Electronic correlations in vanadium chalcogenides: BaVSe$_3$ versus BaVS$_3$

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Abstract

Albeit structurally and electronically very similar, at low temperature the quasi-one-dimensional vanadium sulfide BaVS$_3$ shows a metal-to-insulator transition via the appearance of a charge-density-wave state, while BaVSe$_3$ apparently remains metallic down to zero temperature. This different behavior upon cooling is studied by means of density functional theory and its combination with the dynamical mean-field theory and the rotationally invariant slave-boson method. We reveal several subtle differences between these chalcogenides that provide indications for the deviant behavior of BaVSe$_3$ at low temperature. In this regard, a smaller Hubbard $U$ in line with an increased relevance of the Hund’s exchange $J$ plays a vital role.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discussion of electronic correlation effects in 3d-transition-metal compounds appears often dominantly reserved for the physics of oxides, e.g. for cuprates, manganites, ruthenates, or more recently cobaltates. However, there is increasing awareness that strong correlation effects are also relevant for many intriguing electronic phase transitions of various chalcogenides such as the metal–insulator transition (MIT) in NiS$_{2-x}$Se$_x$ [1], the charge-density-wave (CDW) transition in NbSe$_3$ [2] or the recent discovery of higher-temperature superconductivity in Fe chalcogenides. In this respect, the vanadium chalcogenides with the quasi-two-dimensional X-VS$_2$ misfit-layer structures [3] and the quasi-one-dimensional (1D) BaV(S, Se)$_3$ systems offer a unique opportunity to study the interplay of correlation effects and effective low dimensionality in these transition-metal compound systems.

Here we want to concentrate on the subtle comparison of the quasi-1D barium vanadium chalcogenide systems. It will become evident that the vanadium selenide BaVSe$_3$ is in effect rather similar to the corresponding vanadium sulfide BaVS$_3$ in many respects. The latter compound has been the subject of various studies concerning its complex electronic structure throughout the last decades [4–12]. This sulfide exhibits three continuous phase transitions with decreasing temperature, one of which is a highlighting metal-to-paramagnetic-insulator transition at $T_{MIT} \sim 70$ K. Although the exact details of the scenario are still to be revealed, strong evidence exists [13, 11] that this transition is associated with a CDW instability. Interestingly, such a transition cannot be found in the similar selenide compound, which remains metallic down to very low temperatures [14]. This raises questions about the delicate electronic and structural differences that anticipate a possible CDW in these chalcogenides. Hence the present investigation is devoted to a detailed comparison between the correlated electronic structure of BaVS$_3$ and BaVSe$_3$.

Concerning the structural properties, many features of BaVSe$_3$ are akin to the ones of BaVS$_3$. At room temperature, both materials exhibit a hexagonal structure in which the vanadium atoms form straight chains in the crystallographic $c$ direction. The intrachain V–V distance is less than half of the interchain distance, so that one is tempted to identify a quasi-1D substructure in these compounds. The chains become slightly distorted in the $ab$ plane with a zigzag distortion in the $bc$ plane at the continuous transition temperature $T_c \sim (240 \text{ K}, 290 \text{ K})$ (sulfide, selenide) [15, 16]. Thus, below this temperature regime, an orthorhombic crystal structure is stabilized for both materials. Furthermore, the additional metal-to-insulator transition of the sulfide is accompanied by a doubling of the unit cell and a transition to the monoclinic crystal system [13], whereas the selenide...
remains orthorhombic down to very low temperature. Both chalcogenides display local-moment behavior at ambient $T$ and a final continuous magnetic ordering transition. While in BaVS$_3$ an incommensurate antiferromagnetic (Néel) order develops below $T_N \sim 30$ K [17], BaVSe$_3$ undergoes a ferromagnetic transition at $T_C \sim 43$ K [16, 18].

The electronic structure of both materials in the low-energy regime is dominated by the nominal V$^{4+}$ valence, so that they can be described as 3$d^1$ compounds with a $t_2$g-like manifold at the Fermi level [5, 10, 12]. The latter consists of an $A_{1g}$-like orbital pointing along the vanadium chain direction as well as two $E_g$-like orbitals pointing in between the neighboring sulfur/seelenium ions, respectively. Due to strong hybridization with S(3p)/Se(4p), the $V(e_g)$ states have mainly high-energy weight and may be integrated out in a first low-energy approximation. Hence the essential physics of these systems can be described within a three-band model approach [12]. The two $E_g$ states are degenerate in the hexagonal structure, but split into an $E_{g1}$ and an $E_{g2}$ state in the orthorhombic regime. Due to their somewhat isolated orbital space, the hybridization with the environment is comparatively small. For this reason, they form very narrow bands that show almost no dispersion. In contrast, the $A_{1g}$ orbitals display a larger dispersion along the V chain direction. Hence, in a minimal model, the physics of these materials essentially boils down to the interplay of an itinerant and two localized states sharing a single electron.

2. Theoretical framework

Due to the obviously delicate electronic systems in BaVS$_3$ and BaVSe$_3$, with narrow bands at the Fermi level and local-moment physics, methods are needed that allow us to take into account many-body effects explicitly, i.e. beyond the standard density functional theory (DFT) in its local density approximation (LDA) to the exchange–correlation energy. In the present work, the opportunity is taken to compare two different approaches for this task, namely the LDA + DMFT [19, 20] framework in conjunction with a highly evolved quantum-Monte Carlo impurity solver as well as the combination of LDA with the rotationally invariant slave-boson formalism (RISB) [21, 22].

The DFT parts of the following calculations have been performed using a mixed-basis pseudopotential (MBPP) code [23], which utilizes norm-conserving pseudopotentials and a combined basis set of plane waves as well as non-overlapping localized functions. From the LDA band structure, by means of the maximally localized Wannier-function construction [24–26], a low-energy Kohn–Sham (KS) Hamiltonian $H^{\text{KS}}_{\text{LDA}}(k)$ within a correlated subspace $C$ is extracted [27]. In this work we restrict all self-energy effects to provide more information about the origin of the apparent CDW instability in BaVS$_3$.

(1) is written in the DMFT approximation, i.e. with a purely local self-energy (for a review see e.g. [28]). The mean-field version of RISB which is put into practice in the present work also has a local self-energy by construction. Moreover, the RISB self-energy only captures the linear term of the frequency dependence, expressed via the quasiparticle weight $Z$, as well as a local static part [12]. Thus, without going into details, the main difference between DMFT and RISB (in the mean-field version) is the neglect of the frequency dependence of the higher-energy excitations in the latter framework. However, as a saddle-point approximation the performance is fairly efficient, with reliable qualitative (and often even good quantitative) results in most cases. It is also important to realize that, although we use here a lattice implementation of the RISB method, this technique may equally well be utilized as an impurity solver for standard DMFT. Due to the inherent local nature at the saddle-point, this specific DMFT impurity solution is then identical to the direct lattice-calculation result.

In the present work, the explicit quantum impurity problem within DMFT is solved using the continuous-time quantum-Monte Carlo (CTQMC) approach employing the hybridization-expansion method [29]. For the actual computations the recent implementation by Ferrero and Parcollet (see [30, 31]) is employed. Both frameworks, i.e., DMFT (CTQMC) and RISB, allow for non-density–density terms in the many-body Hamiltonian, which we restrict in the present case to spin-flip and pair-hopping processes. Thus the following interacting Hamiltonian for the minimal modeling may be used:

