Orbitally Driven Spin Pairing in the 3D Non-Magnetic Mott Insulator BaVS₃: Evidence from Single Crystal Studies

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Static electrical and magnetic properties of single crystal BaVS₃ were measured over the structural (Tₐ = 240K), metal–insulator (TMI = 69K), and suspected orbital ordering (TX = 30K) transitions. The resistivity is almost isotropic both in the metallic and insulating states. An anomaly in the magnetic anisotropy at TX signals a phase transition to an ordered low-T state. The results are interpreted in terms of orbital ordering and spin pairing within the lowest crystal field quasi-doublet. The disordered insulator at TX < T < TMI is described as a classical liquid of non-magnetic pairs.

Spatial ordering of the occupancy of degenerate electronic orbitals plays important role in the diverse magnetic phenomena of transition metal compounds. To cite a well-known example: the interplay of magnetic and orbital long range ordering, and strong coupling to the lattice, account for the metal–insulator transitions of the V₂O₃ system. In contrast, the metal–insulator transition of the S = 1/2, 3d⁵ electron system BaVS₃ is not associated either with magnetic long range order, or with any detectable static spin pairing. As an alternative, the possibility of an orbitally ordered ground state was discussed, while other proposals emphasized the quasi-one-dimensional character of the material. The crystal structure is certainly suggestive of a linear chain compound since along the c axis, the intrachain V–V distance is only 2.81 Å, while in the a–b plane the interchain separation is 6.73 Å. It is thus somewhat surprising that our present studies show that electrically BaVS₃ is nearly isotropic. This means that BaVS₃ provides one of the few realizations of a Mott transition within the non-magnetic phase of a three-dimensional system. Since this case (or rather its D → ∞ counterpart) is much studied theoretically, but scarcely investigated experimentally, a good understanding of BaVS₃ should be valuable for strong correlation physics in general.

BaVS₃ has a metal-insulator transition at TMI = 69K, accompanied by a sharp spike in the magnetic susceptibility. The high temperature phase is a strongly correlated metal with mean free path in the order of the lattice constant. There is no sign of a sharp Fermi-edge in the UPS/XPS spectra and instead of a Pauli-susceptibility it exhibits Curie-Weiss like behavior. Though the magnetic susceptibility is similar to that of an antiferromagnet, no long-range magnetic order develops at the transition. The transition is clearly seen in the thermal expansion anomaly, and in the specific heat. The d-electron entropy right above TMI is estimated as ~ 0.8Rln 2, and it seems that a considerable fraction of the electronic degrees of freedom is frozen even at room temperature. It appears that the 69K transition is not symmetry breaking: it is a pure Mott transition which does not involve either magnetic order or any static displacement of the atoms.

Hints of long range order were found well below TMI, at TX = 30K, in recent NMR and NQR experiments. It was suggested that orbital order may develop here, but it could not be decided whether the TX phenomenon is a true phase transition, or purely dynamical. In any case, the associated entropy change must be very small since it escaped detection. In this work we prove that there is a phase transition, by finding its signature in static magnetic properties.

In order to clarify the nature of BaVS₃, we performed single crystal experiments, searching for macroscopic anisotropy in the electrical and the magnetic properties. Our results exclude the quasi-1D interpretations and supply direct evidence for the dominant role of e(t₂g) orbitals tilted out from the chain direction. The static magnetic susceptibility χ, and more markedly, its anisotropy χ_e – χ_a, show clear anomalies both at TMI and TX.

Single crystals of BaVS₃ were grown by Tellurium flux method. Powders of BaVS₃ and sublimated tellurium 99.99% Ventron were mixed in a molar ratio 1 : 50 and heated up to 1050 °C in an evacuated silica ampoule. Then it was slowly cooled down to 55°C at the rate of 1°C/hour. The crystals, obtained from the flux by sublimation, have typical dimensions of 3 x 0.5 x 0.5 mm³.

For the longitudinal (c-direction) resistance measurement standard four probe contact arrangement was applied. The conduction anisotropy was determined by the Montgomery method. Experiments performed on several crystals from various preparation batches showed...
deviation only at low temperatures, which we attribute to the different purity of the samples (see later). The magnetic susceptibility was measured by Faraday-balance, the anisotropy measurements were carried out on a sensitive torque magnetometer [15].

