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Charge-gap formation in the insulating states of $AV_{10}O_{15}$ (A = Ba, Sr)

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We measured the optical conductivity spectra of $SrV_{10}O_{15}$ with $V^{2.8+}$, which exhibits an insulating behavior without any phase transition, and compared the results with those of $BaV_{10}O_{15}$, which shows orbital ordering below $T_c = 123$ K. We found that a soft gap opens at the lowest temperature but it collapses with increasing temperature in $SrV_{10}O_{15}$, in contrast to a finite charge gap (~0.3 eV) in $BaV_{10}O_{15}$ below T_c. We also found that the difference of the conductivity spectra between $SrV_{10}O_{15}$ and $BaV_{10}O_{15}$ evolves even above T_c of Ba, indicating that the fluctuation of orbital ordering produces a pseudogap in $BaV_{10}O_{15}$.

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I. INTRODUCTION

There are various origins of insulating states in solid states. The most common origin is the formation of a band gap, where the periodic potential in the crystal affects the dispersion relation of itinerant electrons and opens a gap in it. Another common origin is the formation of a Mott gap, where the on-site Coulomb interaction induces a localization of electrons and opens a gap in the density of states. An important aspect of this Mott-gap formation is that the number of electrons per site needs to be integer; otherwise, additional electrons (or holes) can move without experiencing the increase of Coulomb repulsion energy and thus a metallic state appears, unless there is another source of the insulating behavior.

It is known that the insulating state of many transition-metal oxides arises from such a Mott-gap formation in the d states of transition metals, and its charge gap has been measured by various spectroscopic techniques, for example, optical and photoemission spectroscopies.[1–4] It is also known that, even if the number of electrons per site becomes away from integer by doping, transition metal oxides often remain insulating.[5–7] One possible origin of the insulating state in the systems with noninteger filling is charge and orbital ordering. In doped perovskite manganites, for example, charge ordering occurs for a wide range of hole concentration, where doped holes order periodically in a stripe shape,[8,9] and a charge gap in such charge-ordered compounds has been measured by various spectroscopic techniques.[10–12] Even if there is no additional periodicity in the system, doped carriers can be trapped as small polarons due to electron-lattice coupling, resulting in the insulating state. Anderson localization arising from disorder is another possible origin of the insulating state in the presence of doped carriers. However, it is usually quite difficult to identify the origin of a charge gap in the insulating state of transition-metal oxides, particularly when the number of electrons per site is not integer.

$AV_{10}O_{15}$ (A = Ba or Sr) is a compound in which V ions form a triangle-based lattice [Fig. 1(a)].[13–17] The average valence of V ions is +2.8; (i.e., there are 2.2 electrons at each V ion on the average). The V ion is surrounded by a O_6 octahedron and those octahedra are edge-sharing with each other. It is known that there is a structural phase transition in $BaV_{10}O_{15}$ at $T_c = 123$ K, where electrical resistivity [$\rho(T)$] jumps by three orders of magnitude [Fig. 1(b)]. Optical reflectivity measurement of $BaV_{10}O_{15}$ indicates that there is a sudden shift of the optical conductivity spectrum [$\sigma(\omega)$] at T_c and a gap of ~0.3 eV opens. It was proposed that V trimerization with the orbital ordering of V t_{2g} states is the origin of the structural phase transition and the formation of a charge gap below T_c. However, even above T_c in $BaV_{10}O_{15}$, $\rho(T)$ increases with decreasing temperature (T) and the $\sigma(\omega)$ spectrum below ~0.5 eV is gradually suppressed; i.e., a typical insulating behavior was observed, though its origin is not understood.

$SrV_{10}O_{15}$ has the same crystal structure as $BaV_{10}O_{15}$ at room temperature, but there is no structural phase transition down to the lowest T. It is known that $\rho(T)$ keeps increasing with decreasing T, and diverges at the lowest T [Fig. 1(b)].[17] It is not understood why $SrV_{10}O_{15}$ shows such an insulating behavior at all the T range in spite of the fractional number of average valence (+2.2) and the absence of long-range ordering, or why $SrV_{10}O_{15}$ does not show a phase transition whereas $BaV_{10}O_{15}$ does.

