Competing itinerant and localized states in strongly correlated BaVS$_3$

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The electronic structure of the quasi-lowdimensional vanadium sulfide BaVS$_3$ is investigated for the different phases above the magnetic ordering temperature. By means of density functional theory and its combination with dynamical-mean field theory, we follow the evolution of the relevant low-energy electronic states on cooling. Hence we go in the metallic regime from the room temperature hexagonal phase to the orthorhombic phase after the first structural transition, and close with the monoclinic insulating phase below the metal-insulator transition. Due to the low symmetry and expected intersite correlations, the latter phase is treated within cellular dynamical mean-field theory. It is generally discussed how the intriguing interplay between band-structure and strong-correlation effects leads to the stabilization of the various electronic phases with decreasing temperature.

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I. INTRODUCTION

Since its first characterization in 1969, the understanding of the complex electronic structure of the vanadium sulfide BaVS$_3$ poses a longstanding problem in condensed matter physics. Numerous experimental and theoretical studies have revealed a delicate coupling between orbital, spin and lattice degrees of freedom over a wide temperature range. On cooling, BaVS$_3$ exhibits three continuous phase transitions, starting with a structural hexagonal-to-orthorhombic transition at $T_3 \sim 240$ K in the metallic regime. The latter vanishes at $\sim 70$ K where a metal-to-insulator transition (MIT), accompanied by a lattice transformation from orthorhombic to monoclinic, to a still paramagnetic phase takes place. A final magnetic transition marking the onset of an incommensurable antiferromagnetic order takes place at $T_X \sim 30$ K.

The underlying driving forces for these transitions and the specific nature of the respective phases is to a large extent still a matter of debate. It was shown that the MIT may be driven to zero temperature at high pressure, and the supression of the insulating phase leads to non-Fermi-liquid and quantum-critical behavior. This observation is not only adding even more complexity to the already existing problems, but also underlines the tricky nature of the electronic structure. At ambient pressure the MIT is early announced by strong precursive behavior such as a large increase of the Hall coefficient and a wide one-dimensional (1D) lattice-fluctuation regime along the c axis of the system. In fact, it seems to be established that the MIT may be described in terms of a charge-density wave (CDW) instability. However, BaVS$_3$ is not a textbook Peierls system. The dc conduction anisotropy is rather small (σ$_c$/σ$_a \sim 3$-4), and the “metallic” phase above $T_{MIT}$ displays a high resistivity (a few mΩcm) and metallic-like behavior ($d\rho/dT > 0$) only above a weak minimum at $\sim 150$ K, below which it increases upon further cooling. Moreover, local-moment behavior is revealed from the magnetic susceptibility, with an effective moment of approximately one localized spin-$1/2$ per two V sites. At $T_{MIT}$, the susceptibility rapidly drops, and the electronic entropy is strongly suppressed.

Because of the nominal V$^{4+}$ valence, BaVS$_3$ belongs to the family of 3$d^1$ compounds with a $t_{2g}$ manifold spanning the low-energy sector. In the hexagonal phase the latter consists (per V ion) of an $A_{1g}$ and two degenerate $E_g$ states. The remaining $e_g$ states are strongly hybridized with the S(3$p$) states and have major high-energy weight. Below $T_3$ the degeneracy of the $E_g$s is lifted in the orthorhombic phase. In both phases the primitive cell includes two formula units, where the V and S ions form chains of face-sharing VS$_3$ octahedra along the c axis. The intrachain V-V distance is less than half the interchain distance. It follows that the $A_{1g}$ orbital is mainly directed along the chain, forming a broader band due to the significant overlap of neighboring intrachain V ions. On the contrary, the lobes of the $E_g$ orbitals point inbetween the sulfur ions, i.e., do not hybridize strongly with their environment, leading to comparably narrow bands. These simple characterizations hold essentially also for the monoclinic insulating phase, yet the primitive cell is doubled and the resulting four V ions in the basis are now all inequivalent by symmetry. The CDW mechanism has led to a tetramerization, yet no evident charge disproportionation among them was detected. The measured charge gaps of about 40 meV is twice as large as the apparent spin gap, pointing once more towards the relevance of electronic correlations.

In Ref. the orthorhombic phase above the MIT was investigated, and it was argued that strong electronic correlations are responsible for a substantial charge transfer within the $t_{2g}$ states, leading also to important Fermi-surface changes in comparison to a weak-correlation treatment. Here we go further by tracing the low-energy states of BaVS$_3$ all the way from room temperature down to 40 K (just above the final magnetic transition). Although the local environment of the V site
does not change dramatically, the electronic structure appears to be rather sensitive to the temperature changes. This originates from the subtle balance of kinetic energy versus Coulomb interaction in the electronic system, a characteristic of strongly correlated materials. In fact, this vanadium sulfide presents an interesting realistic realization of one of the basic problems in strongly correlated physics: there is nominally one electron in the low-energy sector and two distinct orbital states, one forming a broader and two forming narrower bands. Hence depending on temperature, nature shall find the best compromise between kinetic energy gain and potential cost due to mutual Coulomb interaction in this multiorbital scenario.

