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Competition between vanadium tetramerization and trimerization in $Ba_{1-x}Sr_xV_{13}O_{18}$

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We studied the transport, magnetic, and structural properties of $Ba_{1-x}Sr_xV_{13}O_{18}$, in which V and O ions form a sodium-chloride lattice with periodically missing sites. We found that the high-temperature insulating phase is characterized by spin-singlet V tetramers, whereas the low-temperature conducting phase is characterized by V trimers, and these two phases are competing in this series of compounds. Various properties substantially change at the phase transition between the two, indicating a drastic reconstruction of the electronic structure.

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The orbital degree of freedom of d electrons yields various types of ordered states. In the series of perovskite manganites, for example, several different types of ordered states (orbital ordering), a ferromagnetic state without orbital ordering, a charge-ordered state with CE-type spin ordering, and a ferro-orbital ordering with A-type spin ordering, are competing with each other.[1,2] Such a competition of different phases results in a large change of physical properties at the first-order phase transition between two phases, and colossal magnetoresistance in its consequence.

Orbital ordering in perovskite manganites is the so-called site-order type, where localized d electrons exist at each site of transition metals with magnetic moment. On the other hand, $LiVO_2$ with V^{3+} ions on the triangular lattice shows a different type of orbital ordering, the so-called bond-order-type orbital ordering.[3] In this compound, V trimerization occurs, in which xy, yz, or zx orbitals form a bond at each side of the V triangles [Fig. 1(a)], and each bonding state accommodates two d electrons in the spin singlet. In $LiVO_2$, these trimers are two-dimensionally aligned on the triangular lattice, but three-dimensional alignment of similar V trimers is observed in $BaV_{10}O_{15}$[4] and $A_2V_{13}O_{22}$ (A = Ba, Sr).[5]

Recently, it has been found that $AV_{13}O_{18}$ (A = Ba, Sr), in which V and O ions form a sodium-chloride lattice with periodically missing sites,[6,7] shows peculiar phase transitions.[8] The high-temperature (T) phase of $AV_{13}O_{18}$ for both A = Ba and Sr is characterized by V "tetramers," where four V ions form two regular triangles on the same plane that are connected at one side [Fig. 1(b)]. In the crystals, six tetramers surround the center V ion in a hexagon shape, as shown in Figs. 1(c) and 1(e). Since a tetramer surrounds another center V ion in the opposite side, i.e., there are two center V ions corresponding to one tetramer, 13 V ions are separated into three tetramers and one center V ion in the high-T phase. $SrV_{13}O_{18}$ undergoes a phase transition at $T_{tr} = 270$ K. As shown in Fig. 1(d), one of the V ions in the tetramer is detached, and two V ions detached from two tetramers form a new V trimer with the center V ion, whereas two tetramers (from each of which a V ion has been detached) change to two trimers. As a result, 13 V ions are separated into three trimers and one tetramer in the low-T phase of $SrV_{13}O_{18}$.[8] $BaV_{13}O_{18}$ shows another type of phase transition at $T_{co} = 200$ K, below which there is no large change of the crystal structure but there appear superlattice peaks at $q = (0,1/2,1/2)$ (in the hexagonal setting) in the electron diffraction, suggesting a charge-ordered state.

In this paper, we study the detailed physical properties of $AV_{13}O_{18}$ including mixed compounds $Ba_{1-x}Sr_xV_{13}O_{18}$. We find that there is a strong competition between the tetramer phase and the trimer phase in this series of compounds, and the electronic structure substantially changes associated with the phase transition between the two phases.

Polycrystalline samples were synthesized by a solid state reaction as described in Ref. 8. Electrical resistivity and Hall measurement was made by a four-probe technique. Magnetic susceptibility was measured by a SQUID magnetometer. Thermopower and thermal conductivity were simultaneously measured by a steady state method. Synchrotron x-ray powder diffraction measurement was performed with an incident wavelength of 0.77477 Å between 90 and 800 K at SPring-8 BL44B2.[10] Rietveld analysis of the diffraction data was made with Rietan-2000.[11]

