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# Opening of a charge gap with V trimerization in $BaV_{10}O_{15}$

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A structural phase transition at $T_c \sim 130$ K in $BaV_{10}O_{15}$ containing modified $V^{3+}$ ($3d^2$) triangular lattices was studied. It was found that the electrical resistivity jumps by three orders of magnitude and a gap opens up in the optical conductivity spectrum at $T_c$. It was also found from synchrotron x-ray powder-diffraction measurement that the trimerization of the V ions occurs below $T_c$. These results indicate that the orbital ordering of V $t_{2g}$ states occurs at $T_c$ and that induces a charge gap near the Fermi level in the electronic states of $BaV_{10}O_{15}$.

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Transition-metal oxides exhibit a variety of phase transitions and ground states. For example, $V_2O_3$ with $V^{3+}$ ($3d^2$) ions exhibits a Mott transition at 200 K, i.e., a phase transition from a high-temperature metallic phase to a low-temperature insulating phase (a Mott insulator) where the charge gap is caused by electron-electron interaction.[1] Another example of phase transitions and intriguing ground states in transition-metal oxides is orbital ordering. For example, $LiVO_2$ having $V^{3+}$ ions on the triangular lattice exhibits a structural phase transition with V trimerization at 500 K, and the low-temperature phase is an orbital-ordered phase in the spin-singlet state, in which the $t_{2g}$ electrons of the V ions form a bond at each side of the V trimer.[2,3]

These phase transitions in transition-metal oxides often induces large changes of electronic structures and their anisotropy. For $V_2O_3$, a drastic change of optical conductivity from a Drude-like spectrum, which is typical of a metallic state, to a spectrum with a ~0.5 eV gap, which is dominated by on-site Coulomb repulsion energy, occurs with the Mott transition.[4] Evolution of anisotropy in an electronic structure is observed in orbital-ordering transitions, which are caused by the anisotropy of the electron transfer between spatially anisotropic *d* orbitals. For example, in $LaVO_3$ with $V^{3+}$ ions, there is an orbital ordering of the $t_{2g}$ states at 141 K, and the anisotropy of the optical conductivity spectra evolves in this orbital-ordered phase, though its crystal structure is a quasicubic one.[5] A similar evolution of the anisotropy of the optical spectrum with orbital ordering is seen in $La_4Ru_2O_{10}$ with $Ru^{4+}$ ($4d^4$).[6]

Though there have been several studies to investigate the change of the electronic structures associated with the phase transitions in transition-metal oxides, the role of the spatial anisotropy in the *d* orbital and the electron-electron interaction in those phase transitions and the details of the ground states are still unclear. In the present Rapid Communication, we report a change of the electronic structure with a structural phase transition in $BaV_{10}O_{15}$.[7–10] In this compound, the average valence of V is 2.8+; nominally four out of five V ions are 3+ ($3d^2$) and the remaining one is 2+ ($3d^3$). The V ions form a lattice where V "boats," each of which is made of five V ions, are connected to each other along the *ab* plane, as shown in Fig. 1(a). This V lattice can be regarded as the V triangular lattice from which V triangles [shown by the dotted circles in Fig. 1(a)] are periodically missing. Each V ion is surrounded by six oxygen ions that are octahedrally coordinated, and $VO_6$ octahedra are edge sharing with each other for $z=0$ and $z=1/4$ (where the directions of the V "boats" are opposite), and also between $z=0$ and $z=1/4$. Thus, there is a large interaction between the V ions on $z=0$ and on $z=1/4$. On the other hand, the position of the V boats on $z=-1/4$ is shifted by $x=1/2$ from that on $z=0$, as shown by the dashed line in Fig. 1(a), and there is only a small overlap between the $z=-1/4$ and $z=0$ layers. Therefore, this $BaV_{10}O_{15}$ can be regarded as a bilayer structure of modified V triangular lattices. According to the previous studies, $BaV_{10}O_{15}$ exhibits a structural phase transition at around 130 K, where there is an anomaly of electrical conductivity.[7,8] On the basis of the structural analysis of a single crystal, it was proposed that a bond formation between two V ions, i.e., V dimerization, is the driving force of the structural transition.[8] However, no detailed study of the physical properties of this compound using single crystals has been made so far.