II. THEORETICAL FRAMEWORK

For the investigation of competing band-structure and many-body effects in realistic materials, the combination\textsuperscript{23,24} of density functional theory (DFT) and dynamical-mean field theory (DMFT) has recently proven to be a powerful approach.

For the DFT part we used the local density approximation (LDA) to the exchange-correlation energy. The corresponding calculations were performed with a mixed-basis pseudopotential code\textsuperscript{25}. It uses norm-conserving pseudopotentials, and plane waves supplemented with some few non-overlapping localized functions in order to represent the pseudo crystal wavefunction.

Since the low-energy physics of BaVS\textsubscript{3} is dominated by the t\textsubscript{2g} states, the so-called LDA+DMFT calculations were performed for the corresponding three-band subset. The latter was derived from the full band structure via the maximally-localized Wannier function (MLWF) construction\textsuperscript{26,27}. Hence the local orbitals which form the impurity in the DMFT context stem from the associated Wannier functions (WFs) and the low-energy LDA hamiltonian \( H(\mathbf{k}) \) is expressed with respect to these orbitals\textsuperscript{28}. To be specific, by making reference to the formalism outlined in Ref.\textsuperscript{14}, in all LDA+DMFT calculations presented here the set of correlated orbitals \( \mathcal{C} \) was identical to the set \( \mathcal{W} \) of the WFs forming the minimal LDA hamiltonian. Hence the impurity Green’s function is computed in DMFT for finite inverse temperature \( \beta \) via

\[
G(i\omega_n) = \sum_{\mathbf{k}} \left[ (i\omega_n + \mu) \mathbb{I} - H^{(C)}(\mathbf{k}) - \Sigma^{(C)}(i\omega_n) \right]^{-1},
\]

where \( \omega_n=(2n+1)\pi/\beta \) are the Matsubara frequencies and \( \Sigma \) is the self-energy matrix for the strongly correlated orbitals. For the local interacting hamiltonian \( H_{\text{int}} \) the following representation restricted to density-density terms only was used:

\[
\hat{H}_{\text{int}} = U \sum_m \hat{n}_{m\uparrow} \hat{n}_{m\downarrow} + \frac{U'}{2} \sum_{m \neq m'} \hat{n}_{m\sigma} \hat{n}_{m'\sigma} + \frac{U''}{2} \sum_{m \neq m'} \hat{n}_{m\sigma} \hat{n}_{m'\sigma}.
\]

Here \( \hat{n}_{m\sigma} = \hat{d}_{m\sigma}^\dagger \hat{d}_{m\sigma} \), where \( m, \sigma \) denote orbital and spin index. The following parametrization of \( U' \) and \( U'' \) has been proven to be reliable\textsuperscript{28,29} in the case of t\textsubscript{2g}-based systems: \( U'=U-2J \) and \( U''=U-3J \). We utilized the quantum-Monte Carlo (QMC) formalism after Hirsch-Fye\textsuperscript{30} to solve the impurity problem.

For hexagonal and orthorhombic BaVS\textsubscript{3} there are only symmetry-equivalent V ions in the primitive cell and moreover interatomic correlation effects are not expected to be of crucial importance. Hence a single-site DMFT approach to describe the strong-correlation effects was employed for those phases. Thereby the inverse temperature was always \( \beta=30 \text{ eV}^{-1} \) and the number of time slices equaled 128 for the QMC method. However, since the paramagnetic insulating regime of the low-temperature monoclinic phase is associated with a CDW state, this approximation appears inadequate. We thus used a cluster formalism (for recent reviews see e.g. Ref.\textsuperscript{31,32,33}), namely the cellular DMFT (CDMFT) approach in a realistic context\textsuperscript{34,35}. More explicitly, the linear cluster formed by the four symmetry-inequalent V ions, each one decorated with a three-orbital \( t_{2g} \) multiplet, was identified as the impurity for the CDMFT scheme. This amounts to a self-energy matrix \( \Sigma(i\omega_n) \) that is not only off-diagonal in the orbital indices, but also in the site indices within the cluster. Note however that intercluster components of the self-energy are neglected. The latter fact results in the breaking of translational symmetry when computing pair correlations for the end sites of our linear cluster. However such a cluster approach should still be sufficient to describe the major qualitative changes in the correlated electronic structure originating from the CDW instability. Since the undertaken cluster investigation is numerically very expensive within QMC (to our knowledge one of the largest up to now performed in the framework of realistic cluster-DMFT) we chose \( \beta=25 \text{ eV}^{-1} \) and used 90 time slices.

III. RESULTS

Stoichiometric BaVS\textsubscript{3} transforms on cooling successively to crystal systems with lower symmetry, giving a hint to the generally low ordering energy. Table\textsuperscript{1} summarizes the basic crystal data for the three different phases that are studied in this work. Both, the hexagonal and orthorhombic phases are associated with the metallic regime, while the monoclinic phase corresponds to the insulating system. Here we only investigated the
FIG. 1: (color online) BaVS$_3$ in the Cmc2$_1$ structure. The V ions are shown as smaller (red/gray) spheres, the Ba ions as larger (blue/dark) spheres.