First, we studied the T dependence of V-V bond lengths in the high-T phase by synchrotron x-ray powder diffraction measurement. As shown in Fig. 2(a), among all the inequivalent nearest-neighbor V-V bonds in $BaV_{13}O_{18}$, three bonds (shown by solid circles) are shorter than the others, i.e., forming a tetramer. Furthermore, their bond lengths show large T dependence, which amounts to 4%–7% between 800 and 200 K. On the other hand, the bond length of other V-V bonds barely changes or even increases with decreasing T, and consequently, lattice constants are reduced only by ~1% from 800 and 200 K (not shown). It is quite unlikely that a simple thermal contraction induces such a large reduction of bond length only for specific V-V bonds. The relative change of the bond length observed in $BaV_{13}O_{18}$ between 800 and 200 K (4%–7%) is comparable to that observed on the phase transition with V trimerization in various vanadates.[4,5,12]

These results suggest that there is some specific mechanism by which the three V-V bonds are shorter than the others and V tetramers are formed, and we speculate that the orbital ordering as illustrated in Fig. 1(b)[8] is such a mechanism existing behind the tetramerization. It should be noted that the orbital ordering

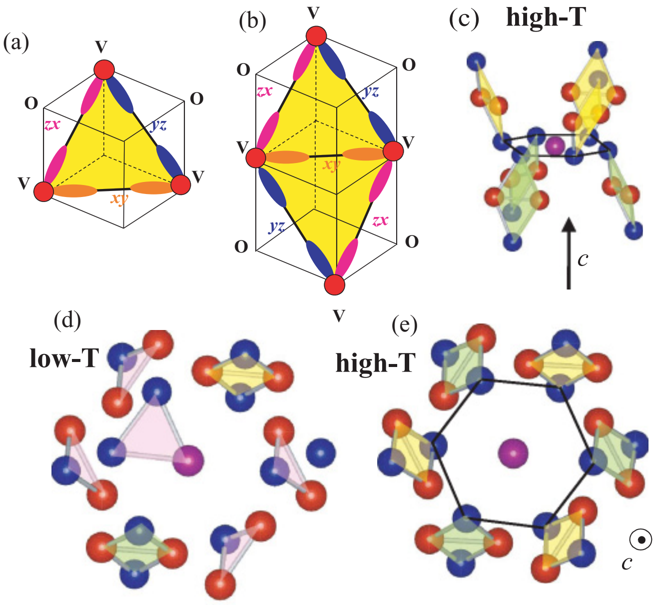

FIG. 1. (Color online) (a) Orbital state of a V trimer. (b) Orbital state of a V tetramer. (c) Configuration of V ions in $BaV_{13}O_{18}$ and $SrV_{13}O_{18}$ above $T_{tr} = 270$ K seen along the *ab* plane. (d) Configuration of V ions in $SrV_{13}O_{18}$ below $T_{tr} = 270$ K seen from the *c* axis. (e) The same as (c) but seen from the *c* axis. (c)–(e) are drawn by VESTA.[9]

