12} = \begin{pmatrix} -2 & -1 & +1 \\ +1 & +2 & +1 \\ +1 & -1 & -2 \end{pmatrix}, \quad \hat{O}_{13} = \begin{pmatrix} +2 & +1 & +1 \\ -1 & -2 & +1 \\ -1 & +1 & -2 \end{pmatrix}, \quad \hat{O}_{23} = \begin{pmatrix} +2 & +1 & -1 \\ +1 & -2 & -1 \\ +1 & +1 & +2 \end{pmatrix}, \quad \hat{O}_{24} = \begin{pmatrix} +2 & -1 & +1 \\ +1 & -2 & -1 \\ -1 & -1 & -2 \end{pmatrix}, \quad \hat{O}_{34} = \begin{pmatrix} -2 & +1 & -1 \\ -1 & +2 & +1 \\ -1 & -1 & +2 \end{pmatrix}. \quad (22) \]

Combining (16-22), the site-orbital resolved self-energies in the \( T^2 \oplus E \) case is as follows.

i) On-site (diagonal blocks), between same orbitals:

\[ \left[ \frac{1}{4} \Sigma^{T^2} (\omega) + \frac{1}{8} \Sigma^E (\omega) \right] \hat{I}_{3 \times 3}, \]

ii) On-site (diagonal blocks), between different orbitals:

\[ \frac{1}{12} \Sigma^E (\omega) \hat{\Delta}_{ii}, \]
iii) Inter-site ($i \neq j$ blocks): $\frac{1}{4}\Sigma T^2(\omega)\hat{I}_{3	imes3} + \frac{1}{6}\Sigma E(\omega)\hat{O}_{ij}$.

Here, we note in passing that $\frac{1}{12}\Sigma E$ is small compared to other terms when $J_H$ is not large ($< 1$ eV), so that terms i) and iii) are dominant contributions, and that the balance between the terms i) and iii) determines whether it is locally (on-site) or non-locally (inter-site) correlated. Plugging (22) into the case iii) above yields an explicit expression of the $ij$-block of $\Sigma$ [$T^2 + E$]. For example, the block between the site 1 and 2 is as follows,

$$
\Sigma \left[ T^2 + E \right]_{12} = \left( \begin{array}{cc}
\frac{1}{4}\Sigma T^2 - \frac{1}{6}\Sigma E & -\frac{1}{12}\Sigma E \\
\frac{1}{12}\Sigma E & \frac{1}{4}\Sigma T^2 + \frac{1}{6}\Sigma E
\end{array} \right),
$$

(23)

where the plus and minus signs in the diagonal components are colored in blue and red to emphasize terms where $\Sigma T^2$ and $\Sigma E$ are adding up and cancelling out, respectively. Among the three diagonal components, the central term ($\frac{1}{4}\Sigma T^2 + \frac{1}{6}\Sigma E$) is between the $d_{yz}$ orbitals at V site 1 and 2, which are forming a strong $\sigma$-type direct overlap, while the other two $\frac{1}{4}\Sigma T^2 - \frac{1}{6}\Sigma E$ are contributing to the $\delta$-like weak overlap between the $d_{xy,xz}$ orbitals. Interestingly, the inclusion of $\Sigma E$ (and $J_H$) affects the inter-site self-energies in an opposite way depending on the orbitals; while the imaginary part of $\frac{1}{4}\Sigma T^2 + \frac{1}{6}\Sigma E$ is enhanced by the nonzero $\Sigma E$ (because causal self-energies should always have negative imaginary parts), it is canceled out in $\frac{1}{4}\Sigma T^2 - \frac{1}{6}\Sigma E$. This implies that the presence of $\Sigma E$ selectively enhances the singlet moment formation within the stronger $\sigma$-bonding, while reducing inter-site correlations in other bondings. In addition, depending on the sign of the real parts of $\Sigma T^2$ and $\Sigma E$, one can either enhance or suppress the real part of the self-energy.

Fig. S7 show the evolution of $\Sigma T^2, E(\omega)$ as a function of the Hund’s coupling $J_H$. Note that the relative signs of the real part of $\Sigma T^2, E(\omega)$ tend to be opposite when $J_H$ is small,
but increasing $J_H$ drives them to be the same. Just after the crossover to the high-spin state happens ($J_H = 1.1$ eV), both the $\text{Re}\Sigma^{T^2,E}(\omega)$ show very similar behavior. This is because of the development of the pole in $\Sigma^E$, signaling the formation of the $E$ local moments, as shown in the lower panels of Fig. S7. As the system goes into the high-spin configuration, both the $\text{Im}\Sigma^{T^2,E}$ should similarly show a well-defined pole, then the shapes of $\text{Re}\Sigma^{T^2,E}(\omega)$ should become similar to each other because of the Kramers-Kronig relation. Hence $\frac{1}{4}\Sigma^{T^2} - \frac{1}{6}\Sigma^E$ within $\Sigma \left[ T^2 \oplus E \right]_{ij}$ tends to cancel better as $J_H$ becomes larger. Since the diagonal parts of the inter-site self energies are most dominant contributions, and we have two $\frac{1}{4}\Sigma^{T^2} - \frac{1}{6}\Sigma^E$ terms compared to just one $\frac{1}{4}\Sigma^{T^2} + \frac{1}{6}\Sigma^E$, the overall self-energy correction to the inter-site hopping terms becomes weaker as the Hund’s coupling becomes enhanced. This is consistent with the observation in the main text that increasing $J_H$ suppresses the degree of $V_4$ clustering, and that while $U$ enhanced the inter-site correlation via $\Sigma^{T^2}$, $J_H$ reduces it by introducing $\Sigma^E$ that cancels $\Sigma^{T^2}$ out.