To investigate the origin of the structural phase transition and its impact on the electronic structure, single crystals of $BaV_{10}O_{15}$, and $SrV_{10}O_{15}$ as a comparison, which does not exhibit a structural phase transition down to the lowest temperature, were grown by the floating-zone technique. Electrical resistivity of the single crystal was measured by a conventional four-probe technique. Magnetization was measured by a superconducting quantum interference device magnetometer. Synchrotron x-ray powder-diffraction measurement was performed for ground single crystals with an incident wavelength of 0.7778 Å at SPring-8 BL02B2.[11] Rietveld analysis of the diffraction data was made with Rietan-2000.[12] Optical reflectivity measurement was performed with a FTIR spectrometer between 0.07 and 0.8 eV and a grating spectrometer between 0.7 eV and 5 eV for the temperature range between 300 and 5 K using a He-gas-flow cryostat.

Figure 2(a) shows the temperature ($T$) dependence of electrical resistivity $\rho(T)$ for $BaV_{10}O_{15}$ along the *a*, *b*, and *c* axes and for $SrV_{10}O_{15}$. The resistivity of $BaV_{10}O_{15}$ sharply

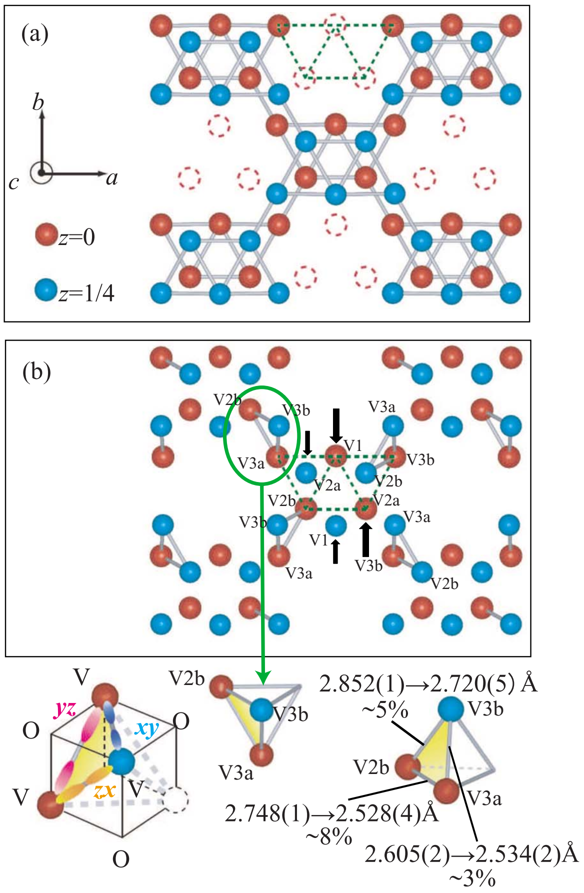

FIG. 1. (Color online) (a) The arrangement of the V ions (circles) in $BaV_{10}O_{15}$ for $z=0$ and $z=1/4$. The dashed circles represent the V triangles missing from the triangular lattice to form the $z=0$ layer. The dashed lines represent the position of the V boat on $z=-1/4$. (b) Bars connecting the circles (V ions) represent the V-V bonds exhibiting a contraction ("trimerization") associated with the structural phase transition. The arrows show the untrimerized V ions. The lower panel shows a contracted V triangle ("trimer") with changes of the bond lengths (300→90 K, right) and the bonds made of the *xy*, *yz*, or *zx* orbitals at each side of the triangle (left). The figures of the crystal structure were drawn by VESTA (Ref. 18).

increases by $\sim 10^3$ times at the structural phase transition ($T_c=123$ K). This change of resistivity is much sharper in the present single crystal than in the polycrystalline samples previously reported,[8] and indicates a large impact of the structural phase transition on the electronic structure.[13] The behavior of $\rho(T)$ below $T_c$ can be regarded as an activation type with the activation energy $\Delta$ is from 0.05 to 0.1 eV depending on the $T$ range, indicating the electronic state with a finite charge gap. On the other hand, the behavior of $\rho(T)$ above $T_c$ is not that of a simple insulating state nor a simple metallic state, as discussed below and in the supplementary material.[14]

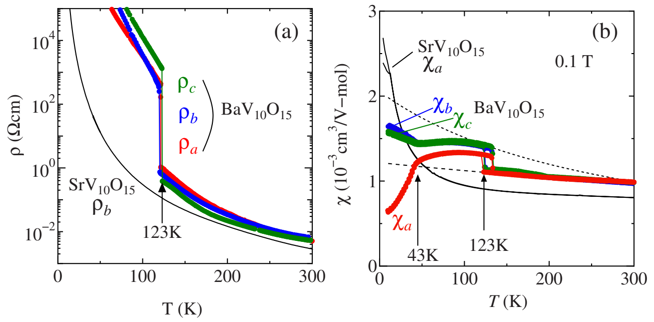

FIG. 2. (Color online) (a) Temperature dependence of resistivity for $BaV_{10}O_{15}$ ($\rho_a$, $\rho_b$, and $\rho_c$) and $SrV_{10}O_{15}$ ($\rho_b$) measured on a cooling run. (b) Temperature dependence of magnetic susceptibility for $BaV_{10}O_{15}$ ($\chi_a$, $\chi_b$, and $\chi_c$) and $SrV_{10}O_{15}$ ($\chi_a$) at 0.1 T. The dashed line corresponds to the fitting by a Curie-Weiss behavior above the transition temperature, and the dotted line to that immediately below the transition temperature (see text).

The $T$ dependence of magnetic susceptibility for $BaV_{10}O_{15}$ also exhibits several anomalies, as shown in Fig. 2(b). First, the magnetic susceptibility exhibits a discontinuous jump by ~20% at the structural phase transition at 123 K. Second, the magnetic susceptibility along the *a* axis, $\chi_a$, decreases whereas $\chi_b$ and $\chi_c$ increase below 43 K. These anomalies indicate an antiferromagnetic ordering with the easy axis along the *a* direction below $T_N=43$ K. Note that the existence of antiferromagnetic ordering itself was confirmed by specific heat and neutron-scattering measurement in previous studies.[10] The $T$ dependence of magnetic susceptibility above $T_c=123$ K can be interpreted in two different ways: one is to attribute it to a Curie-Weiss behavior, $\chi(T) = C/(T-\theta)$. A Curie constant $C=1.46$ K cm$^3$/V-mol and a Weiss temperature $\theta=-1.20\times 10^3$ K were obtained by the fitting, which are almost the same as those in the previous study.[8] The Curie constant $C$ is consistent with the spin state in which all the *d* electrons on the V ions are localized in the high-spin configuration, namely, four out of five are $S=1$ ($3d^2$) and the remaining one is $S=3/2$ ($3d^3$), resulting in $C=1.175$ K cm$^3$/V-mol. Another possibility is a Pauli paramagnetic behavior; we found that the absolute value of $\chi \sim 1\times 10^{-3}$ cm$^3$/V-mol is comparable to that of $V_2O_3$ in the metallic state,[1] where Pauli paramagnetism is enhanced because of the electron correlation effect. The density of states at the Fermi energy by the LDA band calculations on this compound[9,15] gives $\chi \sim 1.3\times 10^{-4}$ cm$^4$/V-mol, and thus, the effective mass is 8 times enhanced by electron correlation on this model.

On the other hand, $SrV_{10}O_{15}$ does not show any anomaly in the resistivity nor magnetic susceptibility, as shown in Figs. 2(a) and 2(b). We found that $\rho(T)$ of $SrV_{10}O_{15}$ obeys a variable-range-hopping $T$ dependence, $\rho(T) = \rho_0 \exp[(E/k_BT)^\alpha]$ with $\alpha \sim 1/3$ over eight digits. The magnetic susceptibility of $SrV_{10}O_{15}$ shows only a small $T$ dependence at high temperatures (>150 K), similarly to $BaV_{10}O_{15}$, but is enhanced at low $T$. By a Curie-Weiss fitting above 150 K, $C=1.61$ K cm$^3$/V-mol, which is comparable to the value of $BaV_{10}O_{15}$, and $\theta=-1.70\times 10^3$ K, which is 1.5 times larger in its absolute value than that of $BaV_{10}O_{15}$, were obtained.

We measured synchrotron x-ray powder diffraction of the ground single crystal and made a Rietveld analysis of the diffraction data.[14] The obtained result is consistent with the previous result of the x-ray diffraction on a single crystal.[8] Here, we focus on the bond length between nearest-neighbor

V ions. We found that three of them exhibit large contractions (by 3%∼8%) with the structural phase transition, whereas others show only small contractions or even elongations. In Fig. 1(b), we plot these three bonds exhibiting large contractions. As illustrated in the lower panel of Fig. 1, the three bonds form a quasi regular triangle. Note that the contraction between V2a and V3a was attributed to the "dimerization" in the previous study.[8] This result indicates that V trimerization (not dimerization) occurs at the structural phase transition in $BaV_{10}O_{15}$, similarly in $LiVO_2$.[3] Thus, a possible scenario for the structural phase transition of $BaV_{10}O_{15}$ is that an orbital ordering of the $t_{2g}$ states occurs, where two $xy$, $yz$, or $zx$ orbitals form a bonding state at each side of the $V^{3+}$ ($3d^2$) triangle, and each bonding state is occupied by two electrons (supplied by three $V^{3+}$ ($3d^2$) ions) and thus is in a spin-singlet state, as shown in the lower-left panel of Fig. 1. Unlike the orbital ordering in $LiVO_2$, where all the V trimers are parallel to each other, the trimers in $BaV_{10}O_{15}$ have four different directions. Furthermore, in $LiVO_2$, all the V ions belong to one of the trimers, whereas two out of five V ions remain untrimerized in $BaV_{10}O_{15}$, as shown by arrows in Fig. 1(b). This untrimerized V ions have magnetic moments and those order antiferromagnetically below $T_N=43$ K.

The increase in magnetic susceptibility at $T_c$ is seemingly inconsistent with the formation of the spin-singlet trimers. One possibility is that a smaller magnetic interaction between the untrimerized V spins (and a smaller absolute value of the Weiss temperature in its consequence) results in the enhancement of the magnetic susceptibility, even though the number of spins is decreased by the trimerization. A Curie-Weiss behavior with $C=0.575$ K $cm^3$/V-mol, which corresponds to the magnetic moment of two untrimerized V ions [$V^{2+}$ ($S=3/2$) and $V^{3+}$ ($S=1$)] among the five, and $\theta=-280$ K can reproduce the magnetic susceptibility immediately below $T_c$, as shown in Fig. 2(b). However, $\chi(T)$ over the whole $T$ range of $T_N<T<T_c$ cannot be fitted by a Curie-Weiss relation. This indicates that the magnetic interaction effectively varies below $T_c$, and $\theta$ varies from $-280$ K (immediately below $T_c$) to $-350$ K (immediately above $T_N$) associated with the evolution of the order parameter of orbital ordering.

To investigate the variation of the electronic structure with temperature, we measured the optical reflectivity spectra of $BaV_{10}O_{15}$ and obtained the optical conductivity spectra $\sigma(\omega)$ by the Kramers-Kronig transformation, as shown in Figs. 3(a)–3(c). At 300 K, there is a finite value of conductivity at around $\hbar\omega=0$ eV, and there is a broad peak centered at around $\hbar\omega=0.5$ eV for all three directions of polarization (=electric field $\boldsymbol{E}$). This low-energy spectrum is neither that of a simple metallic state (the so-called Drude spectrum), where $\sigma(\omega)$ monotonically decreases with increasing $\hbar\omega$, nor that of an insulating state, where $\sigma(\omega)$ is zero up to a certain value of $\hbar\omega$. A similar spectrum has been observed in $\sigma(\omega)$ of transition-metal oxides showing a charge-ordering transition at low temperatures.[16] With decreasing temperature, $\sigma(\omega)$ below 0.5 eV is suppressed, and at 130 K immediately above $T_c$, the extrapolation of $\sigma(\omega)$ almost crosses the origin, indicating a "zero-gap" insulating state. It should be noted that the increase of dc resistivity with decreasing $T$ above $T_c$ shown in Fig. 2(a) is dominated by this rapid suppression of $\sigma(\omega)$ below 0.5 eV.[14]