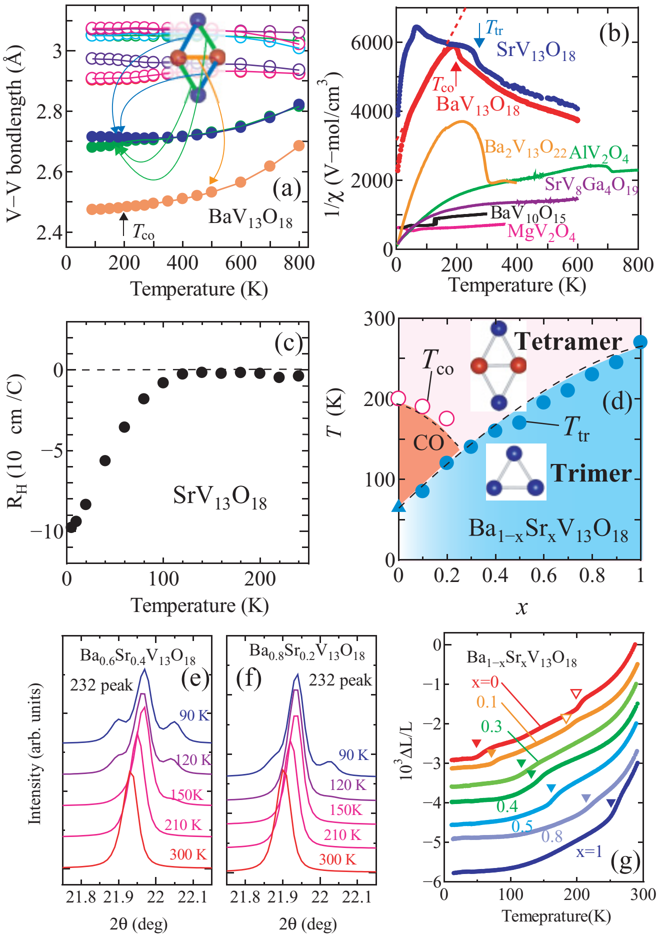

FIG. 2. (Color online) (a) T dependence of V-V bond length for $BaV_{13}O_{18}$. The solid circles correspond to the bonds that form tetramers, whereas open circles to those that do not. The arrow shows T_{co}. (b) T dependence of inverse magnetic susceptibility for various vanadates. (c) T dependence of the Hall coefficient for $SrV_{13}O_{18}$. (d) A phase diagram of $Ba_{1-x}Sr_xV_{13}O_{18}$ in the x-T space. (e), (f) 232 peak in the x-ray diffraction at various temperatures for (e) $x = 0.4$ and (f) $x = 0.2$. (g) T dependence of strain at various values of x. Closed triangles correspond to T_{tr} and open triangles to T_{co}.

in $AV_{13}O_{18}$, if it exists, is not accompanied by a phase transition but occurs as a crossover, since the orbital-ordered state (tetramers) does not break the symmetry of the original crystal structure. Similar crossover behavior of V trimerization was observed in vanadates with a magnetoplumbite structure.[13]

We also found an anomalous T dependence of magnetic susceptibility (χ) in the high-T phase of both $BaV_{13}O_{18}$ and $SrV_{13}O_{18}$. As shown in Fig. 2(b), where inverse magnetic susceptibility is plotted as a function of T, the absolute values of χ around 300 K are much smaller ($1/\chi$ is larger) than those of other vanadates having V^{3+} ions, and χ gradually increases ($1/\chi$ decreases) with increasing T. Such an anomalous temperature dependence of χ ($d\chi/dT < 0$) can be explained by assuming a spin-singlet formation of V ions. Namely, the magnetic susceptibility is suppressed because of the singlet formation on the V-V bonds of tetramers, but thermally induced spins gradually appear with increasing T, resulting in the increase of χ.

Next, let us discuss the low-T phase of $SrV_{13}O_{18}$ below $T_{tr} = 270$ K. In this phase, three trimers, each of which accommodates 6 electrons, and one tetramer, which accommodates 10 electrons, can contain 28 d electrons and thus, 31 (total number of d electrons for 13 V ions) $-28 = 3$ electrons per 13 V ions are not accommodated either in the trimer or tetramer, which can contribute to the electric conduction. We performed the Hall measurement of $SrV_{13}O_{18}$, and the Hall coefficient R_H is plotted as a function of T in Fig. 2(c). As can be seen, R_H is negative and shows a large T dependence below 100 K. The absolute value at 5 K is $\sim 1.0 \times 10^{-2}$ cm^3/C, corresponding to 0.015 carriers per V. This number is much smaller than 3 electrons per 13 V. Furthermore, the sign of R_H at low T (negative) is different from the sign of the Seebeck coefficient at the same T range (positive), as discussed later. These results indicate a semimetallic state of this low-T phase, where a small number of electrons and holes (with different scattering rates) exist and give rise to the T-dependent R_H. It should be pointed out that the unit cell is doubled in the low-T phase of $SrV_{13}O_{16}$, and thus, there are 6 electrons that are not accommodated in either trimers or tetramers in a unit cell, which can form a semimetallic state.

As to the state below $T_{co} = 200$ K in $BaV_{13}O_{18}$, $\chi(T)$ shows a distinctly different T dependence below T_{co}, which can be interpreted by a Curie-Weiss behavior $\chi = C/(T + \theta)$ with $C = 6.0 \times 10^{-2}$ cm^3 K/V mol and $\theta = 190$ K, as shown by a dashed line in Fig. 2(b). The magnitude of Curie constant C is much smaller than the value expected when $S = 1$ spins exist at all the V sites, $C = 1.0$ cm^3 K/V mol, but is comparable to that when $S = 1$ or $S = 1/2$ spins exist only 1 out of 13 V ions, $C = 7.7 \times 10^{-2}$ cm^3 K/V mol or 2.9×10^{-2} cm^3 K/V mol, respectively. Thus, it can be speculated that spin-singlet V tetramers survive below T_{co}, but the d electrons on the center V [surrounded by 6 tetramers in Fig. 1(e)] become localized; i.e., charge ordering occurs, and the localized moment on the center V gives rise to the Curie-Weiss behavior.