TABLE I: Experimental crystal data used for the investigation of BaVS$_3$.

|          | RT     | 100 K  | 40 K   |
|----------|--------|--------|--------|
| crystal system | hexagonal | orthorhombic | monoclinic |
| space group  | P6$_3$/mmc | Cmc2$_1$ | Im     |
| a (a.u.)     | 12.71  | 12.77  | 12.78  |
| b (a.u.)     | 22.01 (=a$\sqrt{3}$) | 21.71  | 21.65  |
| c (a.u.)     | 10.63  | 10.58  | 21.15  |
| $\beta$ (°) | $-90.045$ | $-90.045$ | $-90.045$ |
| experiment   | Ref. 36 | Ref. 36 | Ref. 8 |

paramagnetic phase of the insulator and excluded the magnetically ordered phase below $T_X$.

A. LDA study of the metallic regime

At room temperature (RT) BaVS$_3$ crystallizes in the hexagonal ($P6_3/mmc$) structure with two formula units in the primitive cell. All symmetry operations of the hexagonal group apply to this structure, and all Ba, V and S ions in the cell form one single symmetry class, respectively. The V ions within the chains are aligned straightly. As noted by Mattheis$^{37}$, the variable parameter $x(S)$ which determines the inplane S-S distances deviates slightly from the ideal hexagonal value, i.e., $x(S)=0.1656$ while $x_{\text{ideal}}=1/6$. This means that the inplane equilateral S-S-S triangle above and below an V ion is contracted and the intrachain S-S bond lengths are decreased in comparison to the interchain lengths.

At $T_X$ the crystal system transforms from hexagonal to orthorhombic, leading to a structure with (Cmc2$_1$) space group. The V chains are now zigzag distorted in the bc plane of the lattice. Although still two formula units form the primitive cell, the symmetry class of the sulfur ions has split into two: both S1 ions are positioned at (4a) apical sites on the b axis, while the four S2 ions occupy (8b) sites (see Fig. 1). From Tab. I it is seen that the structural transformation results in only minor changes in the lattice parameters, with a maximum 1.5% per cent contraction of the b axis. There are several LDA studies for BaVS$_3$ above the MIT$^{18,22,37,38}$. In addition to those, a direct comparison of the LDA low-energy electronic structure for the hexagonal and orthorhombic phases via Wannier construction for the $t_{2g}$ manifold is presented here.

Figure 2 displays the LDA density of states (DOS) for the two crystal structures. In each case the dominance of the $t_{2g}$ states at low energy, with a prominent peak right at the Fermi energy, is evident. For the $A_{1g}$ band the dispersion is indeed reminiscent of 1D characteristics, however below the Fermi energy features are changed due

FIG. 2: (color online) Total and local LDA DOS for BaVS$_3$ in (a) the $P6_3/mmc$ structure and (b) the Cmc2$_1$ structure.
FIG. 3: (color online) (top) LDA band structure and (bottom) derived $t_{2g}$ Wannier bands for $P6_3/mmc$-BaVS$_3$. Color coding for (a): $A_{1g}$ (blue), $E_{g1}/E_{g2}$ (red).

to hybridization with the $S(3p)$ states. The weight of the latter states is reduced in the energy range $[-1,0]$ for the $Cmc2_1$ structure compared to the $P6_3/mmc$ structure. One might interpret this as some decoupling of $A_{1g}$ and $S(3p)$ throughout the structural transition. The very large DOS at the Fermi energy, common to both structures, due to the $E_g$ states render instabilities towards broken-symmetry phases very likely.

The LDA band structures in Fig. 3a and Fig. 4a, with “fatbands” exhibiting the weight of the respective $t_{2g}$ states on the different bands, show the folded character of the $A_{1g}$ band due to the two-formula unit primitive cell. The $A_{1g}$ bandwidth is dominated by the dispersion along $\Gamma$-$\text{(A,Z)}$, i.e., along the $c^*$ axis. While for the higher-symmetry $P6_3/mmc$ structure the folding propagates gapless through $A$, the corresponding bands are separated at $Z$ for the $Cmc2_1$ structure. This hybridization between $A_{1g}$ and $E_g$ is obvious in the upper triangle $A$-$H$-$L$ and $Z$-$E$-$T$. Clearly seen is the hybridization of $A_{1g}$ with $S(3p)$ resulting in “jumps” of the $A_{1g}$ character between different bands in the lower triangle $\Gamma$-$K$-$M$ and $\Gamma$-$C$-$Y$. For both structures the $A_{1g}$ band cuts the Fermi level $\epsilon_F$ close to the zone boundary, leading to a nearly filled lower part of the folded band complex. It was noted in former works that for $Cmc2_1$ this filling renders a CDW instability within the $A_{1g}$ band along $\Gamma$-$Z$ impossible.

The $E_g$ states form very narrow, in some regions even nearly dispersionless, bands right at $\epsilon_F$. An important difference occurs between the Fermi surface (FS) of the two metallic phases (see Fig. 5). Although in both cases the FS consists of two sheets, the one for $P6_3/mmc$ is entirely located at the zone boundaries with a dominant $A_{1g}$ sheet and smaller $E_g$ pockets around $L$. On the contrary the FS for $Cmc2_1$ shows as the first sheet a substantial $E_{g2}$ electron pocket centered at $\Gamma$ and $E_{g1}$ pillar-like structures on the $b^*$ axis extending along $c^*$. The FS is completed by the $A_{1g}$ sheet, now extending deeper into the Brillouin zone (BZ). Despite the latter observation,

FIG. 4: (color online) (top) LDA band structure and (bottom) derived $t_{2g}$ Wannier bands for $Cmc2_1$-BaVS$_3$. Color coding for (a): $A_{1g}$ (blue), $E_{g1}/E_{g2}$ (red).