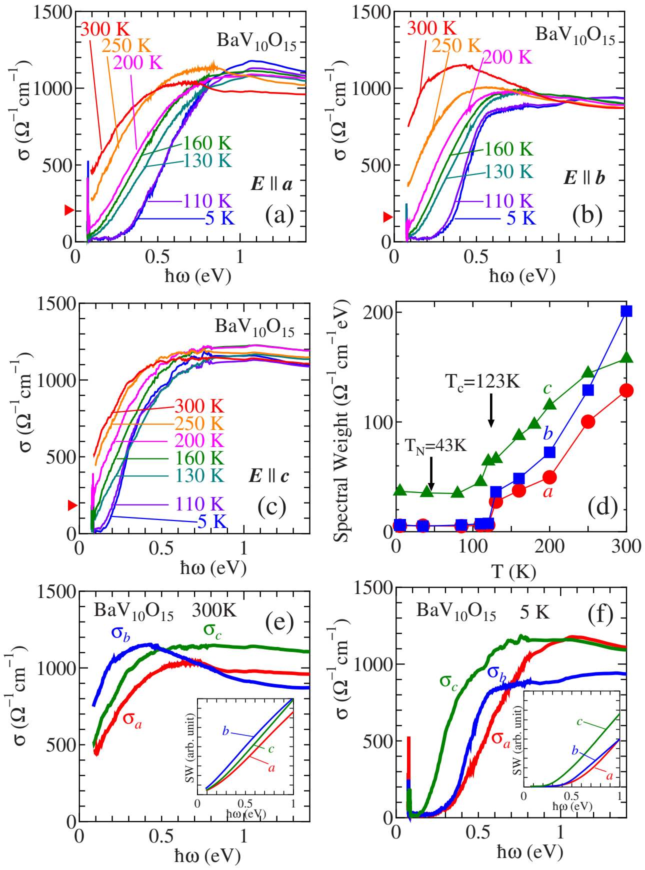

FIG. 3. (Color online) (a)–(c) Optical conductivity of $BaV_{10}O_{15}$ for (a) $\boldsymbol{E}\|\boldsymbol{a}$, (b) $\boldsymbol{E}\|\boldsymbol{b}$, and (c) $\boldsymbol{E}\|\boldsymbol{c}$. Solid triangles on the $y$ axis indicate the values of dc conductivity at 300 K. (d) Temperature dependence in the spectral weight of $\sigma_a$, $\sigma_b$, and $\sigma_c$ between 0.1 and 0.3 eV. (e) and (f) Optical conductivity for three different polarization ($\boldsymbol{E}$) directions at (e) 300 and (f) 5 K. Each inset shows the integration of $\sigma(\omega)$ for three $\boldsymbol{E}$ directions at each temperature.

When $T$ crosses $T_c$, the spectrum suddenly shifts to higher energies and a finite-size gap, which is estimated as ∼0.3 eV for $\sigma_b(\omega)$, opens below $T_c$. With further decreasing temperature, $\sigma(\omega)$ barely changes even across $T_N$. To see this $T$ dependence more clearly, $\sigma(\omega)$ between 0.1 and 0.3 eV is integrated and the obtained spectral weight is plotted as a function of $T$ in Fig. 3(d). A gradual decrease of the spectral weight and a discontinuous jump at $T_c$ are clearly seen. These results indicate that a charge gap opens near the Fermi level in $BaV_{10}O_{15}$ at $T_c$ caused by the orbital ordering of the V $t_{2g}$ states. One possible scenario for the gradual decrease of the spectral weight above $T_c$, i.e., the suppression of $\sigma(\omega)$ below 0.5 eV, is the fluctuation of this orbital ordering.