On the basis of these results, let us see the result of mixed compounds, $\mathrm{Ba}_{1-x}\mathrm{Sr}_x\mathrm{V}_{13}\mathrm{O}_{18}$. We first performed strain measurement [Fig. 2(g)] to identify the transition temperatures. $T_{\mathrm{tr}} = 270$ K in $\mathrm{SrV}_{13}\mathrm{O}_{18}$ can be detected as a small decrease of $\Delta L/L$ ($x = 1.0$), and the temperature of the anomaly decreases with decreasing x, as shown by solid triangles in Fig. 2(g). We confirmed by synchrotron powder x-ray diffraction of several samples that this anomaly corresponds to the same type of structural phase transition, i.e., V trimerization, as that observed in $\mathrm{SrV}_{13}\mathrm{O}_{18}$ [Figs. 2(e) and 2(f)]. On the other hand, $T_{\mathrm{co}} = 200$ K in $\mathrm{BaV}_{13}\mathrm{O}_{18}$ ($x = 0$) can also be detected as a small decrease of $\Delta L/L$, and a similar anomaly is observed also for $x = 0.1$, as shown by an open triangle. For a small x regin ($x \leqslant 0.2$), two successive phase transitions occur, from the high-T tetramer phase to the so-called charge-ordered (CO) phase at T_{co}, and the CO phase to the trimer phase at T_{tr}. This is summarized as a phase diagram in the x-T space in Fig. 2(d).[14]

The T dependence of resistivity (ρ) for $\mathrm{Ba}_{1-x}\mathrm{Sr}_x\mathrm{V}_{13}\mathrm{O}_{18}$ is shown in Fig. 3(a). For $\mathrm{SrV}_{13}\mathrm{O}_{18}$ ($x = 1.0$), ρ increases with decreasing T at high temperatures, but decreases below T_{tr} (shown by a solid triangle). When x is decreased, the drop of ρ at T_{tr} (solid triangles) becomes more pronounced. This result indicates that the trimer phase ($T < T_{\mathrm{tr}}$) is more conducting than the tetramer phase ($T > T_{\mathrm{tr}}$), and these two phase are competing with each other. In $\mathrm{BaV}_{13}\mathrm{O}_{18}$ ($x = 0$), ρ increases at T_{co}, and a similar increase of ρ is observed also for $x = 0.1$, as shown by open triangles. Thus, for $\mathrm{Ba}_{1-x}\mathrm{Sr}_x\mathrm{V}_{13}\mathrm{O}_{18}$ with $x = 0.1$, ρ first increases at T_{co}, and then decreases at T_{tr}. At lower T (<50 K), ρ increases with decreasing T for all the samples. As discussed below, the Seebeck coefficient shows a metallic behavior in this T range (except for $x = 0$), and probably, this insulating behavior in $\rho(T)$ arises from charge localization by disorder or from the Kondo effect.

The T dependence of magnetic susceptibility (χ) has also been measured, as shown in Fig. 3(b). At T_{tr} (shown by solid triangles), χ decreases, and at T_{co} (open triangles), χ slightly decreases and then increases with further decreasing T. For the samples having both T_{tr} and T_{co} ($x = 0.1$ and 0.2), χ first increases at T_{co} and then decrease at T_{tr} more pronouncedly than the other samples having only T_{tr} ($x \geqslant 0.4$). This result indicates that the CO phase ($T < T_{\mathrm{co}}$) has a magnetic moment (most likely at the center V ion) but the moment disappears in the trimer phase (T_{tr}), where all the V ions form trimers or tetramers in a spin-singlet. Below ~50 K, all the samples show an upturn of χ. Recent NMR measurement of $\mathrm{SrV}_{13}\mathrm{O}_{18}$ indicates no sign of anomaly around 50 K,[15] and thus, this upturn may arise from the impurity spins existing in the sample.

We also measured thermopower, and the T dependence of Seebeck coefficients, S, is shown in Fig. 3(c). In the high-T phase, S is negative and its absolute value increases with decreasing T, which amounts to 40–80 μV/K. Such a T dependence is a typical behavior in the semiconducting state. However, S is drastically suppressed below T_{tr} shown by solid triangles, and even changes its sign at low T; S becomes positive. With further decreasing T, S approaches zero almost linearly to T, a typical behavior of S in the metallic state. Note that the sign of S at low T is different from that of the Hall coefficient R_H shown in Fig. 2(c), indicating the existence of both electrons and holes as conduction carriers. On the other hand, at T_{co} shown by open triangles, the absolute values of S increase, indicating a decrease of the carrier number. This is consistent with the charge-ordered state below T_{co}.