FIG. 5: (color online) (a) hexagonal and orthorhombic Brillouin zones as well as LDA Fermi surface for BaVS$_3$ in (b) the $P6_3/mmc$ structure and (c) the $Cmc2_1$ structure from different perspectives.
this quasi-1D sheet is neither strongly flattened nor have both parts the proper distance for nesting with the experimental CDW vector ($q^{\text{exp}} = 0.5c^*$).

The dispersions according to the derived three-band hamiltonian on the basis of the maximally-localized procedure are shown in Fig. 6b. Because of the entanglement of the V(3$d$) bands with the S(3$p$) ones, the dominant $A_{1g}$-like band does not coincide with the true LDA bands in this minimal model. Still such a three-band approach should carry the essential physics in the low-energy regime. Figure 6 pictures the corresponding $V(t_{2g})$ Wannier orbitals in the crystal-field basis, i.e., with vanishing onsite hybridization. For both phases it is seen that the $E_{g1}$ orbitals leak out on the S2 ions, while the $E_{g2}$ orbitals have weight on the apical S1 atoms (recall that $S1,S2$ are symmetrically equivalent only in the hexagonal phase). The $A_{1g}$ orbital hybridizes with the $3p$ orbitals on both sulfur-ion types. That this hybridization is indeed weakened in the $Cmc2_1$ structure may be derived from the reduced spread of the $A_{1g}$ WF shown in Tab. III. Interestingly, the spread is now even below the values for the $E_g$ states. Note also that the

TABLE II: Wannier centers $R_w$ and spread ($r^2$) of the $t_{2g}$-like MLWFs constructed from a $(6 \times 6 \times 6)$ $k$-point mesh. The positions of the symmetrically equivalent V sites in cartesian coordinates (in a.u.) read for $P6_3/mmc$: $R_{V1}=(0.00,0.00,0.00)$ and $R_{V2}= (0.00,0.00,5.30)$ ; as well as for $Cmc2_1$: $R_{V1} = (0.00,0.46,-0.01)$ and $R_{V2} = (0.00,-0.46,5.28)$. The $V(2)$ site is symmetry-related to the $V(1)$ site by the symmetry operation $C_{2}^{\perp}R_{V1}+0.5$. In the following only the data for $V1$ is shown.

| structure    | $R_w$ - $R_{V1}$ (a.u.) | ($r^2$) (a.u.$^2$) |
|--------------|-------------------------|-------------------|
| $P6_3/mmc$   | $A_{1g}$: 0.00, 0.00, -0.00 | 18.62             |
|              | $E_{g1}$: 0.00, 0.00, 0.00 | 17.10             |
|              | $E_{g2}$: 0.00, 0.00, 0.00 | 17.10             |
| $Cmc2_1$     | $A_{1g}$: 0.00, 0.30, -0.16 | 16.60             |
|              | $E_{g1}$: 0.00, 0.19, 0.35 | 17.55             |
|              | $E_{g2}$: 0.00, 0.56, -0.31 | 17.53             |

TABLE III: Hopping integrals between the $t_{2g}$ Wannier orbitals of BaVS$_3$ in the crystal-field basis. The first value corresponds to the $P6_3/mmc$ structure and the second to the $Cmc2_1$ structure, respectively. The term '002$^\perp$' shall denote the hopping to the nearest-neighbor V site within the unit cell. One of the nearest-neighbor V ions in the $ab$ plane is located at '100', while '110' and '110' are closest V ions along $a$ and $b$, respectively. Energies in meV.

|          | $A_{1g}$ | $A_{1g}$ | $E_{g1}$ | $E_{g2}$ | $A_{1g}$ | $E_{g1}$ | $A_{1g}$ | $E_{g2}$ | $E_{g1}$ | $E_{g2}$ |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 000      | -755     | -423     | 500      | 200      | 0        | 0        | 0        | 0        | 0        | 0        |
| 002$^\perp$ | -587     | -511     | 90       | 44       | -90      | -12      | 0        | -146     | 0        | 0        |
| 001      | -61      | -86      | 8        | 5        | 14       | -3       | 0        | -7       | 0        | 0        |
| 000      | -49      | -35      | 8        | 14       | 14       | -26      | 0        | -32      | -32      | 14       |
| 110      | -49      | -26      | -63      | -76      | 31       | 29       | -37      | -28      | 0        | -2       |
| 110      | 3        | 1        | 0        | 2        | 0        | -5       | 0        | -2       | 0        | 0        |

WF centers are identical with the V positions only for the hexagonal structure, while there are some shifts for the orthorhombic structure. The main qualitative difference in the hopping integrals (Tab. III) between the two structures is the emerging substantial hybridization between $A_{1g}$ and $E_{g1}$ for $Cmc2_1$. Note that generally the $E_g$ hoppings are rather isotropic, whereas the dominating hopping along the $c$ axis in the case of $A_{1g}$ is obvious.