FIG. 1. Temperature dependence of the resistivity \( \rho_c(T) \), and the conduction anisotropy \( \sigma_c/\sigma_a \) in BaVS\(_3\). The arrows indicate \( T_S \), \( T_{MI} \) and \( T_X \), respectively.

Figures 1 and 2 show the temperature dependence of the resistivity and the conduction anisotropy of single crystals. BaVS\(_3\) is a “bad metal” with \( \rho_{RT} = 0.7 \) m\( \Omega \) cm. With decreasing \( T \) a slight change of slope reflects the structural transition at \( T_S = 240 \) K (Fig. 1, upper panel). The resistivity has a minimum at 125 K. A sharp metal–insulator transition sets in at \( T_{MI} = 69 \) K (Fig. 2 inset). Below \( T_{MI} \) the resistivity increases steeply and it varies 9 orders of magnitude down to about 20 K. Crossing \( T_X \) does not influence \( \rho(T) \) as it is obvious also from the Arrhenius plot (Fig. 2). We deduce a gap \( \Delta \approx 600 \) K for the insulator (\( \Delta \) is not well defined due to a slight curvature in the \( \ln \rho - 1/T \) plot). The overall behavior of \( \rho(T) \) agrees well with that of high purity polycrystalline samples [3].

The conduction anisotropy, defined as the ratio of conductivities measured along and perpendicular to the chain direction, is surprisingly low, \( \sigma_c/\sigma_a \approx 3 \). It is temperature independent in the metallic phase and there is only a small jump at the metal–insulator transition. Below \( T_{MI} \) the anisotropy has the same small value over a broad temperature range down to about 30 – 40 K. Note that in this range of \( T \) the resistivity increases about 6 orders of magnitude in both directions. The low temperature upturn is related to impurities, the two most different results obtained on different samples are plotted in Fig. 2 (lower panel). It seems that impurity donated carriers enhance the \( c \)-direction conduction, and for this process the activation energy is about 70 K.

FIG. 2. Arrhenius plot of the resistivity and the conduction anisotropy. The latter is shown for two crystals of different purity. Inset: the peak of \( d \ln \rho/d(1/T) \) defines \( T_{MI} \).

Figure 3 summarizes the results of the magnetic susceptibility measurements. Along the chain direction, \( \chi_c(T) \) agrees well with previous data on stoichiometric samples; the Curie–Weiss behavior in the metallic phase (\( \mu_{\text{eff}} = 1.2 \mu_B \); the small \( \Theta < 10 \) K may vary slightly with the range of fit) is followed by a steep decrease in the susceptibility below \( T_{MI} \). \( \chi_c \) and \( \chi_a \) look very similar (therefore we show only \( \chi_c \)), and both are fairly smooth at \( T_X \). However, we find a sharp peak in the temperature derivative of the \( a \)-axis susceptibility \( d\chi_a/dT \), and a sudden break in the anisotropy \( \chi_c - \chi_a \) at \( T_X \approx 30 \) K. These give convincing evidence of a phase transition within the insulating phase. We suggest that the transition temperature \( T_X \) be defined by the sharp peak in \( d\chi_a/dT \) [16].

Discussing the results first we interpret the low value of the conduction anisotropy. For the present purposes, we assume that the simple ionic picture holds (Ba\(^{2+}\)V\(^{4+}\)S\(_2\)\(^{-3}\) ionic state, 3\( d^1 \) configuration). Figure 4a shows the crystal field splitting of the vanadium \( d \)-levels. The sulphur octahedra surrounding nearest neighbor vanadium ions are face-sharing along the \( c \)-axis. Above \( T_S = 240 \) K, there is a trigonal distortion along the \( c \)-axis; for \( T < T_S \), an additional orthorhombic component appears. The main effect is the trigonal splitting of the \( t_{2g} \) level, which lifts the \( d_{x^2} \) level (the \( z \)-axis being now the trigonal axis)
above the two degenerate $e(t_{2g})$ orbitals. The remaining degeneracy is lifted by the orthorhombic distortion: below $T_S$, the low-energy crystal field states can be thought of as a quasi-doublet with a small splitting.