To understand the insulating behavior of these two compounds, it is informative to study the electronic structure by a spectroscopic technique and to investigate the characteristic of a charge gap. In this paper, we measured the optical reflectivity spectra for $SrV_{10}O_{15}$, and compared the results with those of $BaV_{10}O_{15}$ in Ref. 17. We found that the optical conductivity spectra derived from the reflectivity spectra in each compound are characterized by a gap formation with a specific origin for the compound.

II. EXPERIMENTS

Single crystals of $BaV_{10}O_{15}$ and $SrV_{10}O_{15}$ were grown by the floating-zone method. The orientation of the crystal was determined by the Laue method, and the ab or ac plane was cut and polished for optical measurement. Electrical resistivity was measured by a four-probe technique. Optical reflectivity was measured between $\hbar\omega = 0.01$ and 5 eV using FTIR spectrometers ($0.01 < \hbar\omega < 0.8$ eV) and grating spectrometers ($0.7 < \hbar\omega < 5$ eV). Optical conductivity spectra were derived by the Kramers-Kronig transformation of the reflectivity spectra.

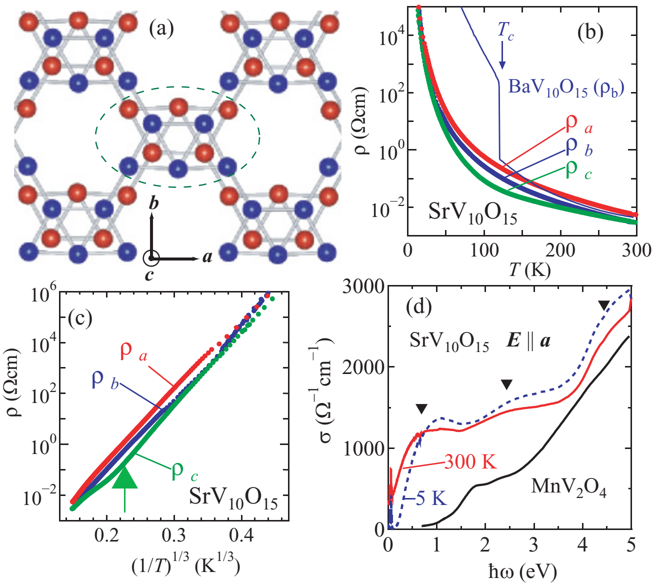

FIG. 1. (Color online) (a) Configuration of V ions (spheres) in the bilayer of $AV_{10}O_{15}$. (b) Temperature (T) dependence of resistivity (ρ) for $SrV_{10}O_{15}$ and $BaV_{10}O_{15}$. (c) Log ρ vs $(1/T)^{1/3}$ for $SrV_{10}O_{15}$. (d) Optical conductivity spectra for $SrV_{10}O_{15}$ at 300 K (solid line) and 5 K (dashed line), and that for MnV_2O_4

III. RESULTS AND DISCUSSIONS

In Fig. 1(b), the electrical resistivity (ρ) of $SrV_{10}O_{15}$ for three different directions is plotted. In Fig. 1(c), ρ in a log scale is plotted as a function of $(1/T)^{1/3}$. The linear relation of ρ_a and ρ_b over 8 orders of magnitude suggests that $\rho(T)$ is dominated by the variable-range-hopping (VRH) mechanism in two dimension, $\rho(T) = \rho_0 \exp[(\Delta/k_B T)^{1/3}]$. It should be pointed out that ρ_c clearly deviates from the linear relation around $(1/T)^{1/3} \sim 0.2\ K^{-1/3}$ ($T \sim 100$ K) as shown by an arrow in Fig. 1(c). This anomaly is related to the $\sigma(\omega)$ peak at finite frequencies, as discussed below.

