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Orbitally driven spin pairing in the three-dimensional nonmagnetic Mott insulator $BaVS_3$: Evidence from single-crystal studies

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Static electrical and magnetic properties of single crystal $BaVS_3$ were measured over the structural ($T_S = 240$ K), metal insulator ($T_{MI} = 69$ K), and suspected orbital ordering ($T_X = 30$ K) transitions. The resistivity is almost isotropic both in the metallic and insulating states. An anomaly in the magnetic anisotropy at T_X 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 quasidoublet. The disordered insulator at $T_X < T < T_{MI}$ is described as a classical liquid of nonmagnetic pairs.

Spatial ordering of the occupancy of degenerate electronic orbitals plays an important role in the diverse magnetic phenomena of transition-metal compounds.[1] 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 V_2O_3 system.[2,3] In contrast, the metal-insulator transition of the $S = 1/2$, $3d^1$ electron system $BaVS_3$ 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,[4] while other proposals emphasized the quasi-one-dimensional character of the material.[5–7] 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.[8,9] It is thus somewhat surprising that our present studies show that electrically $BaVS_3$ is nearly isotropic. This means that $BaVS_3$ provides one of the few realizations of a Mott transition within the nonmagnetic phase of a three-dimensional system. Since this case (or rather its $D \to \infty$ counterpart) is much studied theoretically, but scarcely investigated experimentally, a good understanding of $BaVS_3$ should be valuable for strong correlation physics, in general.

$BaVS_3$ has a metal-insulator transition at $T_{MI} = 69$ K, accompanied by a sharp spike in the magnetic susceptibility.[5,10] 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 ultraviolet photoemission/x-ray photoemission spectra[6] and instead of a Pauli susceptibility it exhibits Curie-Weiss-like behavior. Though the magnetic susceptibility is similar to that of an antiferromagnet,[10,11] no long-range magnetic order develops at the transition.[9,12] The transition is clearly seen in the thermal expansion anomaly,[5] and in the specific heat.[7] The d-electron entropy right above T_{MI} is estimated as $\sim 0.8R \ln 2$, and it seems that a considerable fraction of the electronic degrees of freedom is frozen even at room temperature.[7] It appears that the 69-K transition is not symmetry breaking:[13] 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 T_{MI}, at $T_X = 30$ K, in recent NMR and NQR experiments.[4] It was suggested that orbital order may develop here, but it could not be decided whether the T_X phenomenon is a true phase transition, or purely dynamical. In any case, the associated entropy change must be very small since it escaped detection.[7] 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 $BaVS_3$, we performed single-crystal experiments, searching for macroscopic anisot-

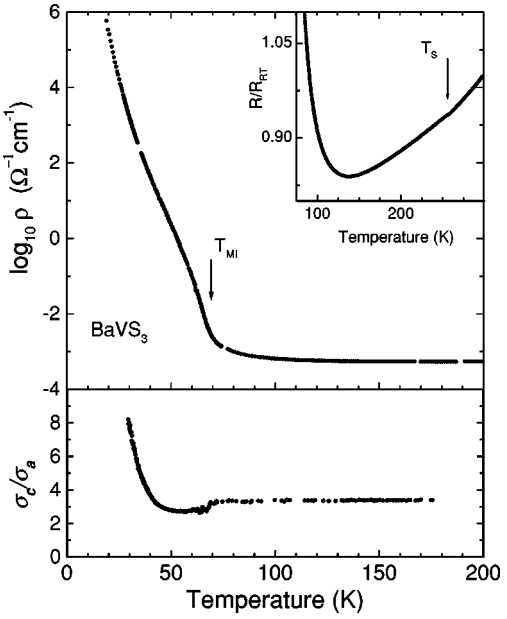

FIG. 1. Temperature dependence of the resistivity $\rho_c(T)$, and the conduction anisotropy σ_c/σ_a in $BaVS_3$. The arrows indicate T_S, T_{MI}, and T_X, respectively.

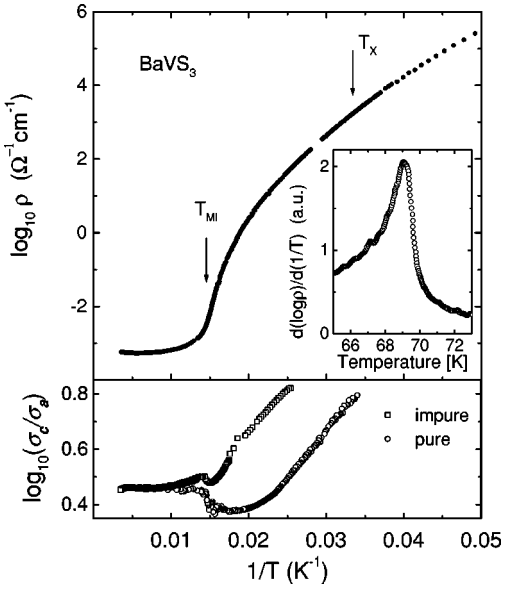

FIG. 2. Arrhenius plot of the resistivity and the conduction anisotropy. The latter is shown for two crystals of different purity. Inset: the peak of $d\ln\rho/d(1/T)$ defines T_{MI}.

ropy in the electrical and the magnetic properties. Our results exclude the quasi-one-dimensional (1D) interpretations and supply direct evidence for the dominant role of $e(t_{2g})$ orbitals tilted out from the chain direction. The static magnetic susceptibility χ, and more markedly, its anisotropy $\chi_c - \chi_a$, show clear anomalies both at T_{MI} and T_X.