In Fig. 4 the lobes of the low-lying orbitals are shown on the background of the crystal structure. The $d_{z^2}$ orbitals have large direct overlap along the chain direction as shown in the left side of Fig. 4b. Taking also into account that the vanadium chains are widely separated, any conduction through the $d_{z^2}$ channel is expected to be extremely anisotropic. In contrast, there is only weak, indirect overlap of the two $e(t_{2g})$ levels and hopping along these channels is almost isotropic. From the observed small conduction anisotropy we conclude that the $d_{z^2}$ orbitals are not involved in the electron transport. In contrast to previous assumptions, the crystal field splitting between $d_{z^2}$ and the $e(t_{2g})$ levels must be large and the band formed from the $d_{z^2}$ orbitals does not overlap with the occupied states.

We believe that the electron propagation along the $c$-axis occurs also through multiple nearest neighbor inter-chain hops involving only the $e(t_{2g})$ orbitals. Extended states of the $d_{z^2}$ band are excited only at low temperatures from impurity levels situated below the broad band. This process is seen in the impurity dependent low-temperature upturn of the anisotropy.

The susceptibility data show that the number of polarizable moments drops drastically upon entering the insulating phase. On the other hand, the metal–insulator transition has no magnetic precursor on the metallic side, $\chi$ closely follows the paramagnetic formula down to $T_{MI}$.

The volume change and the onset of an $ab$-plane rearrangement of the V sublattice at the transition indicate that the state of the system changes profoundly, and the effective spin–spin interaction may be completely different from that in the metallic phase. It seems that the insulator phase does not arise from a magnetic instability of the metallic phase. Let us recall the case of V$_2$O$_3$ where the onset of orbital order leads to an insulating state whose magnetic ordering pattern cannot be anticipated from the short range order found in either of the neighboring phases. We propose a similar picture for BaVS$_3$: the metal–insulator transition involves both the spin and orbital degrees of freedom, and considering only the effect on spins, it amounts to a change of the spin hamiltonian. It is the consequence of the frustrated structure (a triangular array of V chains), and of the form of the relevant crystal field states, that the intermediate ($T_X < T < T_{MI}$) phase is not an ordered magnet, but an overall non-magnetic state with peculiar spin and orbital short range order.
short range rules for the relative orientation of the pairs. Due to the small energy difference between the various configurations the singlet pair formation at $T_{MI}$ is not accompanied by true long range order, but instead a spin–orbital liquid develops. Thermal averaging over the (exponentially large number of) accessible configurations gives rise to a homogeneous state with low susceptibility. Moreover, in accordance with NMR/NQR results~\cite{4}, no static pairing is expected over a broad temperature interval below $T_{MI}$. Long range static order is reached only at the much lower temperature $T_X$, as shown by the present susceptibility data, and also by anomalies in microscopic measurements~\cite{20}. Due to the pre-existing short range order, this transition is not accompanied by any significant entropy change.

![FIG. 5. Some of the energetically favorable pair arrangements in the triangular $ab$ plane.](image)

The pictures in Fig. 5 may remind us of the resonating valence bond state of frustrated Heisenberg models~\cite{1}. We emphasize that the situation is completely different here. Within each pair, those orbitals are occupied which give rise to a strong intrapair exchange, and thus each cluster state belongs to a different effective spin Hamiltonian. Considering the shape of the $e(t_{2g})$ orbitals one finds that pair formation does not quite saturate the exchange interaction, but there are residual interactions which govern farther-neighbor correlations, and cause a weak resonance. However, this resonance is much weaker than in the pure $S=1/2$ Heisenberg models, and the $T_X < T < T_{MI}$ phase of BaVS$_3$ is better described as a thermal average over valence bond solids, than as a resonating valence bond liquid. The finding of a $T$-dependent spin gap, which vanishes at $T_{MI}$~\cite{21}, is consistent with our scenario.