B. LDA+DMFT study of the metallic regime

The LDA approach presented in the last section underlies the assumption that the mutual interactions between the electrons may be cast into a static local exchange-correlation potential within an effective single-particle description. However it is known that for strongly correlated systems such a description is likely to fail. Since one indeed expects rather strong correlations within the quarter-filled $V(t_{2g})$ states of BaVS$_3$, also due to the specific characteristics of very narrow $E_g$ bands and the broader $A_{1g}$ band, we employed the LDA+DMFT framework to explicitly include many-body effects in the electronic structure.
By identifying the derived $t_{2g}$ WFs in the crystal-field basis as the subspace of correlated orbitals, we derived the $k$-integrated (local) spectral functions $\rho(\omega)$ shown in Fig. 7. Clearly seen is the transfer of spectral weight from the quasiparticle (QP) peaks to lower/higher energies in comparison to the local LDA DOS, especially for the $E_g$ states. This corresponds to an inclusion of the atomic-like excitations important for states with substantial localized character, which is missing in the standard LDA picture. By varying $T$ one observes additionally that the strength of the $E_g$ QP peak changes also more significantly. Thus the corresponding electrons are effectively localized for a wide temperature range due to incoherence effects.

Since the correlation effects influence the subtle energetic balance in this system, they are moreover responsible for a substantial charge transfer between the relevant orbitals\textsuperscript{14,22}, resulting in different orbital-resolved fillings compared to the LDA ones (see Tab. IV). The LDA filling of the $A_{1g}$ band is close to 70% in the hexagonal structure and does not change much for temperatures where the DMFT study was elaborated. A reasonable choice\textsuperscript{22} for the Hubbard parameters $U$ and $J$ leads to a significant transfer of charge from $A_{1g}$ to $E_g$, in order the overcome the large potential energy cost for occupying mainly the former orbital. The new fillings for $E_{g1}$ and $E_{g2}$ differ slightly due to a marginal hybridization between $A_{1g}$ and $E_{g1}$ in the Wannier Hamiltonian already for the hexagonal structure. Note that filling in LDA+DMFT is not equivalent to pure band filling in the LDA sense, because the atomic-like excitations are now also included. The essential change for the orthorhombic structure below $T_S$ (which was here treated at same $T$ within the QMC solver of DMFT) is the effective reduction of the three-band to a dominant two-band problem. Due to the now substantial $A_{1g}$-$E_{g1}$ hybridization the charge transfer is dominantly taking place between those two orbitals. Yet the overall occupation of the $A_{1g}$ orbital is only little smaller than in the hexagonal phase. The $E_g$ filling is now close to 50%, in good agreement with the experimentally observed local magnetic moment of about one free spin every other V ion.

Besides the orbital-resolved filling, the change of the respective FS sheets in the metallic regime is also of large interest. However keep in mind that there is no straightforward relation between those two issues, as only the total Fermi-surface volume is invariant when turning on correlations and no unique rule of how the individual sheets have to change can be derived. But this change can of course be calculated, which was done for the orthorhombic phase with the Wannier basis in Ref. 14, and the change of the FS sheets is indeed in line with what one expects from the overall charge transfers (s. Fig. 8). More explicitly, a strong Fermi-surface deformation was revealed, placing parts of the renormalized $A_{1g}$ sheet

| structure   | $U$ (eV) | $J$ (eV) | $E_{g1}$ (eV) | $E_{g2}$ (eV) |
|-------------|----------|----------|---------------|---------------|
| $P6_3/mmc$  | 0.4, 0.9 | 0.45     | 0.16          | 0.16          |
|             | 3.5, 0.7 | 0.29     | 0.27          |               |
| $Cmce_2$    | 0.4, 0.9 | 0.31     | 0.10          |               |
|             | 3.5, 0.7 | 0.14     |               |               |

TABLE IV: Orbital-resolved fillings for BaVS$_3$ from LDA+DMFT within the crystal-field Wannier basis. The QMC solver was used for $T=390$ K.

![FIG. 7: (color online) (right) Local spectral functions from LDA+DMFT in comparison to (left) the local LDA DOS for the $t_{2g}$ WFs in the crystal-field basis, for (a) the $P6_3/mmc$ structure and (b) the $Cmce_2$ structure. The QMC solver was used for $T=390$ K.](image)

![FIG. 8: (color online) comparison between (a) the LDA FS of orthorhombic BaVS$_3$ and (b) the corresponding QP FS derived from LDA+DMFT.](image)
now in reasonably good position for a possible nesting with the experimentally determined \( \mathbf{q} \) vector. An important observation was that the nesting should mainly take place away from the high-symmetry directions in the BZ, i.e., the \( A_{1g} \) band along the \( \Gamma-Z \) direction should not be strongly involved in the direct nesting. As pointed out, one expects the \( E_g \) states to be essentially localized for higher temperatures, rendering the definition of a sharp FS rather difficult. For this reason, no renormalized FS was computed for the hexagonal phase. Due to the missing \( A_{1g}-E_{g1} \) hybridization one would however expect that for this phase the overall \( A_{1g} \) sheet is shifted more or less coherently in the BZ, contrary to the orthorhombic case.