The T dependence of thermal conductivity κ is shown in Fig. 3(d). κ decreases with decreasing T in the high-T phase, but increases below T_{tr}. Anomaly of κ is barely seen at T_{co}. A similar behavior of κ to that seen in the present compounds around T_{tr} is observed in various compounds showing charge ordering or orbital ordering.[16,17] This can be interpreted in such a way that the mean free path of acoustic phonons decreases above the transition temperature because phonons are heavily scattered by the fluctuation of the ordering, but such fluctuation disappears below the transition temperature, resulting in the enhancement of the mean free path of acoustic phonons and phonon thermal conductivity. Another possible origin of the enhancement of κ below T_{tr} is the appearance of the thermal conduction by itinerant electrons.

These experimental results indicate that the phase transition from the tetramer phase to the trimer phase substantially affects various properties. The change of the properties is more pronounced for the compounds with lower T_{tr}, as seen in Fig. 3. To show this tendency more clearly, we take the T derivative of log ρ, χ, S, and κ, and plot them in the x-T space (Fig. 4). The T derivative at T_{tr} is positive for log ρ and χ and negative for S and κ, but for all of the quantities, the absolute values of the T derivative at T_{tr} (solid lines in Fig. 4) are enhanced as x decreases.

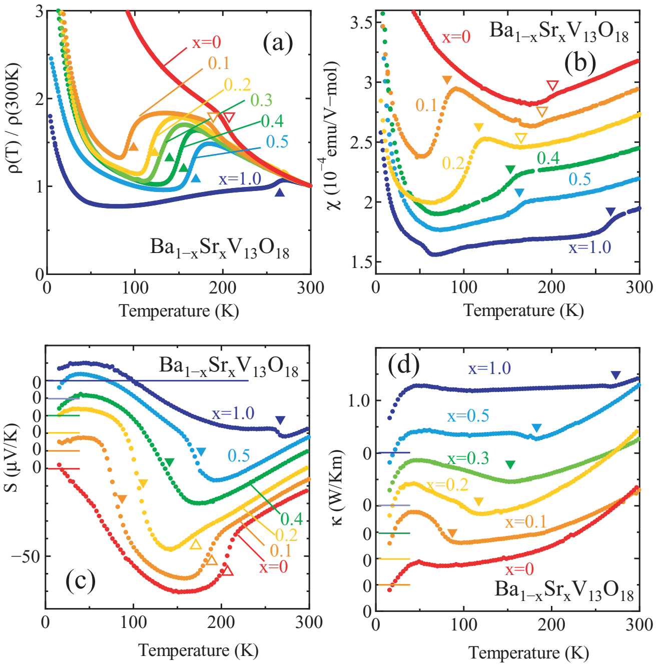

FIG. 3. (Color online) T dependence of (a) resistivity ρ, (b) magnetic susceptibility χ, (c) Seebeck coefficient S, and (d) thermal conductivity κ for $\mathrm{Ba}_{1-x}\mathrm{Sr}_x\mathrm{V}_{13}\mathrm{O}_{18}$ at various values of x. For all the figures, closed triangles correspond to T_{tr} and open triangles to T_{co}. The data in (b)–(d) are offset for clarity.