Figure 1(d) shows overall features of the optical conductivity spectra [$\sigma(\omega)$] for $SrV_{10}O_{15}$ at 300 and 5 K. In the same figure, the $\sigma(\omega)$ spectrum of spinel MnV_2O_4 is also plotted, in which VO_6 octahedra are edge sharing with each other (similarly to $AV_{10}O_{15}$), but there are only V^{3+} ($3d^2$) ions. Three peaks are observed below 5 eV in the $SrV_{10}O_{15}$ spectrum, at 0.5, 2.5, and 4.5 eV, as shown by triangles, whereas only two peaks exist in the MnV_2O_4 spectrum at 2 and 4 eV. As to MnV_2O_4, two peaks can be assigned to the Mott excitation between V $3d$ states (at 2 eV) and the charge-transfer (CT) excitation from the oxygen $2p$ to V $3d$ state (at 4 eV). A similar assignment has been proposed for perovskite RVO_3 also having only V^{3+} ions.[18] Thus, the 2.5- and 4.5-eV peaks in $SrV_{10}O_{15}$ can be similarly assigned to the Mott and CT excitation. Accordingly, the 0.5-eV peak in $SrV_{10}O_{15}$ should be assigned to the in-gap state arising from the fractional number of average valence for V ions [i.e., the excitation between the V^{3+} ($3d^2$) and V^{2+} ($3d^3$) states].

Figures 2(a)–2(c) show $\sigma(\omega)$ spectra for $SrV_{10}O_{15}$ with three different polarization directions at various T. For all the polarization directions the $\sigma(\omega)$ spectra below ~0.5 eV are gradually suppressed whereas those at higher energies are enhanced with decreasing T. Unlike the case of $BaV_{10}O_{15}$, where a charge gap with ~0.3 eV opens in the $\sigma(\omega)$ spectrum at the lowest T [as shown by dashed lines in Figs. 2(a)–2(c)], only a soft gap (i.e., a gap with a size close to zero) is observed even at the lowest T in $SrV_{10}O_{15}$. It should be noted that the spectral change with T occurs in the range of the in-gap state (the excitation between V^{2+} and V^{3+}) in $AV_{10}O_{15}$. Such a gap formation in the in-gap state (in terms of the original Mott gap) was reported for $La_{2-x}Sr_xNiO_4$ showing a charge-ordering transition.[19]