$$
\hat{H}^{\text{int}} = \sum_m \hat{n}_{m\uparrow} \hat{n}_{m\downarrow} + \frac{1}{4} \sum_{m-m', \sigma} [U' \hat{n}_{m\sigma} \hat{n}_{m'\bar{\sigma}} + (U' - J) \hat{n}_{m\sigma} \hat{\bar{n}}_{m'\bar{\sigma}}] + \frac{1}{4} \sum_{m-m', \sigma} [J \hat{d}_{m\sigma}^\dagger \hat{d}_{m'\bar{\sigma}} + J_C \hat{d}_{m\sigma}^\dagger \hat{d}_{m'\sigma} + J_C \hat{d}_{m\bar{\sigma}}^\dagger \hat{d}_{m'\bar{\sigma}} + J_C \hat{d}_{m\bar{\sigma}}^\dagger \hat{d}_{m'\sigma}].
$$

(2)

where $\hat{n}_{m\sigma} = \hat{d}_{m\sigma}^\dagger \hat{d}_{m\sigma}$, with $\hat{d}_{m\sigma}^\dagger$ as the electron annihilation (creation) operator for orbital $m$ and spin $\sigma$. Throughout the calculations, the choice $U' = U - 2J$ and $J_C = J$, appropriate for $t_2g$ systems, is made.

3. Results

3.1. LDA studies

The following LDA comparison between BaVS$_3$ and BaVSe$_3$ builds up on the orthorhombic crystal structure (space group $Cmcm2_1$), since we are mainly interested in elucidating the possibility of the CDW state in both systems. Note that the CDW instability is not only absent in the selenide compound, but also vanishes in the sulfide at high pressure [9]. This raised the suspicion that the selenide compound may be interpreted as the high-pressure analog of the sulfide compound [14]. In any case, theoretically investigating BaVSe$_3$ should surely also provide more information about the origin of the apparent CDW instability in BaVS$_3$. 

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The existence of the orthorhombic phase of the selenide has been reported already on the occasion of its first synthesis by Kelber et al [16], but to the present authors’ knowledge no detailed experimental structural data is available in the literature. For this reason, the atomic positions used for Cmc2_1-BaVSe_3 are revealed by structural relaxation within the LDA using the MBPP code, while the crystal parameters are based on similar recent calculations performed by Akrap et al [14]. In contrast, structural data obtained by neutron diffraction by Ghedira et al [32] are used for BaVS_3. Note that an LDA structural relaxation of these experimental data for Cmc2_1-BaVS_3 results in only marginal changes of the atomic positions; therefore, an influence thereof on the following studies cannot be found. The crystal parameters (a, b, c) for one unit cell consisting of two formula units of BaVS_3 or BaVSe_3, respectively, in au, read (12.77, 21.71, 10.58) for BaVS_3 and (13.34, 22.68, 11.06) for BaVSe_3. For both materials the ideal quasi-1D chains of vanadium ions are slightly distorted in the orthorhombic phase, leading to zigzag chains. This effect turns out to be slightly larger in the selenide (relative displacement: 0.025) than in the sulfide (0.021). Concerning the electronic structure, figure 1 shows the LDA density of states (DOS) of BaVSe_3 in a comparatively large energy window around the Fermi level. Analogous to BaVS_3 [12], it can be seen that the low-energy physics of the material may be dominantly described by the abovementioned t_2g manifold. Thus a downfolding to an effective three-band model consisting of a broader A_1g-like level and narrower E_g1-like and E_g2-like levels is a suitable approximation for the essential physics. The accordance with the LDA DOS of the sulfide (shown in [12]) on this level of comparison is rather striking and only minor differences show up. Figure 2 compares the band structure of BaVSe_3 and of BaVS_3 in a smaller energy window, with ‘fatbands’ showing the weight of the symmetry-adapted t_2g states on the specific bands. Again, both band structures are similar, yet subtle differences may be observed. First the Se(4p) band at the Γ point is much closer to the Fermi level than the corresponding S(3p) band in BaVS_3, which may lead to a smaller Hubbard U for the minimal three-band model due to increased screening. Furthermore, the bandwidth difference between the three t_2g bands is reduced, i.e. the A_1g-like bands become narrower and the E_g-like ones broader. Hence the total t_2g bandwidth in BaVSe_3 is slightly smaller (~2.4 eV) than in BaVS_3 (~2.7 eV). This may be explained by the fact that, since the larger Se ions give rise to increased interatomic distances, a smaller A_1g-like hopping amplitude along the chains results. As a general feature, the overall A_1g contribution to the bands seems somewhat more

