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Symmetry breaking in the metal-insulator transition of BaVS₃

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It has been believed for a long time that the metal-to-insulator (MI) transition of BaVS₃ is not accompanied by any spatial order of the spin and lattice. We have carried out x-ray-diffraction measurements of BaVS₃ single crystals using a laboratory x-ray source as well as synchrotron radiation, and found that superlattice reflections which double the lattice constant exist below the transition temperature. The most probable space group at the low-temperature insulator phase contains two inequivalent vanadium sites, and thus a charge disproportionation of the vanadium ions is considered the main cause of the MI transition.

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A metal-to-insulator (MI) transition is one of the interesting subjects in condensed-matter physics, and is observed in many real materials. According to the dimensionality, band filling, bandwidth, and a certain degree of freedom which shows symmetry breaking, there are a wide variety of transitions, some of which are still controversial in the mechanism; for instance, the Verwey transition in magnetite.²,³

The MI transition in BaVS₃ is one such unresolved issue. In spite of intensive investigations over three decades,⁴⁻¹⁷ the character of the transition is not well understood. One of the largest problems is the driving force of the MI transition. No breaking of symmetry, such as magnetic ordering and structural distortion, which accompanies the MI transition has been reported to date.⁸,⁹ Hence the order parameter of the transition has been vague, and it is even suggested that the transition is a realization of the pure Mott transition.¹⁴,¹⁵ Another problem is the nature of the insulator phase below the MI transition at $T_{MI} = 70 \text{ K}$. The magnetic susceptibility shows a Curie-Weiss like behavior above $T_{MI}$, and decreases steeply below $T_{MI}$ with decreasing temperature.⁵,¹¹,¹⁵ This large reduction of the susceptibility is not caused by magnetic ordering. Neutron powder diffraction measurements revealed that no magnetic Bragg reflection appears just below $T_{MI}$.⁹,¹⁶ Instead, Nakamura et al. found that long-range incommensurate magnetic order sets in at $T_X = 30 \text{ K}$, well below $T_{MI}$.¹⁶ The ordered moment was estimated to be $0.5 \mu_B$/V ion. Therefore, the insulator phase between $T_{MI}$ and $T_X$ is a phase which has no magnetic long-range order and suppressed magnetic moments. Nevertheless, the ground state is not a complete singlet and 50% of spins are still magnetic. A model of the MI transition in BaVS₃, therefore, must interpret this complicated magnetic behavior simultaneously. Such a coherent picture of the insulator phase has not been obtained so far.

In this paper, we have performed single-crystal x-ray-diffraction measurements in order to find the hidden order parameter of the MI transition in BaVS₃. Rather surprisingly, it was a structural phase transition, which has long been believed to be absent. We found superlattice reflections which double the unit cell along the c axis, and confirmed that the intensity of the reflections disappears at $T_{MI}$. We also carried out a preliminary check of the space group using synchrotron radiation. Based on the obtained results, the origin of the MI transition is discussed.

BaVS₃ crystallizes into a hexagonal structure (space group $P6_3/mmc$, $a = 6.719 \text{ Å}$, and $c = 5.619 \text{ Å}$) at room temperature, which is characterized by VS₃ chains running along the c axis [Fig. 1(a)]. A structural phase transition takes place at $T_S = 240 \text{ K}$, and the crystal system becomes orthorhombic. Since the transition is of second-order type, the space group below $T_S$ is considered $Cmcm$ or its subgroups.⁹,¹³ We use the space group $Cmcm$ in this paper, because the suggested space group $Cmc2_1$ is incompatible with our observation. As already mentioned, BaVS₃ undergoes a MI transition at $T_{MI} = 70 \text{ K}$ from the high-temperature metallic phase to the low-temperature insulator phase, which is followed by a magnetic phase transition with a propagation vector $Q = (0.226, 0.226, 0)$ in a hexagonal setting at $T_X = 30 \text{ K}$ [Fig. 1(b)].

FIG. 1. (a) Crystal structure of BaVS₃ at the orthorhombic phase ($Cmcm$). Large and small shaded spheres show barium and vanadium ions, respectively. The sulfur ions reside at the vertices of the octahedra. (b) Structural, transport, and magnetic properties of BaVS₃ as a function of temperature. AF is the antiferromagnetically ordered phase.
T is single-domain below the structural transition at \( T_{MI} \). Due to the large sample size, the sample was a multidomain below \( T_{MI} \). Superlattice reflections are observed on \( l = n + \frac{1}{2} \) lines. Three superlattice points are shown by arrows.

Single crystals in needlelike shapes were synthesized by a tellurium flux method, and then were annealed in the presence of sulfur vapor in order to compensate for deficient sulfur. The x-ray-diffraction measurements were carried out using a two-axis diffractometer at IMRAM, Tohoku University. Mo \( K\alpha \) radiations from a rotating anode (50 kV, 60 mA) were monochromatized by a pyrolytic graphite 002 crystal. The scattered x rays were detected by an image plate as well as a sodium-iodine scintillation detector. A single crystal, the dimensions of which are about \( 0.2 \times 3 \) mm\(^2\), was mounted on the cold finger of a closed-cycle He refrigerator. Due to the large sample size, the sample was a multidomain below the structural transition at \( T_S \). The sample mosaic spread also became broad from 0.13° (300 K) to 1.5° (25 K).

We also performed synchrotron x-ray-diffraction measurements at beamline BL02B1 of SPring-8. Synchrotron radiations were monochromatized by a Si 311 double-crystal monochromator, and higher harmonics were eliminated by the use of mirrors. The x-ray energy was 30 keV. A small single crystal was mounted on the cold finger of a closed-cycle He refrigerator on a four-circle diffractometer. Because of the small sample size (100×100×150 \( \mu \)m\(^3\)), the sample was single-domain below \( T_S \). The sample mosaic was about 0.16° at low temperatures. In addition, the transmission of x-rays at 30 keV through BaVS\(_3\) of 100 \( \mu \)m thick is about 75%, and hence the absorption correction to the diffracted intensity is not very significant for this small crystal.

We first took oscillation photographs at 100 K (above \( T_{MI} \)) and at 25 K (below \( T_{MI} \)) using an image plate. The \( c \) axis of the sample was vertical to the scattering plane, and the sample was rotated about the \( c \) axis by 30°. The results are shown in Fig. 2. The vertical direction of the photograph corresponds to the crystalline \( c^* \) axis, while the horizontal direction is the superposition of the \( a^*, b^* \) plane. Thus Bragg reflections \( hkl \) appear as horizontal lines with different values of \( l \) in the photographs. Above \( T_{MI} \), no significant intensity is observed other than the fundamental Bragg lines. In contrast, well below \( T_{MI} \), weak superlattice reflections are clearly observed just midway between the Bragg lines, indicating a structural phase transition which doubles the \( c \) axis exists below \( T_{MI} \). We then measured Weissenberg photographs of the \( (h,k,0) \), \( (h,k,\frac{1}{2}) \), and \( (h,k,1) \) planes at 25 K. In the \( (h,k,0) \) and \( (h,k,1) \) planes, only fundamental reflections were observed at \( h+k = 2n \). No additional peak was found. On the other hand, in the \( (h,k,\frac{1}{2}) \) plane, superlattice reflections were observed at \( h+k = 2n + 1 \). Accordingly, the reflection condition is \( h+k+2l = 2n \) for \( hkl \), and thus it was found that the superlattice is an \( I \) lattice (body-centered lattice). In the \( (h,k,\frac{1}{2}) \) plane, superlattice reflections are intense around the \( b^* \) axis, while no peak is found around the \( a^* \) axis.

In order to show that the observed structural distortion is associated with the MI transition, the intensity of a superlattice reflection was measured as a function of temperature using a scintillation detector. As shown in Fig. 3, the integrated intensity at (0, 11, \( \frac{1}{2} \)) decreases smoothly with increasing temperature, and vanishes just at the transition temperature \( T_{MI} \) (70 K).

![FIG. 3. Integrated intensity of the superlattice reflection 0 11 ½ as a function of temperature. The intensity decreases with increasing temperature, and vanishes just at the transition temperature TMI (70 K).](image-url)
Laue symmetry, possible space groups are $I_{\text{m}2m}$, $P_{\text{i}2_{1}2_{1}}$, $P_{\text{i}2_{1}1}$, and $I_{\text{m}}$. The intensity mainly arises from the displacement of the heavy Ba ions parallel to the $a$ axis. In the space group $I_{\text{m}2m}$, the Ba ions are at $2a (0,y,0)$, $2b (0,0,y,\frac{1}{2})$, and $4c (0,y,z$ and $0,y,z)$ sites, and actually there is no displacement from highly symmetric positions along the $a$ axis. Accordingly, the best candidate for the space group below $T_{M1}$ is $I_{\text{m}11}$. We also think that the space group $I_{\text{m}2m}$ (the supergroup of $I_{\text{m}11}$) already contains major features of the transition, because superlattice reflections appear at this space group. In the following discussion about the order parameter of the MI transition, we postulate that the space group below $T_{M1}$ is $I_{\text{m}2m}$.

A notable difference between the space groups $C_{\text{mc}}m$ and $I_{\text{m}2m}$ is the number of vanadium sites. All vanadium ions occupy the equivalent $4a$ site in $C_{\text{mc}}m$, whereas in $I_{\text{m}2m}$ the vanadium ions are divided into two crystallographically independent $4c$ sites (we refer to them as $V_{A}$ and $V_{B}$) and pairs of the same kind of the vanadium ions align along the $c$ axis in an alternative manner $-V_{A}-V_{A}^*-V_{B}^*-V_{B}$. It is therefore likely that a charge disproportionation (CD) of the vanadium ions is the major driving force of the MI transition in BaVS$_3$. The CD is probably partial, i.e., $2V^{4+}\rightarrow V^{4+}+\delta V^{4+}-\delta V^{4-}$. If $\delta \approx 1$, a large modulation of the spin density along the $c$ axis is expected, because $V^{3+}$ ions have no magnetic moment. However, such a modulation was not observed in neutron-diffraction experiments.\textsuperscript{16}

One might regard this charge (and structural) modulation along the $c$ axis as being caused by a Peierls-type transition due to the chain-like structure of BaVS$_3$. However, the electronic conductivity of BaVS$_3$ is not highly anisotropic and rather three dimensional.\textsuperscript{15} A band structure calculated by Mattheiss also exhibits only weak anisotropic features.\textsuperscript{22} The MI transition in BaVS$_3$ may not stem from a Peierls-type instability.

The huge reduction of the susceptibility at $T_{M1}$ is still an open question. In the space group $I_{\text{m}2m}$, the vanadium ions make pairs along the $c$ axis. The atomic coordinates of the vanadium ions are $(0,y,z)$ and $(0,y,\bar{z})$, and thus the vanadium ions are no longer equidistant along the vanadium chain (the $c$ axis). We consider $V_{A}-V_{A}$ and $V_{B}-V_{B}$ pairings here. Supposing that the coupling between $V_{A}$ spins is antiferromagnetic, the suppression of the magnetic susceptibility at the MI transition can be ascribed to the formation of singlet pairs. On the other hand, the coupling between the $V_{B}$ spins must be ferromagnetic (otherwise the ground state becomes a singlet) and the surviving $V_{B}$ spins cause a magnetic long-range order at 30 K. However, this scenario also results in a large modulation of the spin density along the $c$ axis and fails to explain the neutron-diffraction results.\textsuperscript{16} Finally, we mention the structure between the chains. In the $z=0$ and $\frac{1}{2}$ planes, the $V_{A}$ and $V_{B}$ ions cause stripes, which show an alternate alignment along the $b$ axis, and an expected positional modulation of the Ba ions caused by this stripe order is consistent with the observed intense superlattice reflections around the $b^*\parallel a$ axis.

In summary, an x-ray-diffraction study of single-crystal BaVS$_3$ has been made, and a structural phase transition

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
(i) & $C_{\text{mc}}m \rightarrow C_{2}2_{1}m1 \rightarrow 12c_{1}1 \rightarrow I_{211}$ & \\
\hline
(ii) & $C_{\text{mc}}m \rightarrow C_{2}m_{2}m \rightarrow I_{\text{m}2m} \rightarrow I_{\text{m}11}$ & \\
\hline
\end{tabular}
\caption{Group-subgroup chains for subgroups of $C_{\text{mc}}m$ which satisfy the reflection condition and the Laue symmetry.}
\end{table}
which accompanies the MI transition was found. The symmetry consideration suggests that a pronounced feature of the insulator phase is two inequivalent vanadium sites, and from this result we propose a charge disproportionation of the vanadium ions as a possible origin of the MI transition. Although the magnetic properties of the low-temperature insulator phase are not fully accounted for as yet, a solid basis for further experimental and theoretical investigations on this MI transition is established.

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