Single crystals of $BaVS_3$ were grown by the Tellurium flux method. Powders of $BaVS_3$ 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 $3\times0.5\times0.5$ mm^3.

For the longitudinal (c-direction) resistance measurement standard four probe contact arrangement was applied. The conduction anisotropy was determined by the Montgomery method.[15] 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.[16]

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 $\rho_{\mathrm{RT}}=0.7$ mΩ 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 $T_{\mathrm{MI}}=69$ K (Fig. 2 inset). Below T_{MI} the resistivity increases steeply and it varies nine 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 $\Delta\approx600$ K for the insulator (Δ 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.[5]

The conduction anisotropy, defined as the ratio of conductivities measured along and perpendicular to the chain direction, is surprisingly low, $\sigma_c/\sigma_a\approx3$. 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 six 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.

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 ($\mu_{\mathrm{eff}}=1.2\mu_B$; 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}. χ_c and χ_a look very similar (therefore we show only χ_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 $T_X\approx30$ 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 $d\chi_a/dT$.[17]

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 ($Ba^{2+}V^{4+}S_3{}^{2-}$ ionic state, $3d^1$ configuration). Figure 4(a) 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_{z^2} level (the

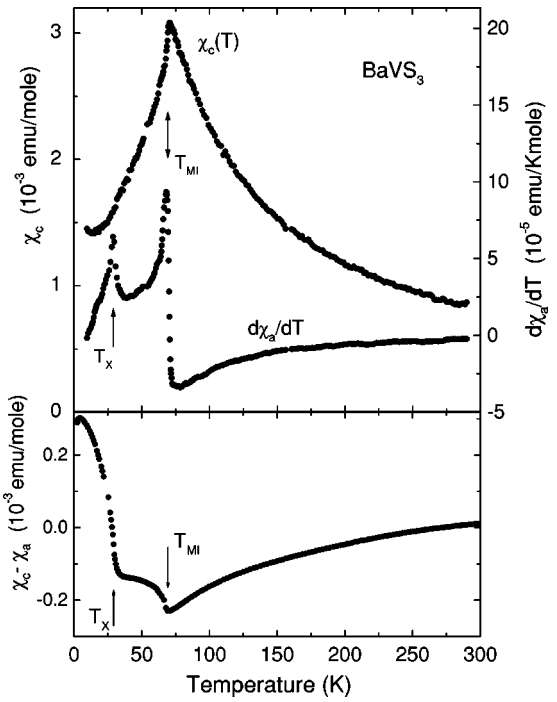

FIG. 3. Temperature dependence of the c-axis magnetic susceptibility χ_c, the derivative of the a-axis susceptibility $d\chi_a/dT$, and the susceptibility anisotropy, $\chi_c - \chi_a$.

z axis being now the trigonal axis) above the two degenerate $e(t_{2g})$ orbitals.[10] The remaining degeneracy is lifted by the orthorhombic distortion: below T_S, the low-energy crystal-field states can be thought of as a quasidoublet with a small splitting.

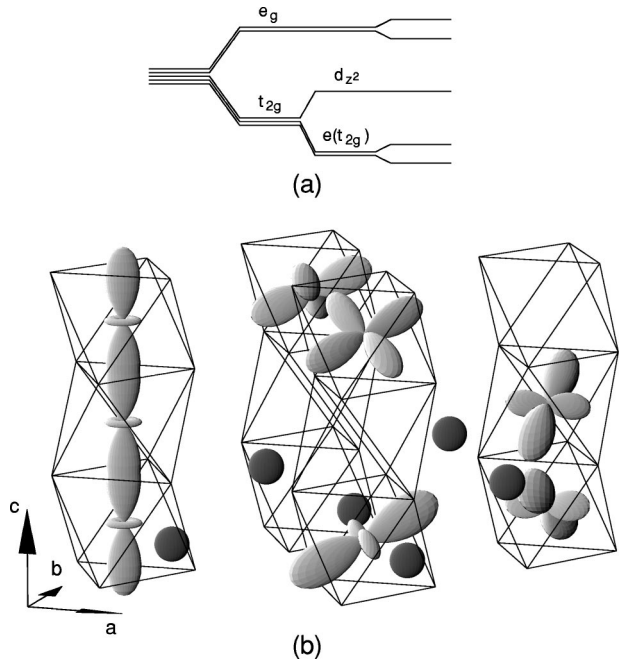

FIG. 4. (a) Crystal-field splitting of the vanadium $3d$ levels due to the symmetry reduction from octahedral→trigonal (distortion along the c direction)→ orthorhombic (zig-zag chain developed below T_S). (b) Perspective view of the crystal structure of $BaVS_3$. The orientation of the low-lying orbitals derived from t_{2g} is also displayed.

