ORIGIN OF THE METAL–INSULATOR TRANSITION IN $BaVS_3$*

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Recent X-ray and neutron diffraction experiments revealed that the metal–insulator transition of $BaVS_3$ at $T_{MI} \simeq 70\,K$ is accompanied by crystallographic superlattice formation along the c axis and nearly uniform reduction of the magnetic moment to approximately half of $S = 1/2$. The origin of the transition is discussed assuming anisotropic conduction bands.

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The metal–insulator transition of a hexagonal perovskite $BaVS_3$ (space group $P6_3/mmc$) at $T_{MI} \simeq 70\,K$ has been known as one of typical phenomena of the quasi-one-dimensional (1D) conductor with $S = 1/2$ spin chains. However recent investigations showed clearly that the conduction of $BaVS_3$ is only weakly anisotropic [1,2] in spite of the much different V intrachain and interchain distances ($\simeq 2.81$ and 6.72 Å, respectively). At high temperature there is metallic conduction in the c plane as well as along the c axis; the conductivity along the c direction is larger by only a factor of 4 than that in the c plane [1], being in good accordance with a theoretical estimation [2]. Furthermore the anisotropy of the conduction does not change markedly at T_{MI} [1]. Thus the issue should be reconstructed as one for a metal with anisotropic (but non-1D) conduction bands with orbital degeneracies; V atoms sense nearly octahedral crystal fields. In this report, we

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summarize recent essential experimental results and discuss a new possible scenario of the metal–insulator transition.

The metal–insulator transition had been believed to be accompanied by no symmetry lowering. However, recent X-ray diffraction measurements of single crystals revealed a superlattice formation at $T_{\mathrm{MI}} \simeq 70\,\mathrm{K}$ [3]. The most probable candidate of the space group below T_{MI} was determined to be monoclinic $Im11$, which is slightly distorted from orthorhombic $Im2m$. At present the atomic coordinates has not been determined successfully. Since the space group $Im2m$ already contains major features of the superlattice, we discuss here physical properties based on $Im2m$. The crystal below T_{MI} contains two inequivalent V sites as shown in Fig. 1. The unit cell is doubled along the c direction, and as a consequence, a 4V period as $-\mathrm{V_A}-\mathrm{V_A}-\mathrm{V_B}-\mathrm{V_B}-$ (see Fig. 1(a)) is formed (the original hexagonal unit cell contains 2 V atoms along the c direction). The body-centered space group (I lattice) implies a 2V period as $-\mathrm{V_A}-\mathrm{V_B}-$ along the [110] direction (in the orthorhombic notation, which corresponds to the a direction in the original hexagonal lattice, see Fig. 1(b)). It is apparent that the site separation of V is not due to the unstable valence such as in $\mathrm{NaV_2O_5}$ because the formal valence of V in $\mathrm{BaVS_3}$ is an integer $+4$. Note that, prior to the superlattice formation at T_{MI}, the hexagonal lattice is deformed to orthorhombic at a higher temperature $T_{\mathrm{S}} \simeq 240\,\mathrm{K}$ [4,5]; degeneracies in the c plane are already lifted as $a > b/\sqrt{3}$.

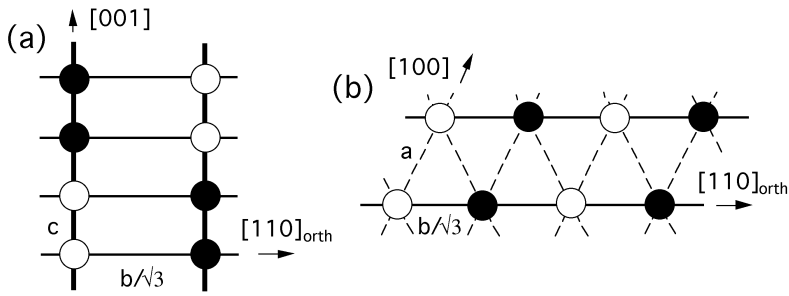

Fig. 1. Schematic representation of V atomic arrangements in $\mathrm{BaVS_3}$ below T_{MI}. Open and closed marks represent different V sites.