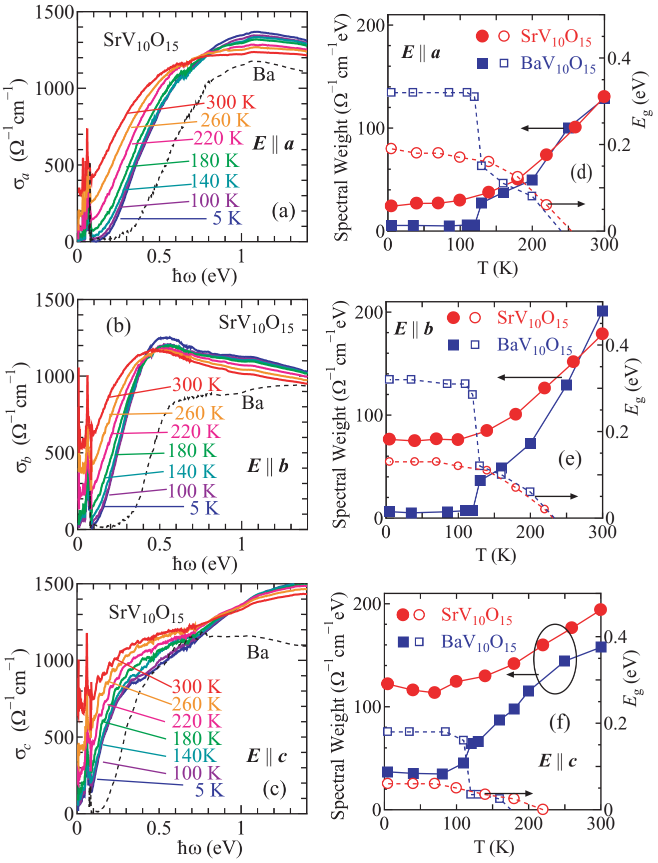

FIG. 2. (Color online) (a)–(c) Optical conductivity spectra for $SrV_{10}O_{15}$ with **E** ∥ (a) **a**, (b) **b**, and (c) **c**. The dashed line in each figure is the optical conductivity spectrum of $BaV_{10}O_{15}$ at 5 K. (d)–(f) Temperature dependence of the spectral weight between 0.1 and 0.3 eV (solid symbols) and the gap magnitude (open symbols) for $SrV_{10}O_{15}$ (circles) and $BaV_{10}O_{15}$ (squares) with **E** ∥ (d) **a**, (e) **b**, and (f) **c**.

As a measure of the low-frequency spectral weight, the integrated values of $\sigma(\omega)$ between 0.1 and 0.3 eV are plotted as a function of T in Figs. 2(d)–2(f), together with those of $BaV_{10}O_{15}$. The spectral weight gradually decreases with decreasing T in $SrV_{10}O_{15}$, in contrast to the existence of an abrupt change at $T_c = 123$ K in $BaV_{10}O_{15}$. In the same figures, as a measure of the gap magnitude, the crossing point of the extrapolation of $\sigma(\omega)$ around $600 \sim 200\ \Omega^{-1}cm^{-1}$ and the x axis is plotted. The gap magnitude jumps at $T_c = 123$ K in $BaV_{10}O_{15}$, but such an anomaly is not observed in $SrV_{10}O_{15}$.

It should also be pointed out that a polarization dependence exists in the $\sigma(\omega)$ spectra (σ_a, σ_b, and σ_c) of $SrV_{10}O_{15}$ shown in Figs. 2(a)–2(c). Namely, for all three polarization directions, the $\sigma(\omega)$ spectra at various T form isosbestic points, but the

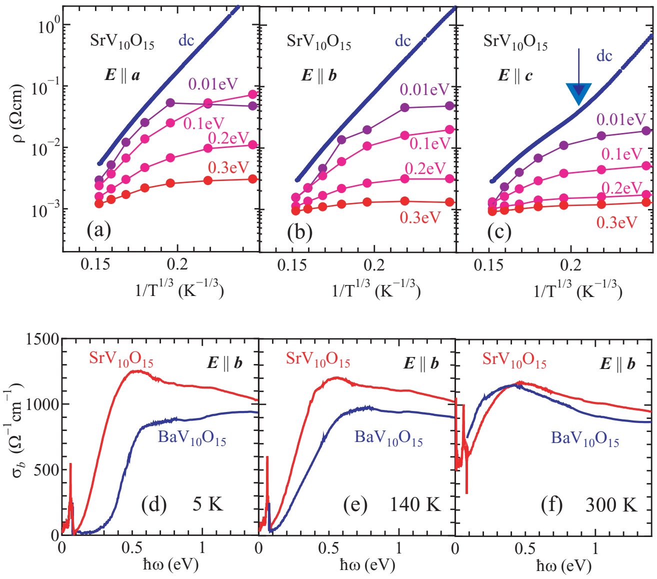

FIG. 3. (Color online) (a)–(c) Temperature dependence of dc resistivity and resistivity at finite frequencies (obtained from optical conductivity spectra) for $\mathrm{SrV_{10}O_{15}}$ with $\boldsymbol{E} \parallel$ (a) $\boldsymbol{a}$, (b) $\boldsymbol{b}$, and (c) $\boldsymbol{c}$. (d)–(f) Comparison of the optical conductivity spectra between $\mathrm{SrV_{10}O_{15}}$ and $\mathrm{BaV_{10}O_{15}}$ at (d) 5 K, (e) 140 K, and (f) 300 K (with $\boldsymbol{E} \parallel \boldsymbol{b}$).

positions of the isosbestic points are different for σ_a, ($\hbar\omega =$ 0.7 eV), σ_b (0.4 eV,), and σ_c (0.8 eV). Furthermore, the isosbestic point appears associated with the collapse of the lowest-energy peak in σ_a (∼1.1 eV) and σ_b (∼0.5 eV), whereas in the $\sigma_c(\omega)$ spectrum, another peak exists at ∼0.3 eV below the isosbestic point at 0.8 eV.

