Symmetry breaking in the metal-insulator transition of BaVS$_3$

T. Inami,$^1$ K. Ohwada,$^1$ H. Kimura,$^2$ M. Watanabe,$^2$ Y. Noda,$^2$ H. Nakamura,$^3$ T. Yamasaki,$^{3,4}$ M. Shiga,$^3$
N. Ikeda,$^4$ and Y. Murakami$^{1,5}$

$^1$Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, Mikazuki, Hyogo 679-5148, Japan
$^2$Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan
$^3$Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan
$^4$Japan Synchrotron Radiation Research Institute, Mikazuki, Hyogo 679-5148, Japan
$^5$Department of Physics, Tohoku University, Sendai 980-8578, Japan

(Received 4 March 2002; published 20 August 2002)

It has been believed for a long time that the metal-to-insulator (MI) transition of BaVS$_3$ is not accompanied by any spatial order of the spin and lattice. We have carried out x-ray-diffraction measurements of BaVS$_3$ 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.

DOI: 10.1103/PhysRevB.66.073108 PACS number(s): 71.30.+h, 61.10.-i, 71.27.+a

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 BaVS$_3$ 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 $T_{\text{MI}} = 70$ K. The magnetic susceptibility shows a Curie-Weiss like behavior above $T_{\text{MI}}$, and decreases steeply below $T_{\text{MI}}$ with decreasing temperature.$^{5,11,15}$ This large reduction of the susceptibility is not caused by magnetic ordering. Neutron powder diffusion measurements revealed that no magnetic Bragg reflection appears just below $T_{\text{MI}}$.$^{9,16}$ Instead, Nakamura et al. found that long-range incommensurate magnetic order sets in at $T_X = 30$ K, well below $T_{\text{MI}}$.$^{16}$ The ordered moment was estimated to be $0.5 \mu_B / V$ ion. Therefore, the insulator phase between $T_{\text{MI}}$ 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 BaVS$_3$, 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 BaVS$_3$. 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 $T_{\text{MI}}$. 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.

BaVS$_3$ crystallizes into a hexagonal structure (space group $P6_3/mmc$, $a = 6.719$ Å, and $c = 5.619$ Å) at room temperature, which is characterized by VS$_3$ chains running along the $c$ axis [Fig. 1(a)]. A structural phase transition takes place at $T_S = 240$ 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.$^{8}$ We use the space group $Cmcm$ in this paper, because the suggested space group $Cmc2_1$ is incompatible with our observation. As already mentioned, BaVS$_3$ undergoes a MI transition at $T_{\text{MI}} = 70$ 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 $T_X = 30$ K [Fig. 1(b)].

![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.](image)

FIG. 1. (a) Crystal structure of BaVS$_3$ 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 BaVS$_3$ as a function of temperature. AF is the antiferromagnetically ordered phase.
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 Kα 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 $d_00.2\times3 \text{ mm}^2$, was mounted on the cold finger of a closed-cycle He refrigerator. Due to the large sample size, 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 radiation experiments were carried out for an estimate of the space group below $T_{\text{MI}}$. We first confirmed the reflection condition. We measured reflections on the $(0,0,1), (0,k,\frac{1}{2}), (h,0,\frac{1}{2})$ and $(h,0,1)$ lines at 30 K, and a weak but finite intensity of superlattice reflections at $(h,0,\frac{1}{2})$ was observed. The total reflection conditions were as follows; for the superlattice $(c'=2c)$, $hkl$: $h+k+l=2n$, $hk0$: $h+k=2n$, $h0l$: $h+l=2n$, $0kl$: $k+l=2n$, $h00$: $h=2n$, $0k0$: $k=2n$, and $00l$: $l=2n$. This shows that the superlattice is an $I$ lattice without any glide plane.

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 $T_{\text{MI}}$ (~70 K).

![FIG. 2. Oscillation photographs of BaVS$_3$. (a) At 100 K (above $T_{\text{MI}}$). The white points are fundamental Bragg reflections $hkl$, and are classified by $l$ from bottom ($l= -2$) to top ($l=2$). (b) At 25 K (below $T_{\text{MI}}$). Superlattice reflections are observed on $l=n+\frac{1}{2}$ lines. Three superlattice points are shown by arrows.](...)
FIG. 4. Rocking curves of four symmetric superlattice reflections in the \(b^* c^*\) plane. The asymmetry of superlattice reflections in intensity suggests that the mirror planes perpendicular to the \(b\) and \(c\) axes and the twofold axes parallel to the \(b\) and \(c\) axes are missing.