The metal–insulator transition affects mainly the spin degrees of freedom: the electronic entropy present at $T$ slightly above $T_{MI}$~\cite{4} is almost exhausted by the spin entropy required by the measured $T > T_{MI}$ susceptibility which can be ascribed to $\sim 70\%$ of the V sites carrying nearly independent localized spins. The primary order parameter of the low temperature phase is the density of the non-magnetic pairs, and the driving force of the transition is the gaining of spin entropy. Sizeable orbital order must exist even above the metal–insulator transition (below $T_{MI}$, it becomes additionally stabilized by the singlet formation as shown by the appearance of an extra component of the orthorhombic distortion~\cite{20}). We emphasize, however, that the entropy which would correspond to the complete absence of short range orbital order is certainly not present even at $T = 300K$~\cite{7}.

In conclusion, we have shown that electron propagation in BaVS$_3$ occurs via nearest neighbor interchain hops involving the $e(t_{2g})$ orbitals only. The metal–insulator transition was described as a transition to a classical liquid of non-magnetic pairs, which shows spin and orbital short range order. We have proposed that though farther-neighbor inter-pair interactions prefer ordered structures, due to the frustrated triangular structure long range order can develop only well below the metal–insulator transition, at $T_X$. Our explanation is in overall agreement with the results of transport, magnetic and thermodynamic experiments.

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\begin{thebibliography}{99}
  \bibitem{1} P. Fazekas, Lecture Notes on Electron Correlation and Magnetism, (World Scientific, Singapore, 1999).
  \bibitem{2} W. Bao et al., Phys. Rev. B 58, 12727 (1998).
  \bibitem{3} L. Paolasini et al., Phys. Rev. Lett 82, 4719 (1999).
  \bibitem{4} H. Nakamura, H. Imai and M. Shiga, Phys. Rev. Lett. 79, 3779 (1997).
  \bibitem{5} T. Graf et al., Phys. Rev. B 51, 2037 (1995).
  \bibitem{6} H. Nakamura et al., Phys. Rev. B 49, 16191 (1994).
  \bibitem{7} H. Imai, H. Wada and M. Shiga, J. Phys. Soc. Jpn. 65, 3460 (1996), M. Shiga, H. Imai and H. Wada, J. Magn. Magn. 177 1347 (1998).
  \bibitem{8} R.A. Gardner, M. Vlasse and A. Wold, Acta Crystallogr. Sec B 25, 781 (1969).
  \bibitem{9} M. Ghedira et al., J. Phys. C 19, 6489 (1986).
  \bibitem{10} O. Massenet et al., J. Phys. Chem. Solids 40, 573 (1979).
  \bibitem{11} M. Takano et al., J. Phys. Soc. Jpn. 43, 1101 (1977).
  \bibitem{12} A. Heidemann and M. Takano, Phys. Stat. Solidi B 100, 343 (1980); H. Nishihara and M. Takano, J. Phys. Soc. Jpn. 50, 426 (1981).
  \bibitem{13} The only known change of symmetry occurs at the hexagonal-orthorhombic transition at $T_S = 240K$. It slightly affects the resistivity, and it is not visible either in the magnetic susceptibility or in the specific heat.
  \bibitem{14} H.C. Montgomery, J.App. Phys. 42, 2971 (1971).
  \bibitem{15} M. Miljak et al., unpublished.
  \bibitem{16} The phase transition would be less visible in $d\chi_e/dT$ which has only a small bump.
  \bibitem{17} The $e(t_{2g})$ orbitals shown in Fig. 4 are the $\pm 1$ eigen-states of the orbital angular momentum $L^z$: $e_g = (x^2 - y^2)/\sqrt{5} - xz/\sqrt{5}$ and $d_g = xy/\sqrt{3/2} + yz/\sqrt{5}$. Note that the coordinate system has been rotated from the octahedral main axes so that now $z$ is along the trigonal axis.
  \bibitem{18} K.I. Kugel and D.I. Khomskii, Usp. Fiz. Nauk 136, 621 (1982) [Sov. Phys. Usp. 25, 231 (1982)].
  \bibitem{19} K. Penc et al., unpublished.
  \bibitem{20} F. Sayetat et al., J. Phys. C 15, 1627 (1982).
  \bibitem{21} H. Nakamura et al., J. Phys. Chem. Solids 60, 1137 (1999).
\end{thebibliography}