Experimental electronic structure and Fermi-surface instability of the correlated 3d sulphide BaVS₃: High-resolution angle-resolved photoemission spectroscopy

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The correlated 3d sulphide BaVS₃ exhibits an interesting coexistence of one-dimensional and three-dimensional properties. Our experiments determine the electronic band structure and shed light on this puzzle.

The correlated transition-metal sulphide BaVS₃ offers a puzzling combination of structural quasi-one-dimensionality (quasi-1D) with 3D character of some fundamental electronic and magnetic properties. Reconciling these features is a challenge for condensed-matter physics. BaVS₃ exhibits several instabilities: a structural hexagonal-to-orthorhombic transition at $T_S=250$ K, metal-to-insulator transition (MIT) at $T_M=69$ K, and an onset of antiferromagnetic long-range order at $T_N=30$ K. Here we concentrate on the MIT and we present angle-resolved photoemission (ARPES) data taken at $T_c<T<T_S$ on both sides of the MIT. For many years, ARPES has been used to experimentally probe the electronic band structure of different materials. This powerful approach, however, requires high-quality single crystals of reasonable size. We grew suitable crystals of BaVS₃ to experimentally determine the band structure and provide a solid background for the understanding of this compound and a framework for all future studies of BaVS₃ properties.

The crystal structure can be envisaged as a triangular lattice of chains of face-sharing VS₆ octahedra, with V-V distances in the a-b plane (6.72 Å) almost 2.4 times as large as in the c direction of the chains (2.84 Å). Naïvely, one would expect this structural quasi-one-dimensionality to be reflected in the electronic structure, with high conductivity along the chain direction and poor conductivity in the perpendicular directions. If this were the case, the MIT could be driven by the tendency of quasi-1D systems to form symmetry-breaking density-wave states. Interestingly, the transport measurements on single-crystal samples reveal conductivity that is essentially isotropic ($\sigma_c/\sigma_a \sim 3$), very low in the metallic phase and only weakly dependent on temperature. This 3D “bad metal” conductivity in the high-temperature phase is accompanied by the Curie-Weiss-type susceptibility, indicating a substantial fraction of localized V sites. On the other hand, the only good candidate so far for the order parameter is 1D in character: Inami et al. find the doubling of the unit cell occurring in the direction of V chains, while Fagot et al. show that this tetrametrization is preceded by strong 1D fluctuations of the lattice in a wide temperature range above the MIT. The MIT instability is interpreted as corresponding to a charge density wave (CDW) of a 1D electron gas with a periodicity of $2k_F = 0.5c$.

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The difficulties in understanding this coexistence of both 1D and 3D metal aspects are in large part due to the unclear character and occupancy of the low-energy electronic band structure. In theionic picture of a single V⁴⁺=3d¹ site, the trigonal component of the crystal field splits the $t_2g$ level into a nondegenerate $a_{1g}$ and a doubly degenerate $e_g$ level. The $a_{1g}$ orbitals have a $z^2$ character, overlapping strongly in the direction of chains. Such a band would be wide and almost 1D. If only these states were filled, we would expect to have a weakly correlated metal, or possibly a semiconductor, and no possibility for the formation of localized momenta. This is obviously not the case. There must be also $e_g$ electrons. In fact, all band structure calculations agree that the Fermi energy level ($E_F$) is lying in the region of the crossing of $a_{1g}$-like and $e_g$-like bands. If both $a_{1g}$ and $e_g$ electrons are indeed present, it is important to have a clear band picture, as complicated scenarios for the MIT may arise.

We performed ARPES on fairly large ($\approx 0.25 \times 0.25 \times 3 \text{ mm}^3$) single crystals of BaVS₃ grown by the slow-cooling technique in melted tellurium. The data were collected at the PGM beamline of the SRC (Stoughton, WI) and with a Scienta-2002 analyzer. The spectra presented were measured with a total energy and momentum resolution of $\Delta E = 15 \text{ meV}$ and $\Delta k = 0.04 \text{ Å}^{-1}$. Clean surfaces were exposed in UHV conditions of the analyzer chamber (10⁻¹¹ mbar range). The temperature of the sample could be controlled in the range from 5 to 150 K. Due to the pronounced needlelike structure, samples were fractured rather than cleaved, making the momenta of electrons poorly defined in the perpendicular directions to the one parallel to V chains. In the latter case, measurements were systematically reproducible.