We then confirmed the Laue symmetry of the lattice. Four superlattice reflections at \((0, \pm 7, \pm 0.5)\) are shown in Fig. 4. Obviously the \(I(\bar{Q})\)s (the diffracted intensity at a momentum transfer \(\bar{Q}\)) are not all identical, although the momentum transfers are symmetric. Since the condition that \(I(\bar{Q})=I(-\bar{Q})\) (the so-called Friedel pair) is fulfilled, that is \(I(0,7,0.5)=I(0,7,0.5)\) and \(I(0,7,0.5)=I(0,7,0.5)\), the effect of absorption is considered rather small in these data. Inequality in the diffracted intensities therefore indicates the lack of mirror planes perpendicular to the \(b\) and \(c\) axes and the twofold axes parallel to the \(b\) and \(c\) axes. We could not obtain convincing data for superlattice reflections including the \(a^*\) axis, because of the weak intensity. Although the observed lattice constant \(a\) was nearly 90°, the data shown in Fig. 4 imply that the crystal structure below \(T_{MI}\) is a monoclinic lattice of the unique \(a\) axis.

Combining the results for the reflection conditions and the Laue symmetry, possible space groups are \(I211\), \(Im\)11, and \(I2/mI\). Since it seems that the MI transition is of second order, the space group below \(T_{MI}\) is a subgroup of the space group above \(T_{MI}\) (\(Cmcm\)). Under this restriction, relations between \(Cmcm\) and the possible low-temperature space groups are summarized in Table 1.\(^{21}\)

It is likely that the overall pattern of superlattice reflections in a monoclinic lattice should be reminiscent of that in its supergroup. In this sense, the space group \(I211\) is not plausible. The space group \(I2/c11\) (the supergroup of \(I211\)) has a reflection condition \(k,l=2n\) for \(0kl\), and hence there is no superlattice reflection at \((0,k,\frac{1}{2})\). However, the observed pattern of superlattice reflections in the \((h,k,\frac{1}{2})\) plane is weak around the \(a^*\) axis and strong around the \(b^*\) axis. On the other hand, the reflection conditions of \(Im\)2\(m\) are the same as the observed ones. In addition, the relatively strong intensity of the superlattice reflections suggests that the intensity mainly arises from the displacement of the heavy Ba ions. The observed weak intensity of superlattice reflections around the \(a^*\) axis indicates that the displacement of the Ba ions parallel to the \(a\) axis is small. In the space group \(Im\)2\(m\), the Ba ions are at \(2a\) \((0,0,0)\), \(2b\) \((0,0,\frac{1}{2})\), and \(4c\) \((0,y,0)\) sites, and actually there is no displacement from highly symmetric positions along the \(a\) axis. Accordingly, the best candidate for the space group below \(T_{MI}\) is \(Im\)11. We also think that the space group \(Im\)2\(m\) (the supergroup of \(Im\)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 \(T_{MI}\) is \(Im\)2\(m\).

A notable difference between the space groups \(Cmcm\) and \(Im\)2\(m\) is the number of vanadium sites. All vanadium ions occupy the equivalent \(4a\) site in \(Cmcm\), whereas in \(Im\)2\(m\) 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 \(-V_A^{-}V_A^{-}V_B^{-}V_B^{-}-V_A^{-}V_A^{-}V_B^{-}V_B^{-}\). 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., \(2V^{4+}\rightarrow V^{4+}+V^{4-}+\delta=0\). If \(\delta=1\), 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.\(^{16}\)

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.\(^{15}\) A band structure calculated by Mattheiss also exhibits only weak anisotropic features.\(^{22}\) The MI transition in BaVS\(_3\) may not stem from a Peierls-type instability.

The huge reduction of the susceptibility at \(T_{MI}\) is still an open question. In the space group \(Im\)2\(m\), the vanadium ions make pairs along the \(c\) axis. The atomic coordinates of the vanadium ions are \((0,0,\frac{1}{2})\) and \((0,0,\frac{1}{2})\), and thus the vanadium ions are no longer equidistant along the vanadium chain (the \(c\) axis). We consider \(V_A^{-}V_A^{-}V_B^{-}V_B^{-}\) 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.\(^{16}\) 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 \(b^*\) axis.

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

<table>
<thead>
<tr>
<th>Table 1: Group-subgroup chains for subgroups of (Cmcm) which satisfy the reflection condition and the Laue symmetry.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
</tr>
<tr>
<td>(ii)</td>
</tr>
</tbody>
</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.

This work was partially supported by Grants-in-Aid for Scientific Research of the Japan Society for the Promotion of Science (11440107, 12640345) and a Grant-in-Aid on priority area “Novel Quantum Phenomena in Transition Metal Oxides” from the Ministry of Education, Science, Sports and Culture (12046243). The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2001A0046ND-np).

*Present address: Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan