Anomalous metallic ground state in BaV$_{13}$O$_{18}$

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We studied single crystals of BaV$_{13}$O$_{18}$, in which V ions with an average valence of $+2.62$ ($3d^{2.38}$) form a quasi-fcc lattice. We found that the ground state of the stoichiometric crystal is insulating, whereas that of the off-stoichiometric crystal is metallic with a large effective mass. This metallic state can be explained by the Kondo coupling between the magnetic moment existing at the lone V ion and itinerant carriers in the V tetramers.

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Recently, it has been reported that hexagonal AV$_{13}$O$_{18}$ (A = Ba,Sr), in which the average valence of V ions is $+2.62$ (the average number of d electrons per V is 2.38), exhibits a variety of phases [1,2]. In this series of compounds, V and O ions occupy a part of the NaCl structure, and thus, V ions form a quasi-fcc lattice with periodically missing sites [3,4]. The high-temperature phase of this series of compounds is characterized by a lone V ion at the center, surrounded by six V tetramers, each of which has a rhombus shape composed of two regular triangles connected at the edge, as illustrated in the upper panel in Fig. 1. Experimentally, these tetramers start to form below $\sim$800 K, and the magnetic susceptibility keeps decreasing with decreasing temperature (T) below 800 K, indicating a spin-singlet formation. This V tetramerization is likely caused by an orbital ordering of V t_{2g} states. The absence of a structural phase transition associated with this orbital ordering can be attributed to the fact that the orbital ordering and the resultant formation of V tetramers do not break the symmetry of the original crystal structure [2].

Among this series of compounds, SrV$_{13}$O$_{18}$ exhibits a structural phase transition at $T_{tr} = 270$ K [1]. Below T_{tr}, the lone V ion at the center forms a V trimer with two V ions of the surrounding two tetramers, and the two tetramers are accordingly changed into two trimers; thus 13 V ions are separated into three trimers and one remaining tetramer. Note that such a trimerization of V ions at low T was observed in various vanadates in which V^{3+} ($3d^2$) ions form a quasi-fcc lattice [5,6] and was attributed to the orbital ordering of V t_{2g} states [7]. The resistivity and magnetic susceptibility of SrV$_{13}$O$_{18}$ decrease at T_{tr}. On the other hand, BaV$_{13}$O$_{18}$ exhibits a different type of phase transition at $T_{co} \sim 200$ K [1]. There is no discernible change in the powder x-ray diffraction, unlike the case of SrV$_{13}$O$_{18}$ at T_{tr}, but superlattice peaks at $(0,1/2,1/2)$ appear in the electron diffraction below T_{co}. This suggests that there is no substantial change in the configuration of V tetramers and lone V ions, but a charge ordering occurs for the lone V ion in BaV$_{13}$O$_{18}$.

Characteristics of the ground state in BaV$_{13}$O$_{18}$ are not clear. The resistivity of polycrystalline BaV$_{13}$O$_{18}$ increases at T_{co} and keeps increasing with further decreases in T, but the absolute value of the resistivity at the lowest T

remains $\sim$1 Ω cm [1], which is much lower than that of other Ba-V-O compounds exhibiting an insulating ground state with V trimerization (BaV$_{10}$O$_{15}$ [5] and Ba$_2$V$_{13}$O$_{22}$ [6]). The magnetic susceptibility of BaV$_{13}$O$_{18}$ exhibits a small drop at T_{co} but increases with further decreases in T, indicating a Curie-Weiss behavior, whose Curie constant is consistent in size with magnetic moments ($S = \frac{1}{2}$–1) existing only on lone V ions. According to the phase diagram of Ba$_{1-x}$Sr$_x$V$_{13}$O$_{18}$ in polycrystalline forms, the transition temperature T_{tr}, which is 270 K for SrV$_{13}$O$_{18}$ ($x = 1$), decreases with decreasing x (increasing the Ba content) but survives even in BaV$_{13}$O$_{18}$ at $\sim$70 K [2]; thus, there are two phase transitions in BaV$_{13}$O$_{18}$. However, anomalies in the resistivity and magnetic susceptibility are barely observed at $T_{tr} \sim 70$ K in polycrystalline BaV$_{13}$O$_{18}$, in clear contrast to the anomalies observed at $T_{co} \sim 200$ K.

It is known that such an orbital/charge ordering is fragile against disorder and that the transport properties of polycrystalline samples are seriously affected by the grain boundaries. In this paper, we report the physical properties of BaV$_{13}$O$_{18}$ single crystals. We studied two single crystals, both of which exhibit a high-T phase transition (T_{co}), but only one of which exhibits a low-T phase transition, at $T_{tr} = 65$. We found that the ground state of the sample exhibiting T_{tr} is insulating, whereas the sample without T_{tr} exhibits a metallic ground state with a large effective mass. This mass enhancement can be explained by the Kondo coupling between localized magnetic moments at the lone V ions and itinerant carriers in V tetramers.

Single crystals of BaV$_{13}$O$_{18}$ were grown by the floating-zone technique. Details of the crystal growth and characterization are given in the Supplemental Material [8]. Electrical resistivity was measured by a conventional four-probe method. Magnetic susceptibility was measured by a SQUID magnetometer. Specific heat was measured by a relaxation method. Optical reflectivity was measured between 0.01 and 0.8 eV by FTIR spectrometers and between 0.7 and 5 eV by a grating spectrometer. In the following, we discuss two single crystals of BaV$_{13}$O$_{18}$ (samples 1 and 2). Thermogravimetric analysis indicates that with the notation of BaV$_{13}$O$_{18+\delta}$, δ is 0.1 for sample 1 and 0.8 for sample 2; sample 1 is close to stoichiometric.

Figures 1(a) and 1(b) show the T dependence of resistivity for the two single crystals with $j \parallel a$ (ρ_a) and $j \parallel c$ (ρ_c). As can be seen, ρ_c is smaller than ρ_a over the whole T range for
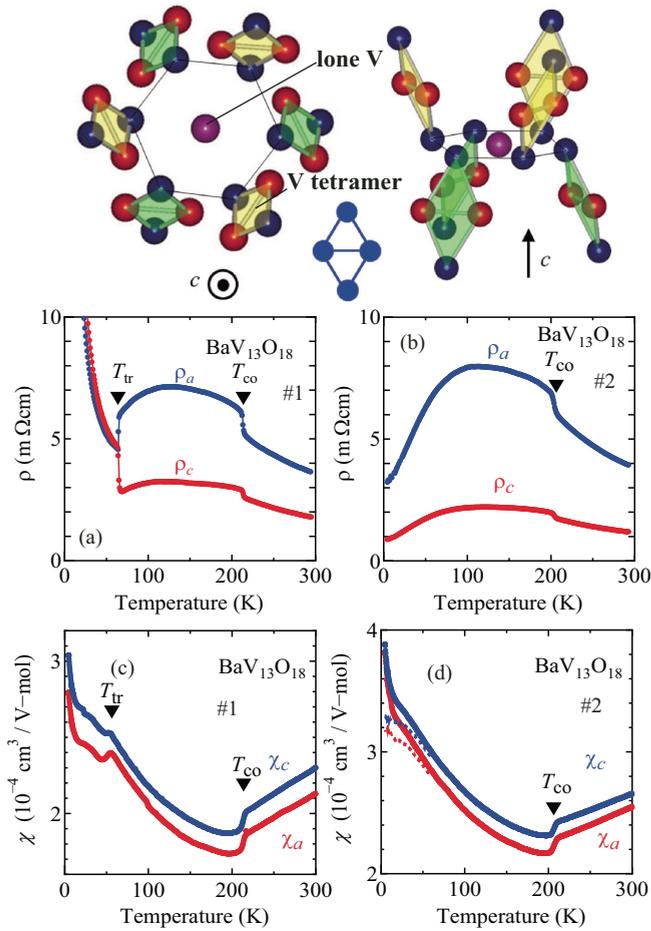
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FIG. 1. (Color online) Top: Arrangement of V ions in $BaV_{13}O_{18}$: the lone V ion at the center and six surrounding V tetramers. The left panel is a top view and the right is a side view. (a, b) Temperature dependence of resistivity for (a) sample 1 and (b) sample 2 of $BaV_{13}O_{18}$. (c, d) Temperature dependence of magnetic susceptibility for (c) sample 1 and (d) sample 2. Dashed lines correspond to the susceptibility from which the low-T Curie component is subtracted.

sample 2 and above 65 K for sample 1. This is likely related to the facts that the electron transfer along the V tetramer is dominant over that between tetramers or between a lone V and a tetramer and that the longer diagonal axis of the tetramer is tilted by only $\sim 19°$ from the c axis (upper right panel in Fig. 1); thus the electrons can travel more easily along the c axis. For both samples (nos. 1 and 2), there is an anomaly of resistivity at $T_{co} \sim 200$ K, where both ρ_a and ρ_c increase with decreasing T. Another anomaly at $T_{tr} = 65$ K exists only in sample 1, where ρ_c increases while ρ_a decreases with decreasing T, but both ρ_a and ρ_c increase with further decreases in T. On the other hand, both ρ_a and ρ_c for sample 2 decrease with decreasing T below ~ 100 K down to the lowest T, indicating a metallic ground state for this sample. We found that the T dependence of ρ below 30 K for sample 2 is given by $\rho = \rho_0 + AT^{1.5}$ for both ρ_a and ρ_c [8].

Magnetic susceptibilities of the two samples are shown in Figs. 1(c) and 1(d). The anisotropy of the magnetic susceptibility for $H \parallel a$ (χ_a) and $H \parallel c$ (χ_c) is less than 10%, and the behaviors of χ_a and χ_c are similar to those of the
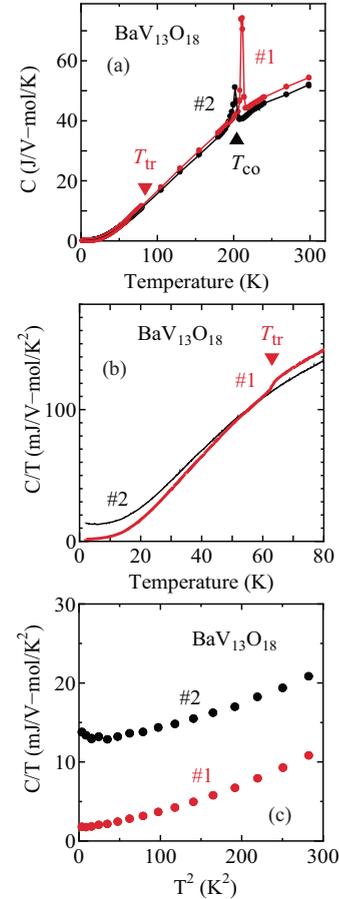

FIG. 2. (Color online) (a) Specific heat (C) vs T below 300 K, (b) C/T vs T below 80 K, and (c) C/T vs T^2 below 55 K for the two crystals (samples 1 and 2) of $BaV_{13}O_{18}$.

polycrystalline samples [1,2]. For sample 1, there is a small drop in χ at $T_{tr} = 65$ K.

The result of specific-heat (C) measurements is shown in Fig. 2. As shown in Fig. 2(a) (C vs T), there is a large peak in $C(T)$ at T_{co} for both samples. For sample 1, a sharp decrease in $C(T)$ is observed at T_{tr}, which is more clearly shown in Fig. 2(b) (C/T vs T). Note that the present specific-heat measurement was performed by a relaxation method, and thus the release of latent heat by the first-order phase transition at T_{tr} may not be fully detected. Figure 2(c) shows C/T as a function of T^2. The T linear coefficient in $C(T)$, γ, arising from the electron specific heat, is ~ 12 mJ/V-mol K^2 for sample 2 and ~ 1 mJ/V-mol K^2 for sample 1. The larger value of γ for sample 2 is consistent with the metallic behavior of the same sample regarding the T dependence of ρ shown in Figs. 1(b).

It is known that orbital ordering, which is accompanied by V trimerization below T_{tr}, is fragile against disorder or carrier doping, and the absence of T_{tr} for sample 2 can be attributed to the hole doping induced by excess oxygen. $BaV_{13}O_{18+\delta}$ with $\delta = 0.8$ means that there are 1.6 holes per 13 V tions, most likely in the three V tetramers. We speculate that these holes in sample 2 are responsible for the suppression of T_{tr} and the metallic ground state.

Although the behavior of the specific heat for sample 2 is consistent with its metallic characteristics, the T dependence

of χ, which indicates the existence of the localized moments, does not seem consistent. For this issue, one can see that the behavior of $\chi(T)$ for sample 2 in Fig. 1(d) below $\sim$50 K can be separated into a saturation behavior (as shown by dashed lines) and the remnant Curie behavior. If we assume that the saturation value of χ, 3.3×10^{-4} cm^2/V-mol, arises from a Pauli paramagnetic susceptibility, the Wilson ratio, i.e., χ/γ in the unit of $3\mu_B^2/\pi^2 k_B^2$, is $\sim$2, a typical value for strongly correlated electron systems. This result, together with the Curie-Weiss behavior above 50 K, reminds us of the Kondo behavior. Namely, in higher T regions ($>$50 K), i.e., above the Kondo temperature (T_K), there are localized magnetic moments, presumably sitting on the lone V ions, and also itinerant carriers, presumably caused by the holes in the tetramers. In this T range, the localized moments act as scattering centers for the itinerant carriers, and this causes the negative value of $d\rho/dT$. However, at low T ($<$50 K), i.e., below T_K, the localized moments and itinerant carriers are coupled and form heavy-mass carriers, which are responsible for the metallic conduction at low T. Assuming that the localized moments exist on lone V ions, and thus, the number of carriers with a heavy mass is only 1/13 the number of total V ions, the electron specific heat $\gamma = 12$ mJ/V-mol K^2 corresponds to an effective mass of $\sim$50m_0, where m_0 is the free electron mass.

We measured the optical reflectivity spectra for no. 1 and 2 crystals polished on the ac plane and for an as-cleaved no. 2 crystal on the $(32\bar{2})$ plane. Note that the $(32\bar{2})$ plane in the present compound corresponds to a (100) plane of the NaCl structure that the V and O ions form. We found that the spectra for the polished and cleaved surfaces of sample 2 are discernibly different below T_{co}. This is caused by the remnant stress applied to the sample surface during polishing. Thus, we only show the data taken on the cleaved surface of sample 2 below. Here, the $(32\bar{2})$ plane contains the axis along the ab plane ($[2\bar{3}0]$ axis) but does not contain the c axis. Thus, we measured the reflectivity on the $(32\bar{2})$ plane with two polarization directions, along the $[2\bar{3}0]$ axis (R_a) and along the one perpendicular to the $[2\bar{3}0]$ axis on the $(32\bar{2})$ plane (R_{ac}), as illustrated in the lower-right panel in Fig. 3. The R_a and R_{ac} spectra at various temperatures are shown in Figs. 3(a) and 3(b). The optical conductivity spectrum along the a axis [$\sigma_a(\omega)$] can be directly obtained by Kramers-Kronig transformation of the $R_a(\omega)$ spectra, whereas that along the c axis [$\sigma_c(\omega)$] can be calculated by both the $R_a(\omega)$ and the $R_{ac}(\omega)$ spectra with a Kramers-Kronig transformation [8].