Figure 1 shows the ARPES intensity map taken in the $\Gamma-Z$
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tion for the unit cell with two $V$ atoms. The measure-
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state. We read off the period 2
constant for the unit cell with two $V$ atoms. The measure-
ment in the vicinity of $E_F$ distinctly resolved, we choose a photon energy
of 50 eV, close to the photoionization cross section maxi-
mum for $V(3d)$ and avoiding the high cross section for $S(3p)$. Except for the temperature broadening and the lead-
ing edge shift close to $E_F$, as we discuss later, we obtain essentially the same intensity maps in the 40–150-K range.
The maps reproduce the theoretical $k$-space periodicity in the
extended zone scheme, indicating that the measurements, in
fact, disclose bulk states. We read off the period 2$\varepsilon_z$ where
$\varepsilon_z = 1/\pi \varepsilon_0 = 0.56$ Å$^{-1}$, $\varepsilon_0 = 5.61$ Å being the $c$-axis lattice
constant for the unit cell with two $V$ atoms. The measure-
ment is in agreement with the latest local density approxima-
tion (LDA) calculations$^{10}$ (see Fig. 1, right). Most of the
bands in the 1–4-eV interval are resolved and match in
width and position with the theory. The low-energy part of
the spectrum ($E_g \leq 1$ eV), requires a more rigorous look.

The $-d^2I/dE^2$ map of Fig. 2(b) shows the details of the
band structure close to $E_F$. We identify the dispersive band
with a minimum at $\Gamma$ and $\sim 1$ eV bandwidth as the $a_{1g}$ band.
In the absence of perpendicular-to-chain measurements, we
can conclude that the $a_{1g}$ band is at least close to quasi-1D
because (i) no distinction could be found in maps of different
measurements, though the perpendicular to $\Gamma-Z$ orientation
of the needlelike crystal was fairly arbitrary, and (ii) we ob-
tained indistinguishably similar dispersions by varying the
photon energy (25–55 eV). This band is traversed by one of
the $S(\pi_z)$ bands with a maximum at $\Gamma$. We associate the
seemingly flat band, just under $E_F$ and most clearly discerned
around $\Gamma_z$, with the $\epsilon_g$ states. One can notice both $\epsilon_g$ and $a_{1g}$
bands in the plot of selected raw energy distribution curves
(EDCs) presented in Fig. 2(c).

Even deep in the metallic phase ($T > T_{MI}$), the EDCs re-
tain the width and peak positions. The width $\Delta E 
\sim 300$ meV is large, and the spectra are pseudogapped, with
no obvious $E_F$ crossing in the metallic phase for any of
the bands. Both indicate that the observed spectral function does
not reflect the “bare” quasiparticle dispersion. Our angle-
resolved data corroborate the results of an angle-integrated
study on polycrystalline samples$^{12}$ which reported the lack of a
Fermi edge above $T_{MI}$. This was attributed to Luttinger
liquid behavior. However, the electronic properties of BaVS$_3$
are far from being purely quasi-1D to permit such an inter-
pretation. In fact, these features are not at all uncommon in
systems where electrons are coupled to collective modes and
are nowadays accepted as one of the signatures that carry
valuable information about the interactions. They have been
observed in quasi-1D metals$^{13,14}$ but also in high-
temperature superconductors$^{15,16}$, layered manganites$^{17}$, and,
some aspects, even in semiconductors$^{18}$.

When electrons couple to collective excitations, the spec-
tral weight on the quasiparticle peak is renormalized$^{15,17}$ and
the extent of the renormalization depends on the strength of
the interactions and the dimensionality of the bands in ques-
tion. If interactions are strong, almost all of the spectral
weight is taken away from the quasiparticle peak. This ap-
ppears to be the case in BaVS$_3$. Taking that into account, the
dispersion map in Fig. 2(b) consists of two regions: (i) the
higher-binding-energy region where EDC peak dispersion
represents accurately the “frozen” lattice dispersion (dashed
lines as guides to the eye) and (ii) the region between $E_F$
and the closest EDC peak—whose position is determined by
interactions—where we observe only flat features (dotted
lines as guides to the eye). Nevertheless, the dispersing qua-
siparticle spectrum is there, and this is directly observable in
momentum distribution curves (MDCs). MDCs are equivalent
to EDCs, but with the advantage of being less sensitive to
interactions.$^{16}$

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**FIG. 1.** (Color online) Left: ARPES intensity map at 40 K taken
in the direction parallel to the structural chains. Brighter color sig-
nifies higher intensity. The spectra were normalized and a back-
ground was subtracted to enhance the features. Right: the corre-
sponding theoretical LDA band dispersion, adopted from Ref. 10.

**FIG. 2.** (Color online) (a) An MDC of an integrated energy
region $E_F < E_b < 50$ meV from an ARPES map at 150 K. A double-
Lorentzian fit determines the position of $k_{F_\pi}$ from both sides of the
BZ. Below is the equivalent MDC plot taken from a map at 40 K
and 80 meV higher in binding energy to account for the gap open-
ing (Ref. 14). The arrows indicate the positions of the second $E_F$
crossing, $k_{F_\pi}$. (b) $-d^2I/dE^2$ plot of the ARPES map at 40 K. The
white dashed and dotted lines guide the eye in following the dis-
persions. Refer to the text for details. (c) Selected raw EDCs in
equidistant steps from the $\Gamma$ to $Z$ point, plotted with an offset.
In Fig. 2(a) we plot an MDC around the \( E_F \) from an ARPES map taken in the metallic phase. The Lorentzian-shaped peaks are a token of quasiparticles. They disclose the \( E_F \) crossings of the \( a_{1g} \) band within the first and second Brillouin zones (BZs). The value from Lorentzian peak fits of the wave vector \( k_F = (0.40 \pm 0.05) \ \text{Å}^{-1} \) is in good agreement with the latest theoretical result, which includes interactions in the band picture, specifically Fig. 4 of Ref. 10. As for the \( e_g \) states, there is only a slight increase of intensity not far from the \( \Gamma \) point in the MDC of Fig. 2(a), which could indicate a crossing of a predicted electron pocket.\(^9\)\(^10\) For better resolution we need to look at the map at a lower temperature (40 K), but to have equivalency of MDCs we take one at higher binding energy to account for the gap opening \( \Delta_{eg} \).\(^14\)

We determine the gap value directly from our spectra, as we describe later. Since we are able to fit the same width and position Lorentzians for \( a_{1g} \) peaks, we trust the correctness of this procedure. The two new peaks that are revealed are symmetric around the \( \Gamma \) point and indicate an electron pocket crossing \( E_F \) at \( k_F = (0.15 \pm 0.05) \ \text{Å}^{-1} \). This is again in good agreement with the value from Ref. 10. Unlike for \( a_{1g} \), where we can follow the dotted line of the dispersion by plotting successive MDCs, we cannot do the same for \( e_g \) states. The dotted line in Fig. 2(b) is only for illustration purposes; the actual states are too narrow to be revealed in MDCs.