On the other hand low-energy powder neutron diffraction experiments showed that long-range magnetic ordering with an averaged moment $\sim 0.5\,\mu_{\mathrm{B}}/\mathrm{V}$ is established at $T_{\mathrm{X}} \simeq 30\,\mathrm{K}$ well below T_{MI} [6]. This is in contrast to earlier neutron diffraction results [7,8] and denies a proposed spin-singlet ground state [9]. The modulation vector was determined to be incommensurate $Q = (0.226\ 0.226\ 0)$ in hexagonal setting; the spin structure is a derivation of the 120° structure in the triangular lattice. Ferromagnetic coupling

along the c axis was confirmed by experiments using a number of needle-like single crystals oriented along the c axis [10]. These results suggest that only half of the high-temperature spin $S = 1/2$ survives below T_{MI}. Although we tried to detect the amplitude modulation of the moment corresponding to the doubling of the crystal lattice, no appreciable reflections have been detected at $(h\ k\ \frac{1}{2})$ within experimental accuracy [10]. Hence complete separation of V atoms to magnetic and nonmagnetic, *i.e.*, partial singlet formation seems to be ruled out. Furthermore the formation of singlet pairs along the c direction seems to be inconsistent with the ferromagnetic coupling along the c direction. Thus the experimental results suggest rather uniform reduction of the V moment to approximately half of the high temperature spin $S = 1/2$. As an interpretation of the superlattice formation, partial charge disproportionation as $2\mathrm{V}^{4+} \rightarrow \mathrm{V}^{4+\delta} + \mathrm{V}^{4-\delta}$ with small δ is the most probable; the corresponding amplitude modulation of the moment cannot probably be detected within the present accuracy of neutron diffraction experiments.

Let us consider here physics of the 1D conductor with a quarter-filled band (0.5 electron on each site). Generally, Peierls-type instability induces $2k_{\mathrm{F}}$-CDW, which gives 4 atomic period in the quarter-filled case. This mechanism may quench spin. In a strongly correlated case, *i.e.*, when the band width W is smaller than the Coulomb repulsion U, we expect a Mott–Hubbard transition. For a 1D quarter-filled band this corresponds to $4k_{\mathrm{F}}$-CDW with 2 atomic period. In this case, the spin degree of freedom remains in the insulating phase. $BaVS_3$ has a characteristic band structure [2], which consists of wide d bands ($W \sim 3$ eV) originating from a d_{z^2} orbital which yields direct overlap along the c axis and narrow (strongly-correlated) d bands ($W \sim 0.7$ eV) made by d_{xy}-type orbitals being responsible for the interaction in the basal plane. The Fermi level locates approximately the center of both of the bands.

If we assume that electrons in each band can be treated independently and that the two-fold degeneracies in the d_{xy}-like bands are lifted being associated with lattice deformation below T_{S}, this system may be regarded as a composite system of above-mentioned quarter-filled 1D metals with different degrees of electron correlations (weak along [001] and strong along [110]). Thus we suggest a new model as the metal–insulator transition of $BaVS_3$ is a cooperative phenomenon of 2 different 1D bands with Peierls-type and Mott–Hubbard-type instabilities; the former and the latter gives 4V period (bond-centered $2k_{\mathrm{F}}$-CDW) along [001] and 2V period along [110], respectively, and only half of spin is quenched at T_{MI} and residual half exhibits magnetic ordering at low temperature.

As mentioned above the long-range magnetic ordering appears only below $T_{\mathrm{X}} \simeq 30$ K. Absence of *static* magnetic ordering above T_{X} was confirmed by μ-SR experiments [11]. It should also be noted that no appre-

ciable entropy change has been detected at T_X [12]. These results indicate that *dynamic* correlations are already established above T_X, probably below $T_{MI} \simeq 70\,K$. The microscopic description of the state between T_{MI} and T_X remains for further studies.

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