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. 4(b). 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,[18] 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,[10] the crystal-field spitting 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 interchain 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, χ closely follows the paramagnetic formula down to T_{MI}. The volume change[5] and the onset of an ab plane rearrangement of the V sublattice at the transition[9] 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_2O_3 where the onset of orbital order[3] leads to an insulating state whose magnetic ordering pattern cannot be anticipated from the short-range order found in either of the neighboring phases.[2] 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 ($T_X < T < T_{\mathrm{MI}}$) phase is not an ordered magnet, but an overall nonmagnetic state with peculiar spin and orbital short-range order.

In order to investigate the electronic structure of the insulating phase, we derived a Kugel-Khomskii-type model[19] starting from the atomic limit, including also the orbital index dependence of the hopping matrix elements, and the spin-orbit coupling.[20] There is a broad range of parameters for which the ground state of an isolated pair of sites is nonmagnetic. Further numerical and variational calculations for clusters of up to 24 sites revealed the presence of a large number of ordered low-energy states. Figure 5 gives examples of these various long-period structures which obey characteristic 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. More-

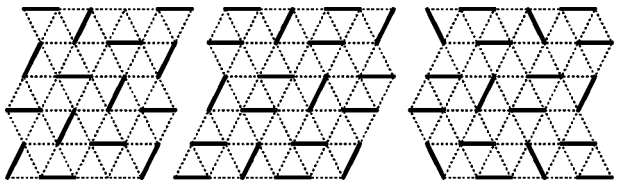

FIG. 5. Some of the energetically favorable pair arrangements in the triangular ab plane.

over, in accordance with NMR/NQR results,[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.[4,14] Due to the pre-existing short-range order, this transition is not accompanied by any significant entropy change.

The pictures in Fig. 5 may remind us of the resonating valence bond state of frustrated Heisenberg models.[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} (Refs. 4 and 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} (Ref. 7) 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 nonmagnetic 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[14]). We emphasize, however, that the entropy which would correspond to the complete absence of short-range orbital order is certainly not present even at $T=300$ K.[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 nonmagnetic pairs, which shows spin *and* orbital short-range order. We have proposed that although farther-neighbor interpair 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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[1] P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism* (World Scientific, Singapore, 1999).
[2] W. Bao *et al.*, Phys. Rev. B **58** 12 727 1998.
[3] L. Paolasini *et al.*, Phys. Rev. Lett. **82**, 4719 (1999).
[4] H. Nakamura, H. Imai, and M. Shiga, Phys. Rev. Lett. **79**, 3779 (1997).
[5] T. Graf *et al.*, Phys. Rev. B **51**, 2037 (1995).
[6] H. Nakamura *et al.*, Phys. Rev. B **49**, 16 191 (1994).
[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. Mater. **177**, 1347 (1998).
[8] R.A. Gardner, M. Vlasse, and A. Wold, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **25**, 781 (1969).
[9] M. Ghedira *et al.*, J. Phys. C **19**, 6489 (1986).
[10] O. Massenet *et al.*, J. Phys. Chem. Solids **40**, 573 (1979).
[11] M. Takano *et al.*, J. Phys. Soc. Jpn. **43**, 1101 (1977).
[12] A. Heidemann and M. Takano, Phys. Status Solidi B **100**, 343 (1980); H. Nishihara and M. Takano, J. Phys. Soc. Jpn. **50**, 426 (1981).
[13] The only known change of symmetry occurs at the hexagonal-orthorhombic transition at $T_S=240$ K. It slightly affects the resistivity, and it is not visible either in the magnetic susceptibility or in the specific heat.
[14] F. Sayetat *et al.*, J. Phys. C **15**, 1627 (1982).
[15] H.C. Montgomery, J. Appl. Phys. **42**, 2971 (1971).
[16] M. Miljak *et al.* (unpublished).
[17] The phase transition would be less visible in $d\chi_c/dT$ which has only a small bump.
[18] The $e(t_{2g})$ orbitals shown in Fig. 4 are the ± 1 eigenstates of the orbital angular momentum L^z: $d_x=(x^2-y^2)/\sqrt{6}-xz/\sqrt{3}$ and $d_y=xy/\sqrt{3/2}+yz/\sqrt{3}$. Note that the coordinate system has been rotated from the octahedral main axes so that now z is along the trigonal axis.
[19] K.I. Kugel and D.I. Khomskii, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)].
[20] K. Penc *et al.* (unpublished).
[21] H. Nakamura *et al.*, J. Phys. Chem. Solids **60**, 1137 (1999).