To see the relation between $\rho(T)$ and the $\sigma(\omega)$ spectra more clearly, the $1/T^{1/3}$ dependence of dc resistivity as well as resistivity at finite frequencies obtained from $\sigma(\omega)$ is plotted in Figs. 3(a)–3(c).[20] For ρ_a and ρ_b, the $1/T^{1/3}$ dependence of logarithmic ρ gradually changes from the linear dependence for dc resistivity to a saturation behavior with T for finite values of ω, and the saturation temperature increases with increasing ω. This suggests that the behavior of dc resistivity is related to that at finite frequencies. In other words, the VRH behavior observed in the dc resistivity is dominated by the collapse of the lowest-energy peak in $\sigma_a(\omega)$ and $\sigma_b(\omega)$ with increasing T. On the other hand, ρ_c at finite frequencies [Fig. 3(c)] shows relatively small values compared with those for ρ_a and ρ_b. This is caused by the existence of a peak in the $\sigma_c(\omega)$ spectra at ∼0.3 eV shown in Fig. 2(c). A possible origin of a dip in the T dependence of dc ρ_c [shown in Fig. 1(c)] is that the sum of a conductivity with a peak around 1.5 eV, which collapses with increasing T, giving rise to the VRH behavior, and that with a peak at 0.3 eV, which persists even with increasing T, giving rise to an activation-type T dependence of dc conductivity, results in a dip in the T dependence of the reciprocal conductivity [$\rho_c(T)$].

Here, let us discuss the possible origin of the insulating state in $\mathrm{SrV_{10}O_{15}}$. The gap opens in the in-gap state, and thus, it cannot simply be regarded as a Mott gap of d states. However, there are 20 V ions in a primitive unit cell, and it is possible to see a bunch of V ions as a molecule with an integer number of electrons and to consider a Mott-insulating state on such molecules. According to the crystal structure shown in Fig. 1(a), 10 V ions marked by a dashed circle form a cluster, and can be regarded as a molecule. These molecules are three-dimensionally connected in the crystal, and thus, one possible origin of the insulating state in $\mathrm{SrV_{10}O_{15}}$ is a Mott gap state based on this molecule.

Since there are 10 V ions, each of which has triply degenerate t_{2g} states, quite a large number of localized d states per molecule are expected near the Fermi level. Indeed, according to band calculations of $\mathrm{BaV_{10}O_{15}}$, many bands cross the Fermi energy.[15,21] It should be pointed out that the VRH behavior of $\rho(T)$ in general comes from the fact that when there are many levels near the Fermi surface with disorder, an electron just below the Fermi level can find a level to be transferred to with a lower energy if it jumps over a longer distance.[5] Accordingly, a large number of localized states at one molecule with various different values of Coulomb repulsion energy in $\mathrm{SrV_{10}O_{15}}$, together with the disorder inherently existing in the crystal, can give rise to the VRH-like behavior as observed experimentally.

In Figs. 3(d)–3(f), the $\sigma_b(\omega)$ spectra for $\mathrm{SrV_{10}O_{15}}$ and $\mathrm{BaV_{10}O_{15}}$ at the same T are shown. At 5 K (below T_c of $\mathrm{BaV_{10}O_{15}}$), the spectrum of $\mathrm{BaV_{10}O_{15}}$ shifts by ∼0.3 eV from that of $\mathrm{SrV_{10}O_{15}}$ caused by the opening of a charge gap at $T_c = 123$ K. At 300 K, on the other hand, σ_b spectra of $\mathrm{BaV_{10}O_{15}}$ and $\mathrm{SrV_{10}O_{15}}$ are almost identical. At 140 K, immediately above T_c of $\mathrm{BaV_{10}O_{15}}$, two spectra are discernibly different; a peak around 0.5 eV exist in the spectrum of $\mathrm{SrV_{10}O_{15}}$, but is barely observed in $\mathrm{BaV_{10}O_{15}}$.