If the Lorentzian peaks in MDCs may truly be regarded as quasiparticles, they should reveal the real gap and show the phase transition. If we plot the position of the leading edge of measured spectral functions versus temperature, we see a monotonic shift—which most likely started above 150 K—and a noticeable nonlinear increase in the shift below 90 K. This is consistent with the results of Ref. 12 and indicative of the opening of a charge gap. We do not see a clear transition associated with the \( T_{MI} = 69 \) K. This is not unusual, particularly in CDW systems when pretransitional fluctuations are present or in systems where conducting, wide-band electrons are strongly scattered by the narrow-band electrons and/or by the localized states placed at energies close to \( E_F \). The gap as seen in photoemission spectra develops in the same range of temperatures where resistivity\(^3\)\(^19\) identifies a “precursor” to the insulating phase and where x-ray diffraction detects large 1D fluctuations.\(^6\) The saturation of the leading edge shift indicates a charge gap of \( \Delta_{eg} = 60-70 \) meV. This is about the same value as the full charge gap from transport measurements.\(^2\)\(^3\)\(^12\)

We examined our experimentally determined band structure to identify a Fermi surface instability which can introduce a gap into the wide \( a_{1g} \) band. We find that the \( a_{1g} \) band alone cannot satisfy the nesting condition as \( 2k_F > Q_{\text{CDW}} = 0.5\text{Å}^{-1} \). An intraband nesting of a half-filled \( a_{1g} \) band would be most prominent in the \( \Gamma-Z \) direction, where strong 1D fluctuations are observed,\(^6\) so it is expected to be discerned in our intensity maps. Therefore, we may conclude that this scenario is not likely for this compound. On the other hand, our results tempt us to consider an instability involving both bands, since our data are in agreement with the condition \( k_F + k_F = Q_{\text{CDW}} \). In this scenario the whole Fermi surface is removed. This is confirmed in the temperature dependence presented in Fig. 3 because we observe the same evolution at both \( k_F \) and \( k_{F'} \). The gap opens across the entire Fermi surface. However, this scenario cannot be fully reconciled with, at least, the x-ray diffraction experiments. Therefore, the nature of the exact mechanism for the MIT remains an open question, but it must include both bands.

**FIG. 3.** Left: EDCs at \( k=k_F \) taken at 140 and 45 K. The charge gap is observable in the shift of the leading edge, where the actual quasiparticle is situated. Right: the shift of the leading edge as a function of temperature. The dashed line in (right) marks the MIT temperature.

ARPES cannot see the empty part of the \( a_{1g} \) band, but judging from the occupied part, its overall width must approach the theoretical value \( W(a_{1g}) \geq 2 \) eV.\(^9\)\(^10\) On the other hand, the width of the \( e_g \) band is very small, as discussed above. We conclude that the intriguing behavior of BaVS\(_3\) results from the fact that two kinds of \( d \) states, strongly correlated narrow-band \( e_g \) states and weakly correlated wide-band \( a_{1g} \) states, coexist at the Fermi level. The isotropic, highly localized, \( e_g \) band explains the Curie-like susceptibility. Lechermann et al. provide the only theoretical work that correctly describes the band structure that we obtain experimentally, by including the correlations\(^10\) and show that the population between the bands is split with the ratio \( n(a_{1g})/n(e_g) = 1/2:1/2 \). Therefore, exactly half of the electrons are localized. Small anisotropy in transport is observed as the quasi-1D \( a_{1g} \)-band influence is reduced through a certain combination of \( e_g-a_{1g} \) scattering, hybridization with sulphur bands, or likely electron-phonon interaction. In fact, the width of the quasiparticle peaks in MDCs allows for the direct determination of the coherence length \( \Delta \ell = (9.7 \pm 0.4) \ \text{Å} \). This value is smaller than two unit cells and explains why the conductivity is much lower in the \( T > T_{MI} \) phase than it would be in a normal metal.

To conclude, we measure the electronic band structure by ARPES in a wide range of temperatures on both sides of the MIT. We find discernible quasiparticle features, even though the spectral function is profoundly influenced by strong interactions. Our results show that the physics of BaVS\(_3\) is governed by the coexistence of weakly correlated wide-band \( a_{1g} \) electrons and strongly correlated narrow-band \( e_g \) electrons near the Fermi energy level. Both bands must be considered to explain the observed 1D instability,\(^7\) as the examined points of the Fermi surface do not support the intraband nesting of the half-filled \( a_{1g} \) band and the charge gap opens over the entire Fermi surface, involving both bands.

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