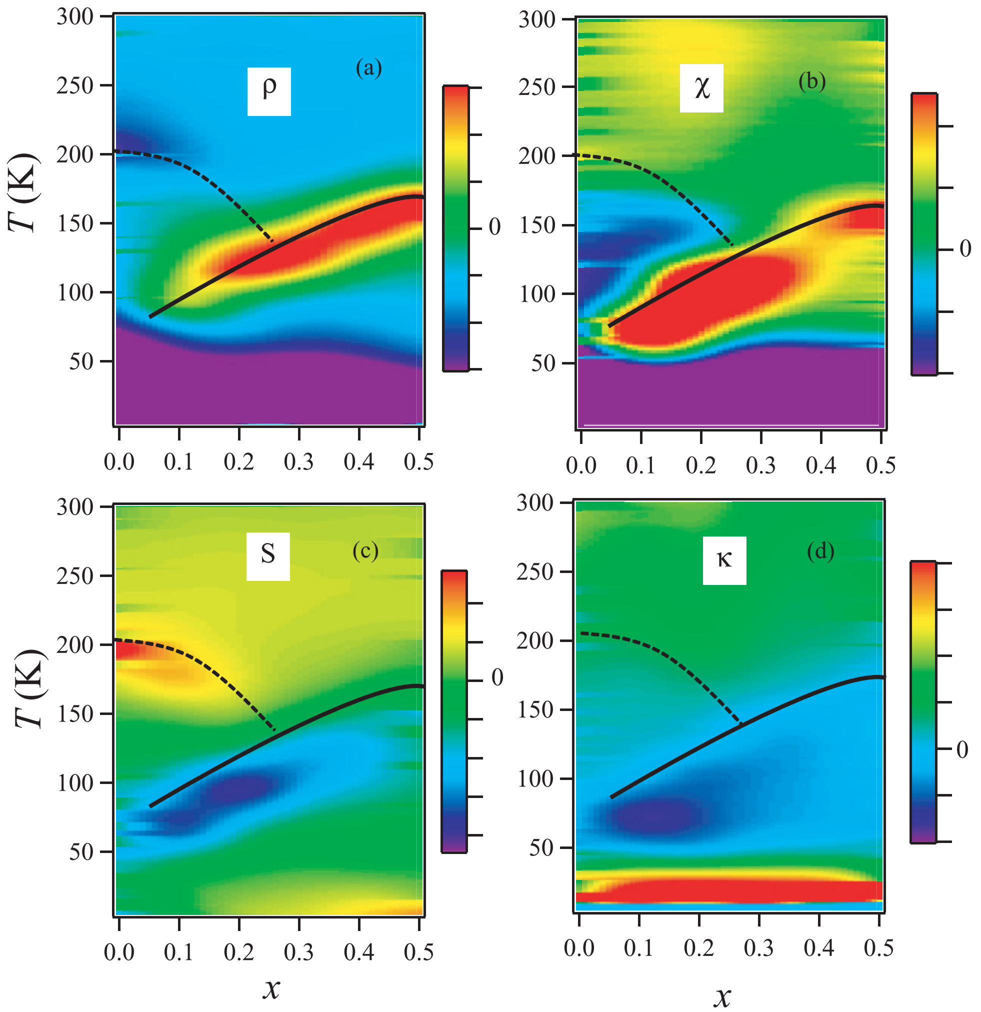

FIG. 4. (Color) Contour plot of (a) $d\log\rho/dT$, (b) $d\chi/dT$, (c) dS/dT, and (d) $d\kappa/dT$, as a function of x and T. The data are convoluted along the x axis. Solid lines refer to T_{tr} and dashed lines to T_{co}.

The overall phase diagram can be interpreted by the competition between an insulating state in the tetramer phase and a conducting state in the trimer phase. In the tetramer phase, among 31 d electrons for 13 V ions, 30 electrons are accommodated in the bonding state of three tetramers (each of which accommodates 10 electrons) in a spin-singlet state, and the one remaining electron at the center V ion contributes to the hopping conduction, but this electron becomes localized below T_{co}. This can explain the insulating behavior in the T dependence of ρ and S, and the anomaly at T_{co} in those two quantities. On the other hand, in the trimer phase, among 31 electrons, 28 electrons are accommodated in three trimers and one tetramer, and the other three electrons contribute to electric conduction. This leads to the decrease of ρ and the sign change of S.

The mechanism of the phase transitions in $AV_{13}O_{18}$ is related to the entropy of the single electron on the center V ion surrounded by six tetramers [Fig. 1(e)], which can be suppressed by breaking the threefold-rotation symmetry and forming a cluster with the other two V ions. This mechanism is analogous to the Peierls transition with dimerization observed in one-dimensional compounds in the sense that symmetry is spontaneously lowered to form a closed-shell structure. What is unique about the present phase transition is that there are six possible directions to form a trimer [see Fig. 1(d)], in contrast to the only two possible configurations of dimerization in the Peierls transition. Accordingly, intriguing dynamics and fluctuation are expected to be associated with the phase transition in $AV_{13}O_{18}$, and should be studied in the future.

In summary, the transport, magnetic, and structural properties of $Ba_{1-x}Sr_xV_{13}O_{18}$ were studied. In the high-T phase of this series of compounds, V tetramers evolve and magnetic susceptibility is suppressed with decreasing T, and these can be explained by an orbital ordering with a spin-singlet state. The low-T phase for $x > 0$ is characterized by V trimers, and is a semimetallic state. The phase transition observed in $BaV_{13}O_{18}$ ($x = 0$) persists up to $x = 0.2$, and is most likely driven by the localization of the carriers at the center V ion with keeping V tetramers. Various properties substantially change at the transition between the tetramer and trimer phase, indicating a reconstruction of the electronic structure.

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