Figure 3(c) shows the overall features of the $\sigma(\omega)$ spectra along the a and c directions at 300 K. There are three structures in both $\sigma_a(\omega)$ and $\sigma_c(\omega)$: a peak at $\sim$0.5 eV, a broad structure between 0.5 and 3 eV, and an edge at $\sim$4 eV. These spectral features are similar to those for BaV$_{10}$O$_{15}$, shown by the dashed line in Fig. 3(c), in which the V ions form a bilayer slab of a quasi-fcc lattice with periodically missing sites, and the three peaks were assigned to the in-gap excitation (between V^{2+} and V^{3+}), Mott excitation (between V^{3+} and V^{3+}), and charge-transfer excitation (between V^{3+} and O^{2-}), respectively [5,9]. This simple structure of the $\sigma(\omega)$ spectrum and the similarity between the spectrum of BaV$_{13}$O$_{18}$ and that of BaV$_{10}$O$_{15}$ indicate that the electronic structures of these compounds are dominated by a local configuration of the V
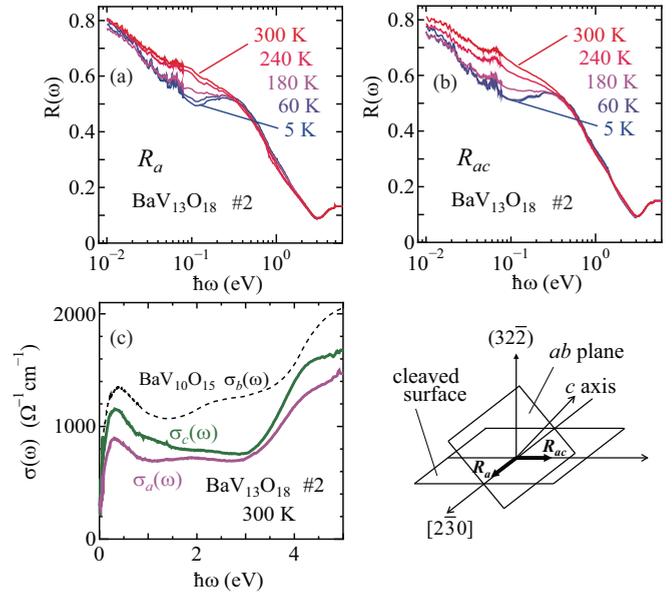

FIG. 3. (Color online) (a, b) Reflectivity spectra at various temperatures on the $(32\bar{2})$ plane with the polarization directions (a) along the $[2\bar{3}0]$ axis and (b) perpendicular to the $[2\bar{3}0]$ axis. (c) Optical conductivity spectra at 300 K derived from the reflectivity spectra, together with that for BaV$_{10}$O$_{15}$ (along the b axis). Data for BaV$_{10}$O$_{15}$ are offset by 200 Ω^{-1} cm^{-1} for clarity. Lower right: Configurations of the cleaved surface, crystal axes, and polarization directions for the optical reflectivity measurement.

and O ions with a Coulomb repulsion in the V d states, rather than the band structure with many branches [10] caused by a large number of ions in a unit cell. Note that the absolute values of σ_c are larger than those of σ_a over the whole $\hbar\omega$ range ($0 < \hbar\omega < 5$ eV) for BaV$_{13}$O$_{18}$, consistent with the lower values of dc resistivity along the c axis.

Figures 4(a) and 4(b) show $\sigma_a(\omega)$ and $\sigma_c(\omega)$ below 1 eV at various temperatures. Both σ_a and σ_c below 0.25 eV decrease with decreasing T. However, the conductivity does not become 0 but maintains a finite value ($\sim$200 Ω^{-1} cm^{-1}) even at the lowest T, indicating the opening of only a pseudogap in BaV$_{13}$O$_{18}$. This is quite different from the formation of a real gap in BaV$_{10}$O$_{15}$ [5], which exhibits a V trimerization and an insulating ground state below 130 K. The integrated value of $\sigma(\omega)$ (spectral weight) below 0.2 eV, which approximately corresponds to the isosbestic point of the conductivity spectra, is plotted as a function of T in Fig. 4(c); the decrease in the spectral weight is correlated with the phase transition at $T_{co} \sim 200$ K, particularly for $\sigma_a(\omega)$. This indicates that the opening of a pseudogap in the $\sigma(\omega)$ spectra is caused by a phase transition at T_{co}. The inset in Fig. 4(c) shows the spectral weight as a function of cutoff $\hbar\omega$ for the 240 and 5 K spectra. The spectral weights for the two temperatures almost merge at $\sim$0.6 eV for both $\sigma_a(\omega)$ and $\sigma_a(\omega)$, indicating that the transfer of the spectral weight occurs within this energy scale. It should be pointed out that this energy scale of spectral-weight transfer is comparable to or smaller than that of various transition-metal oxides exhibiting charge ordering at around 200 K [11–14].