![Figure 1. LDA density of states of BaVSe_3.](image1)

![Figure 2. Left: LDA band structure of BaVS_3 (top) and BaVSe_3 (bottom). The fatband broadening depicts the weight of t_2g orbitals on the bands. Color coding: A_1g, blue/dark, E_g1, red/medium, and E_g2, green/light. Right: Brillouin zone of the orthorhombic structure with relevant points/directions.](image2)
Figure 3. LDA Fermi surfaces of BaVS$_3$ (top) and BaVSe$_3$ (bottom) from different perspectives.

Figure 4. Dispersions of the effective three-band model (red/gray), obtained by means of a maximally localized Wannier-function construction, for BaVS$_3$ (top) and BaVSe$_3$ (bottom). Black: original LDA band structure.

Figure 5. LDA t$_{2g}$ Wannier fatband plots for BaVS$_3$ (top) and BaVSe$_3$ (bottom) along a closed path in the first Brillouin zone, connecting $\Gamma$, ‘M/2’, ‘A/2’ and Z (see figure 2). Color coding: $A_{1g}$, blue/dark, $E_{g1}$, red/medium, and $E_{g2}$, green/light.

Figure 4 shows the respective three-band dispersion of the correlated subspace obtained from a maximally localized Wannier construction [24] for strongly hybridized bands [25]. It should be mentioned that this construction yields for the selenide a larger spread of the Wannier functions (i.e. in the range of 23 au$^2$ for the $E_{g}$-like ones in BaVSe$_3$ compared to about 18 au$^2$ for the same ones in BaVS$_3$). This can be attributed to a stronger hybridization of the $t_{2g}$ system with the Se(4p) electrons. Note that for the further use of this Wannier representation we rotated the original maximally localized Wannier Hamiltonian into the crystal-field basis, i.e. the basis where the on-site part thereof takes on a diagonal form.

Concerning the susceptibility towards the CDW state it is important and evident to note that the nesting vector mentioned above is not necessarily located along the $\Gamma$–Z high-symmetry line [27, 12]. In order to take this fact into account, the low-energy band structure is computed along a Brillouin zone (BZ) path containing a line parallel to the $\Gamma$–Z line, shown in figure 5. The points ‘M/2’ and ‘A/2’ are located halfway between the $\Gamma$- or Z-point, respectively, and the edge of the first BZ (see figure 2). From the displayed fatbands it can be seen that the hybridization between $A_{1g}$ and $E_{g1}$ on the resulting bands along M/2–A/2 as well as along $\Gamma$–Z is significantly larger in the selenide than in the sulfide. Thus a clear notion of exclusive ‘$A_{1g}$ bands’ or ‘$E_{g1}$ bands’ becomes even more difficult for BaVSe$_3$. This fact also impedes the assignment of the distinct FS sheets to a single definite orbital character.