C. LDA study of the paramagnetic insulating regime

\( \text{BaVS}_3 \) below \( T_{\text{MIT}} \) is insulating with a monoclinic \( Im \) structure involving four formula units in the primitive cell. The system is described as a CDW state with a dominant 2\( k_F \) distortion. Figure 9 displays the four inequivalent vanadium ions along the chain together with numbers indicating the shift of the atomic positions with reference to the \( Cmc2_1 \) structure above the MIT (at \( T=100 \text{ K} \)). It is seen that the shifts for \( V \) along the chain are relatively small, on the scale of 4\% at most. Nonetheless, a dominant distortion pattern for this CDW state may be identified. The mainly shifted ions are \( V1 \) and \( V3 \) in our notation, whereas \( V2 \) and \( V4 \) only marginally change their positions. Since \( V1 \) and \( V3 \) are shifted towards each other, with \( V4 \) inbetween, the tetramerization appears as an effective trimerization, isolating the \( V2 \) site. As a result, the \( V-V \) distances in decreasing order are: \( V2-V3, V1-V2, V1-V4 \) and \( V3-V4 \). To a smaller extent, the average \( V-S \) distance (taking into account only the six nearest-neighbor sulfur ions, respectively) also varies. Again, the averaged distance \( \Delta \bar{d}_{VS} \) is largest for the \( V2 \) ion and smallest for the \( V4 \) ion.

Although the CDW phase is experimentally known to be paramagnetic insulating, the LDA calculation finds it to be metallic (see Fig. 10). Hence whereas the insufficiency of LDA for the metallic regime required a closer band-structure study, the failure due to the neglection of strong correlations is now obvious. Still the LDA approach may deliver relevant information about the kinetic part of the hamiltonian and the changes of the electronic structure due to the CDW distortion.

The total LDA DOS for the \( Im \) structure is rather close to the \( Cmc2_1 \) one. We plotted in Fig. 10 only the Wannier bands for the low-energy regime on top of the full LDA band structure. The lowest and highest \( t_{2g} \) bands still have the strongest \( A_{1g} \) weight, and the hybridization between \( A_{1g} \) and \( E_{g1} \) is significant especially at higher energy. However no clear distinction between the individual electronic character of the \( V \) ions can be made on the level of simple projection onto local orbitals.

A bit more insight is obtained when going to the Wannier representaion, again using the crystal-field basis as the choice of reference. Figure 11 indicates that from a low-energy perspective the \((V1,V2)\) and \((V3,V4)\) ions have similar characteristics, especially in the occupied part of the DOS. The \( A_{1g} \) occupation compared to the \( E_{g1} \) one is larger for the \((V3,V4)\) ions. Because of the way of the shifts of the atomic positions in the monoclinic structure it is not so surprising to find that already on an LDA level the \((V3,V4)\) and \((V1,V2)\) ions appear to form somehow two different classes. Since the \((V1,V2)\) ions are more isolated, the larger \( E_{g1} \) filling makes sense when being the more localized state. In spite of these differences it is seen in Tab. V that the LDA crystal-field splitting within the \( t_{2g} \) manifold is greatly reduced in the CDW state. Note also that the spread of the \( A_{1g} \) WF is significantly enhanced in the LDA description of

| \( A_{1g} \) | \( E_{g1} \) | \( E_{g2} \) |
|---|---|---|
| \( V1 \) | 478 | 17.61 | 200 |
| \( V2 \) | 473 | 18.04 | 200 |
| \( V3 \) | 460 | 18.39 | 200 |
| \( V4 \) | 477 | 17.54 | 200 |

Note also that the spread of the \( A_{1g} \) WF is significantly enhanced in the LDA description of
D. LDA+DMFT study of the paramagnetic insulating regime

In order to overcome the obvious failure of LDA in describing the paramagnetic insulating state of BaVS$_3$ an LDA+CDMFT approach was employed. Because of the revealed different behavior of the inequivalent V ions already on the LDA level, the minimal cluster has to include all four V ions along the chain. Such a four-site cluster leads in the present case to the description within an effective twelve-band model on the basis of the derived Wannier hamiltonian. The same values for $U$ and $J$ as for the metallic regime were used ($U=3.5$ eV, $J=0.7$ eV), no explicit interatomic Coulomb repulsion term was introduced. Due to the large computational effort for the QMC impurity solver, the lowest temperature with a still reasonable statistics we achieved was $T=460$ K.

Figure 12 exhibits the site- and orbital-resolved local spectral function obtained from CDMFT. It is seen that within this description the system can be interpreted to be in an insulating state. The partially still remaining minor spectral weight at zero energy is due to the limitation concerning the handable temperature with the QMC solver. Remember that the experimental charge gap from precise optics measurements equals only $\Delta_{ch}=0.42$ meV.

Obviously the strong correlations lead to a substantial renormalization of the crystal-field splitting, since the $E_g$ twofold is now widely separated in energy, shifting the $E_{g2}$ state towards higher energy and somehow “out of the picture”. The different tendencies in the character of the inequivalent V ions seen in LDA, are now much more strongly enhanced. Thus the (V1,V2) ions have now nearly exclusively $E_{g1}$ weight, while the (V3,V4) ions show some mixed $A_{1g}/E_{g1}$ occupation. This interesting result is also summarized in the site- and orbital-resolved occupations shown in Tab. VII. Hence the charge transfer that was observed in the metallic regime due to strong correlations, takes place also in the insulating state, however now in a site-dependent manner. Whereas the (V1,V2) ions loose their $A_{1g}$ occupation nearly completely and become orbitally polarized, the (V3,V4) ions fall more in the regime of orbital compensation, with the V4 ion gaining some extra $E_{g1}$ weight. On average, roughly speaking the $E_{g1}$ orbital is the winner of the CDW transition, since it replaces the $A_{1g}$ orbital as the dominant orbital in the system. Concerning the question of charge order, the data does not provide a strong argument for either side. Albeit from the numbers there appears to be the slight tendency to put some minor extra charge on the (V1,V2) ions, due to the restrictions in quantitative accuracy of the formalism this may be within the error bars. Remember that experimentally no charge order was found.

$Im$-BaVS$_3$ (see Fig. VII).
The LDA+CDMFT method gives access to more quantities than solely the spectral functions and onsite densities. To find out more about the nature of the CDW transition and the insulating state in BaVS$_3$, investigating the behavior of the self-energy $\Sigma(i\omega_n)$ is very instructive. Note that in the present case $\Sigma$ corresponds to a $12 \times 12$ matrix, including information not only about onsite but also intersite correlations within the four-site cluster.

It is seen in Fig. 13 that the onsite self-energies for the various V ions display the expected behavior. While $\Sigma_{A_{1g}}$ and $\Sigma_{E_g}$ have rather different amplitude and zero-frequency slope for (V1,V2), they scale similar for (V3,V4). The large negative increase of $\text{Re } \Sigma_{E_g}$ close to zero frequency for (V1,V2) leads to the strong shift of theQP spectral weight to lower energies observed in Fig. 12. An important qualitative finding is that none of the Im $\Sigma$ diverges at $\omega_n=0$. Hence the opening of the gap in BaVS$_3$ is due to shifts of theQP states away from zero energy.

The inspection of the nearest-neighbor self-energy $\Sigma_{V-V}$ (see Fig. 14) reveals more details of the CDW state. For the (V3,V4) ions $\text{Re } \Sigma_{V-V}$ displays a salient increasing behavior when approaching zero frequency. Such a tendency for the intersite self-energy is a strong indication for the importance of intersite correlation effects leading to interatomic dimer formation. However, within the crystal-field basis (derived from the LDA hamiltonian) the occupation on (V3,V4) is of mixed $(A_{1g},E_g)$ character. Diagonalizing the interacting cluster Green’s function thus may lead to an orbital basis which corresponds to this dimer symmetry. On the other hand, the V1-V2 pair does not show strong intersite correlations. Thus these dominant $E_g$ occupied ions do not tend to form a spin singlet. It follows therefrom that the apparent spin gap in the insulating system is not originated from the direct correlated coupling of the neighboring $E_g$ spins on (V1-V2). However, one observes for the V2-V3 self-energies a minor tendency for singular behavior, especially for the $E_g-A_{1g}$ channel. One may conclude from this that the $E_g$ spins on (V1,V2) are somewhat effectively pinned by the neighboring dimers within the overall tetramerized state. This would explain the large drop in the magnetic susceptibility and excess entropy below the MIT.

It has to be noted that the intersite $\Sigma_{V-V}$ for V4-V1 is not a true pair self-energy as the others. Since the cellular DMFT approach we applied here breaks translational invariance, this special intersite self-energy connecting the surface of the cluster may not be obtained accurately. Thus for completeness we plotted in Fig. 14 instead $\Sigma_{V1-V4}$. The issue of translational-invariance breaking is surely a drawback of the used method. However since the V4-V1 pair is expected to be in an intermediate state between V1-V2 and V3-V4, we believe that the qualitative result of how the V ions electronically relate to each other remains unchanged. Note that one option to restore the periodicity in the present context would have been to perform calculations in the chain-DMFT framework. However, there the different treatment of inter- and intrachain hopping might cause other problems for BaVS$_3$, since the 1D character (as stated) is not very strongly indicated from the band hamiltonian.
IV. SUMMARY AND CONCLUSIONS

The puzzling physics of BaVS$_3$ is dominated by the competition between the more itinerant $A_{1g}$ state and the quasi-localized $E_g$ states, which form together the $t_{2g}$ manifold of the V(3$d$) shell. Some theoretical models in the early days tried to rule out one or the other of those orbital sectors for playing an essential role. However, several recent experimental and theoretical studies revealed clearly the importance of the existence of both orbital types in order to find a way of understanding the complex electronic phases of this system. Thus BaVS$_3$ appears to be a manifest multiorbital system, and if at all some orbital degrees of freedom might just freeze out at very low temperatures.

LDA approaches to the electronic structure of BaVS$_3$ tend quite naturally to overestimate the itinerant character of the system. The $A_{1g}$ associated Wannier orbital has an LDA filling of around 70% for the RT hexagonal structure, while the inclusion of strong electronic correlations within the LDA+DMFT reduce this filling to about 50%. This is because a dominant $A_{1g}$ filling becomes just too costly in the presence of reasonable mutual Coulomb interactions between the electrons. The balanced occupation of $A_{1g}$ and $E_g$ seems to be stable when going to the orthorhombic structure below $T_S$, yet the LDA+DMFT calculations revealed some tendency towards increasing the $E_g$ filling even more. Note however that there is still some arbitrariness in what one calls an $A_{1g}/E_g$ orbital, especially in the metallic regime and between different phases, and hence some margin in the derived numbers. Nonetheless, it was shown that in the paramagnetic insulating phase with the monoclinic structure the average $E_g$ occupation finally reaches about 70%.

The $E_g$ states show a low QP coherence temperature and are expected to be effectively localized for elevated temperatures in the metal. Though the LDA approach (even when extended by linear expansions of the DMFT self-energy) shows $E_g$ FS sheets, it is very likely that the $E_g$ QPs do not participate in the true Fermi surface in a well-defined manner. Hence due to the rather large difference in the coherence temperatures, one may describe BaVS$_3$ to be in an effective orbital-selective insulating regime. As there is substantial hybridization between $A_{1g}$ and $E_g$ below $T_S$, the low metallicity of BaVS$_3$, and especially the bad-metal regime below 150 K, may result from the scattering processes for the (quasi-)itinerant electrons. The origin of the hexagonal-to-orthorhombic transition appears to be closely related to the $A_{1g}$-$E_g$ hybridization. It was shown that the $E_g$ Wannier orbital connects to the $S_2$ ions, while the $E_g$ hybridizes with only one apical S1 ion. It is likely that this imbalance favors the susceptibility for growing symmetry-breaking $A_{1g}$-$E_g$ hopping. Thereby the large DOS close to the Fermi level is partly reduced when lifting the $E_g$ degeneracy, and this driving force leads via the final zigzag intrachain distortion to a new energetic minimum. Albeit many details of the MIT are still open, as discussed in Ref. [1] the correlation-induced flattened $A_{1g}$ FS sheets away from the high-symmetry directions in the BZ are good candidates for a meaningful matching with experimental findings. Further experimental studies of the low-energy regime close to the MIT are needed to reveal more details.

We revealed with LDA+CDMFT calculations that the insulating CDW state does not stay behind in terms of complexity of the electronic structure in comparison with the metallic regime. The tetramerization of the V ions, structurally an effective trimerization, leads to quite different behavior. While the (V3,V4) pair apparently forms a correlated dimer with mixed $A_{1g}/E_g$ occupation, the (V1,V2) ions are strongly orbitally polarized with major $E_g$ occupation and negligible coupling. Note however that this picture is of course basis dependent, and we worked always in the Wannier basis derived from the LDA hamiltonian. Hence a new orbital basis may be found in the interacting regime where e.g. the occupation for (V3,V4) has also polarized character. Concerning the “free” spins on (V1,V2), note that they are still coupled to the neighboring dimers, whereby their degrees of freedom are substantially reduced. The latter effect may serve as an explanation of the quenched local moments observed below $T_{MIT}$. Fagot et al. proposed from anomalous x-ray measurements a dominant $E_g$ occupation on V1 and an additional dominant occupation of $A_{1g}$ on V3, as well as no definite preferential occupation on (V2,V4). This would describe an orbital order modulated with 2c along the chain. Our picture differs by the fact that we do not find a dominant $A_{1g}$ occupation, but rather two ions, i.e., (V1,V2), with dominant $E_g$ weight. Although from a local structural point of view the former proposition appears meaningful, the intersite correlation effects appear efficient in singling out dimer and isolated behavior. Note that dimer formation and nearest-neighbor spins may also be energetic favorable, since the former brings in some residual hopping whereas the latter yields energy from spin exchange. Recently, Fazekas et al. proposed a minimal one-dimensional model, expecting thereby also nearest-neighbor $E_g$ spins. However the orbital degeneracy of the $E_g$ multiplet, ascribed to spin-orbit coupling, was kept in that model.

The aspect of the spin degree of freedom in BaVS$_3$ was so far only scarcely discussed. Albeit it is expected that the former is an important ingredient in the understanding of the physics, its role in the different phases is still quite open. Nakamura and coworkers reported anomalies in the temperature derivative of the magnetic susceptibility not only at $T_{MIT}$ but also at the onset of the bad-metal regime (∼160 K). Hence the detailed role of the local $E_g$ spins in the metal still poses important questions. Our study of the insulator renders it difficult to make precise statements about possible long-range order effects for the spin and orbitals, thus leaving questions concerning the classification of the electronic phase open. Furthermore, the mechanisms in conjunction with
the famous magnetic transition at $T_X$ need to be addressed. LDA+(C)DMFT computations may still help in delivering some further information associated with these problems. For instance, the calculation of magnetic susceptibilities in the insulating regime, the study of exchange interactions, as well as the investigation of the influence of the interchain coupling especially on the spin arrangement. More sophisticated model studies for multiorbital chains, perhaps with therefore well-adapted theoretical tools like density matrix renormalization group (DMRG), may also deliver important new insights.

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