As discussed above, the dc resistivity measurement indicates a metallic characteristic of sample 2 below 50 K. In
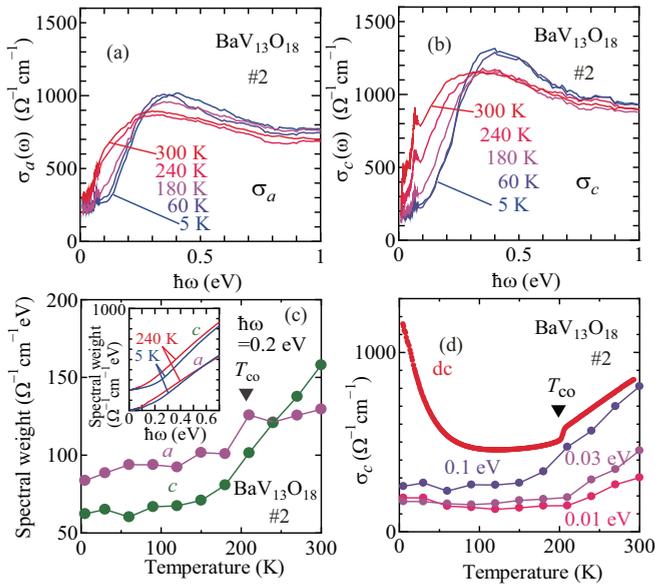
FIG. 4. (Color online) (a, b) Optical conductivity spectra at various temperatures along (a) the a axis and (b) the c axis. (c) Integrated value of optical conductivity up to 0.2 eV as a function of temperature. Inset: Spectral weight as a function of cutoff $\hbar\omega$, where data are offset for clarity. (d) Value of optical conductivity at various values of $\hbar\omega$ and dc conductivity as a function of temperature.

Fig. 4(d), the values of optical conductivity at various values of $\hbar\omega$ and dc conductivity are plotted as a function of T. The increase in conductivity below 50 K observed for the dc values, indicative of Kondo-singlet formation below T_K, is not observed in the optical conductivity down to $\hbar\omega = 0.01$ eV. This indicates that the Drude component responsible for metallic conduction below 50 K exists only below 0.01 eV [8]. Assuming that the number of carriers is 1/13, the total number of V ions, and that the effective mass of the carriers is 50

times the free electron mass as derived from the specific heat measurement, the estimated Drude weight [integrated value of $\sigma(\omega)$] is 20 Ω^{-1} cm^{-1} eV. This is nearly consistent with the possible Drude weight for the $\sigma_c(\omega)$ spectrum at 10 K below 0.01 eV, which reaches 1200 Ω^{-1} cm^{-1} at 0 eV. Note that in various heavy-fermion compounds, a small Drude spectrum appears below T_K in the $\hbar\omega$ range far below 0.01 eV [15–20].

It should be pointed out that a spontaneous separation of spin-singlet clusters and magnetic moments in the crystal has been observed in several transition-metal oxides, for example, spinel AlV_2O_4, where spin-singlet V heptamers and lone magnetic V^{3+} ions are formed [21], and $Ba_2V_{13}O_{22}$, where spin-singlet V trimers and lone magnetic V^{4+} ions are formed [6]. However, the ground state of such compounds is insulating, meaning that the magnetic moments remain localized down to the lowest T. In this sense, $BaV_{13}O_{18}$ with oxygen offstoichiometry belongs to a new class of materials in which the magnetic moments that are separated from the spin-singlet clusters (V tetramers) at high temperatures are coupled with itinerant carriers again and form heavy-mass quasiparticles at low temperatures.

In summary, two single crystals of $BaV_{13}O_{18}$ were studied, one of which is close to stoichiometric and exhibits two phase transitions, at $T_{co} \sim 200$ K and $T_{tr} = 65$ K, and the other of which is rather off-stoichiometric and exhibits only the high-T phase transition at T_{co}. It was found that the ground state of the crystal exhibiting the low-T phase transition (T_{tr}) is insulating, while the crystal in which T_{tr} is absent exhibits a metallic ground state. For the latter crystal, the localized magnetic moments that appear below T_{co} act as scattering centers for the itinerant carriers above 50 K but are coupled with itinerant carriers and form heavy-mass quasiparticles below 50 K. It was also found that the phase transition at T_{co} induces a pseudogap in the optical conductivity spectrum for $BaV_{13}O_{18}$.

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