To see the anisotropy of the optical conductivity more clearly, the optical conductivity spectra along the $a$, $b$, and $c$ axis at the same temperature (300 and 5 K) are plotted in the same panel [Figs. 3(e) and 3(f)], together with the integration of them in the inset. At 300 K in the high-$T$ phase, $\sigma_b$ has the largest spectral weight below 0.5 eV, then $\sigma_c$, and $\sigma_a$ has the smallest. On the other hand, at 5 K in the low-$T$ phase, $\sigma_c$ has the largest spectral weight below 0.5 eV, then $\sigma_b$, and $\sigma_a$. This change of anisotropy with temperature indicates that the structural phase transition causes an anisotropic electronic structure.

Here, let us discuss the electronic structure below $T_c$ based on the V trimerization model. In this model, there are a bonding state and an antibonding state of the *xy*, *yz*, or *zx* orbitals at each side of the triangle. In this case, the lowest (and the only) excitation is that from the bonding state to the antibonding state, and only the electric field parallel to the V-V bond contributes to this excitation. Thus, for one V trimer, the spectral weight (SW) with the electric field of the light $\boldsymbol{E}$ can be given as

$$\mathrm{SW} \propto \sum_{i=1}^{3} |\boldsymbol{E}\cdot\boldsymbol{l}_i|^2, \quad (1)$$

where $\boldsymbol{l}_i$ $(i=1,2,3)$ is the unit vector along three V-V bonds on a trimer. It should be noted that, even though there are V trimers with four different directions in $\mathrm{BaV_{10}O_{15}}$, if $\boldsymbol{E}$ is along the $a$, $b$, or $c$ direction, the SW given by Eq. (1) becomes the same for all the V trimers. Accordingly, the ratio of the SW of $\sigma_a$, $\sigma_b$, and $\sigma_c$ can be calculated based on Eq. (1) and the result becomes 3:7:8. Experimentally, the order of the magnitude of the integrated $\sigma(\omega)$ for the three polarization directions is such that $c>b>a$ below 1 eV at 5 K, as shown in the inset of Fig. 3(f). This means that the estimate of SW based on Eq. (1) is qualitatively consistent with the experimental result. The gap formation with $T$ and a large spectral weight above the gap along the $c$ direction indicates the importance of the bond formation away from the *ab* plane. Namely, not dimerization but trimerization is necessary to account for the electronic structure below $T_c$. For more quantitative discussion on the anisotropy of the spectral weight and the spectral shape of the optical conductivity, the interaction between the V trimers and the untrimerized V ions, on-site Coulomb repulsion, and the charge-transfer excitation between oxygen and V ions have to be taken into account.[17]

In summary, we studied the structural phase transition of $\mathrm{BaV_{10}O_{15}}$ at $T_c \sim 130$ K using single crystals. It was found that the electrical resistivity jumps by three orders of magnitude at $T_c$, and the magnetic susceptibility also exhibits an anomaly at $T_c$. Synchrotron x-ray powder-diffraction measurement indicates that V trimerization occurs at $T_c$. It was also found that the optical conductivity spectrum at low frequency ($\hbar\omega < 0.5$ eV) is gradually suppressed with decreasing temperature, and a gap suddenly opens up at $T_c$. These experimental results indicate that the orbital ordering of the V $t_{2g}$ states occurs at $T_c$, and that results in the structural phase transition, the charge gap near the Fermi level, and the anisotropy of the electronic states in $\mathrm{BaV_{10}O_{15}}$.

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[13] $T_c=123$ K of the present single crystal estimated by the anomaly on the cooling run is by several degrees lower than that of the sample with "$T_c=135$ K" reported in Ref. 8, whose differential scanning calorimeter data has a peak at 127 K on the cooling run. It is speculated that this difference is caused by a small amount of excess oxygen existing in our crystal.

[14] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.81.060405 for the detailed result of the crystal structure and the analysis of resistivity and optical conductivity.

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[17] In the vanadate Mott insulators, the Mott excitation (between neighboring V ions) and the excitation between V and oxygen ions exist above 1 eV (Refs. 4 and 5). We speculate that in the present $\mathrm{BaV_{10}O_{15}}$, the excitation between trimerized V ions and untrimerized V ions, and between V and oxygen ions, are dominant in the $\sigma(\omega)$ spectra above 1 eV.

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