3.2. Inclusion of correlation effects

Besides the apparent metal-to-insulator transition in BaVS$_3$, already the complex magnetic behavior in both systems (with
It is visible that the $A_{1g}$ filling is generally reduced by the simplified RISB technique. Concerning the trend in the (minor) differences, especially concerning the frequency dependence of the high-energy excitations. But also the neglect of the explicit quantum fluctuations within RISB, surely differ somewhat between both approaches due to the small correlation-induced charge transfer mainly from $A_{1g}$ to $E_{g1}$ in the selenide than in the sulfide. In order to compare BaVS$_3$ and BaVSe$_3$ in this respect, the calculated orbital-resolved fillings are shown in figure 6 for varying values of $U$ and fixed Hund’s exchange $J = 0.7$ eV. First note the very good agreement between the DMFT (CTQMC) and the RISB treatment of the correlation effects. Both methods clearly show the correlation-induced charge transfer mainly between the $A_{1g}$ and $E_{g1}$ orbitals [33, 12]. The actual numbers clearly show the correlation-induced charge transfer mainly from $A_{1g}$ to $E_{g1}$ in BaVSe$_3$. The latter is due to the fact that these terms lead to a smaller orbital polarization. It can further be seen that the spin-flip and pair-hopping terms have only a small influence on the occupation numbers, resulting qualitatively in a slightly smaller orbital polarization. In summary, the system could be understood as an effective two-band system, since the effective $E_{g2}$ orbital is almost empty, with an even larger correlation-induced charge transfer from $A_{1g}$ to $E_{g1}$ in the selenide than in the sulfide. It can further be seen that the spin-flip and pair-hopping terms have only a small influence on the occupation numbers, resulting qualitatively in a slightly smaller orbital polarization. The latter is due to the fact that these terms lead to a further reduction of the integrated effective $U$ compared to the density–density only case. Moreover, since the present systems mainly reside in the local single-particle sector, the influence of spin-flip and pair-hopping matrix elements on the charge fluctuations remains minor.

Figure 7 shows the density of states derived from the original Wannier functions compared to the local spectral functions from DMFT for both systems. On the LDA level, the plot shows the reduced bandwidth of the selenide compound, with the orbital-resolved effective widths within the $E_{g2}$ manifold becoming more similar. Furthermore, the overall stronger hybridization (note the use of the crystal-field basis) between $A_{1g}$ and $E_{g1}$ in BaVSe$_3$ is clearly visible. This also leads to a more pronounced $A_{1g}$ quasiparticle peak right at the Fermi level in the DMFT local spectral function.

As explained in [33, 12], the importance of explicit many-body effects in deforming the LDA Fermi surface appears as a crucial ingredient for the onset of the CDW in BaVS$_3$. Therefore, figure 8 shows the DMFT (CTQMC) quasiparticle Fermi surfaces for both chalcogenides. Correspondingly, figure 9 displays the quasiparticle dispersion for the closed path in the first BZ connecting the points ‘M/2’ and ‘A/2’ (see expected from the Fermi-surface discussion. This result is also apparent from table 1, where the occupation numbers are displayed for selected interaction strengths. In this context, a smaller Hubbard interaction $U = 2.5$ eV for BaVSe$_3$ seems reasonable in the end. However, for direct comparisons we also include the case $U = 3.5$ eV in the computations. Note that $J$ is usually not strongly affected by the crystal environment and to a good approximation can remain constant. Hence, if not stated differently, we generally fixed the Hund’s coupling to the value $J = 0.7$ eV used in previous studies [12], which is in line with what was utilized in similar investigations for vanadium oxides [34–36]. Note that a suitable energetic range for $J$ proved to be sufficient to describe the key low-energy physics of BaVS$_3$ [33].

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| $U$ (eV) | $H_{int}$ | $A_{1g}$ | $E_{g1}$ | $E_{g2}$ |
|---------|-----------|---------|----------|----------|
| BaVS$_3$ | 3.5 RI    | 0.37    | 0.53     | 0.10     |
|        | 3.5 RI    | 0.37    | 0.53     | 0.10     |
| BaVSe$_3$ | 2.5 DD    | 0.40    | 0.46     | 0.14     |
|        | 2.5 RI    | 0.45    | 0.45     | 0.14     |

Table 1. Orbital-resolved fillings from LDA + DMFT (CTQMC). Vanishing Hubbard $U$ marks the LDA result. ‘DD’: only density–density interactions, ‘RI’: additional inclusion of spin-flip and pair-hopping interactions.
Figure 7. Comparison of the LDA Wannier DOS (left) and local spectral functions from LDA + DMFT (right) for BaVS$_3$ with $U = 3.5$ eV (top) and BaVSe$_3$ with $U = 2.5$ eV (bottom).

Table 2. Relation of the spatial components of squared Fermi velocities in BaVS$_3$ and BaVSe$_3$ on the LDA level and within LDA + DMFT (CTQMC) for a given $U$ (in eV).

|           | BaVS$_3$ (LDA) | BaVS$_3$ (LDA) | BaVS$_3$ (CTQMC) | BaVSe$_3$ (LDA) | BaVSe$_3$ (LDA) | BaVSe$_3$ (CTQMC) |
|-----------|----------------|----------------|------------------|-----------------|-----------------|------------------|
| $\langle v^2_y \rangle / \langle v^2_z \rangle$ | 3.7            | 4.8            | 8.3              | 4.8             | 9.9             | 10.2             |
| $\langle v^2_x \rangle / \langle v^2_z \rangle$ | 2.7            | 5.2            | 9.9              | 5.2             | 9.9             | 10.2             |

Figure 8. Quasiparticle Fermi surfaces of BaVS$_3$ with $U = 3.5$ eV (top) and BaVSe$_3$ with $U = 3.5$ eV (middle) and $U = 2.5$ eV (bottom).

Figure 9. Effective $t_{2g}$ Wannier band structure with (red/gray) and without (black/dark) renormalization from LDA + DMFT along the closed path including ‘M/2’ and ‘A/2’ (see figure 2) for BaVS$_3$ (top) and BaVSe$_3$ with $U = 3.5$ eV (middle) and $U = 2.5$ eV (bottom).

In order to get a quantitative comparative understanding of the degree of quasi-one-dimensionality of the two materials, we investigated the theoretical order of magnitude of the anisotropy in the DC conductivities in LDA as well as in the strongly correlated case. To this end, table 2 summarizes the relation of the spatial components of the averaged Fermi velocities squared ($\langle v^2_y \rangle = \langle v^2_x \rangle + \langle v^2_y \rangle + \langle v^2_z \rangle$), whereas $y$ denotes the spatial direction in which the zigzag distortion of the vanadium chains can be observed. Note that the LDA values obtained for the sulfide are in perfect agreement with the earlier result from Mattheiss [37]. Surprisingly, the selenide shows an even larger formal DC anisotropy in LDA compared to the sulfide compound. In contrast, it is also obvious that within the many-body approach of LDA + DMFT the renormalization of the anisotropy, especially in the dominant
The growing electron localization. Note that in the ratio $U/J = 5$ was chosen. (a), (b) Total and orbital-resolved diagonal spin–spin expectation value. (c), (d) Off-diagonal spin–spin correlation between the effective $t_{2g}$ orbitals.

The respective on-site spin-correlation functions from the LDA + RISB computations for constant ratio $U/J = 5$. Concerning the diagonal spin–spin expectation value, as expected, the magnitudes evolve according to the nominal orbital occupations. Hence $\langle S^2 \rangle$ for the effective $E_{g1}$ orbital dominates over the corresponding value for the effective $A_{1g}$ orbital in the strong-interaction limit. In this respect, again quantitatively $\text{BaVS}_3$ exceeds $\text{BaVS}_5$ due to the increased $E_{g1}$ occupation. The total $\langle S^2 \rangle$ increases with larger $U$ due to the growing electron localization. Note that in the present problem the magnitude of this diagonal quantity can exceed the atomic-limit value of a single electron, i.e. $\langle S^2 \rangle_{\text{at}} = \frac{1}{4} (\frac{1}{4} + 1) = \frac{5}{4}$, although we have nominally one electron in the 3d shell of the chalcogenides. This is due to the fact that at some point a strong Hund’s coupling may tolerate an occupation of two electrons in the local three-orbital manifold of a metal. Since two electrons with parallel spin alignment form an $S = 1$ system, the resulting $\langle S^2 \rangle$ is bigger than the sum of two individual single-electron occupied sites. The interorbital spin–spin correlations again prove the dominant $A_{1g}$–$E_{g1}$ hybridization, which also leads to a significant spin coupling. However, it may be observed that in the minimal modeling for both systems the first Hund’s rule is violated close to $U = 0$, i.e., the off-diagonal $\langle S_{A1g} S_{Eg1} \rangle$ becomes smaller than zero in this regime.

It also has to be noted that these interorbital spin–spin correlations are rather sensitive to the degree of approximation of the rotational invariance in the interaction. While the diagonal spin–spin expectation value is not strongly affected by the inclusion of spin-flip and pair-hopping terms in the local Hamiltonian, the off-diagonal $\langle S_{A1g} S_{Eg1} \rangle$ is strongly enhanced in this case by a factor of two to three. Thus, whereas integrated one-particle quantities such as occupation numbers and local spins do not strongly suffer from density–density only descriptions, the two-particle functions, i.e. susceptibilities, may be substantially different. Figure 11 displays the same spin–spin functions, but for the (more realistic) case of a constant $J = 0.7$ eV. Of course, the strongest response may be observed for smaller $U$ since then the Hund’s coupling is most effective. Note again the differences for the density–density only interactions, leading to an even qualitatively different behavior for small $U$, where $\langle S_{A1g} S_{Eg1} \rangle$ is eventually dominated by $\langle S_{Eg1} S_{Eg1} \rangle$. In the more sound close to rotationally invariant description however, $\langle S_{A1g} S_{Eg1} \rangle$ is always clearly strongest. Because of the supposedly different $U/J$ ratio for $\text{BaVS}_3$ and $\text{BaVS}_5$ we hence expect for the selenide compound a more distinct magnetic behavior. Note that the interorbital spin–spin correlations decay in any case for large $U$, contrary to what is known for half-filled systems (there $\langle S_{A1g} S_{Eg1} \rangle$ actually increases with $U$). This is due to the fact that the ground state for a multi-orbital problem with a single-electron filling corresponds at large $U$ to the localization of that electron within a single orbital.
4. Discussion

From the above calculations, it turns out that BaVS$_3$ and BaVSe$_3$ are in many respects very similar materials. The differences between them are rather subtle, but still large enough to be resolved by the applied methods. The picture that arises thereof is not totally unambiguous, but several hints can be given why the formation of a charge-density wave is hindered in BaVSe$_3$. Already on an LDA level, it can be seen that hybridization effects among the bands of the t$_{2g}$ multiplet, as well as with the corresponding S(3p)/Se(4p) electrons, are the highlighting renormalizations in the t$_{2g}$ manifold in BaVSe$_3$ acts somewhat more cooperatively although the orbital differences are obvious, it seems as if electronic correlations are not irrelevant in discussion, no clear answer to this question may be conveyed. Nevertheless, spin–spin correlations should shed more light onto this.

In the end, the present study within standard LDA + DMFT is not in the definite position to clearly assign the different experimental facts of these surprisingly similar compounds from a theoretical perspective. However, although the situation is very subtle, we believe we have shown several indications that may explain to a certain extent why the present compounds behave so differently at lower temperatures. There seem to exist two main possible instabilities in these chalcogenides, namely the CDW one and the (ferro)magnetic ordering instability. As the driving forces towards these broken-symmetry states compete, a tailored renormalization-group study could reveal the finally dominating instability channel for each compound. Hence it is expected that the minor differences revealed in the present investigation show up more evidently within a renormalized scaling scenario. Still it has to be appreciated that, though not fully comprehensive, the LDA + DMFT method is nowadays on a level where it is feasible to reveal fine details between rather similar materials.

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