To see how this difference between $\mathrm{BaV_{10}O_{15}}$ and $\mathrm{SrV_{10}O_{15}}$ evolves with T, the difference of the $\sigma(\omega)$ spectrum for $\mathrm{BaV_{10}O_{15}}$ and that for $\mathrm{SrV_{10}O_{15}}$ with the same polarization at the same T was taken [i.e., $\Delta\sigma(\omega) = \sigma_{\mathrm{Ba}}(\omega) - \sigma_{\mathrm{Sr}}(\omega)$], and

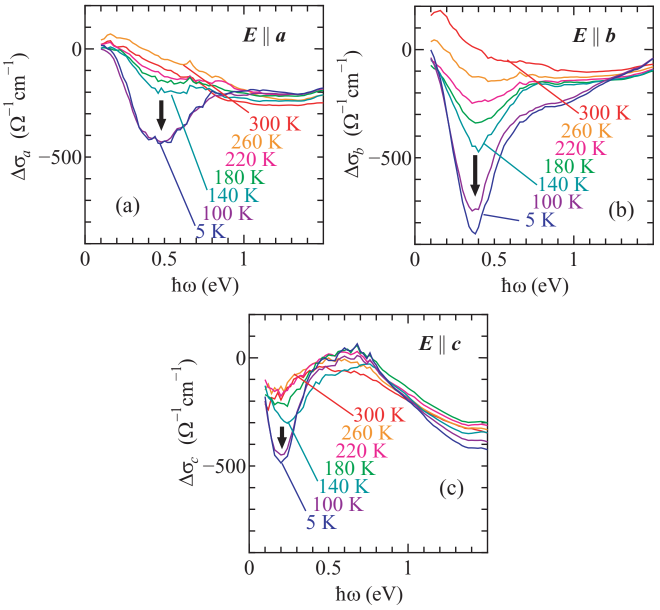

FIG. 4. (Color online) (a)–(c) Optical conductivity spectra of $\mathrm{BaV_{10}O_{15}}$ minus that of $\mathrm{SrV_{10}O_{15}}$ at the same T for $\boldsymbol{E} \parallel$ (a) $\boldsymbol{a}$, (b) $\boldsymbol{b}$, and (c) $\boldsymbol{c}$. The thick arrows indicate that T crosses $T_c = 123$ K from the high-T to low-T side between those two spectra.

$\Delta\sigma(\omega)$ spectra are plotted in Figs. 4(a)–4(c). A large dip at 5 K was observed at ∼0.4 eV for $\boldsymbol{E} \parallel \boldsymbol{a}$ and $\boldsymbol{E} \parallel \boldsymbol{b}$ and at ∼0.2 eV for $\boldsymbol{E} \parallel \boldsymbol{c}$, which arises from the opening of a charge gap in $\mathrm{BaV_{10}O_{15}}$. As can be seen, this dip evolves far above $T_c = 123$ K of $\mathrm{BaV_{10}O_{15}}$ for all the polarization directions. Furthermore, the energy scale of the dip above T_c is comparable to that below T_c. This analysis indicates that the dip above T_c arises from a pseudogap, whose origin is similar to that of the real gap below T_c. Namely, the fluctuation of orbital ordering exists in $\mathrm{BaV_{10}O_{15}}$ even above T_c and that produces a pseudogap in the density of states.[22,23] It should be pointed out that the raw spectrum of $\sigma(\omega)$ is dominated by the density of states and the matrix elements in the optical process as a function of ω, and thus, a pseudogap formation with T will be easily masked by the structures arising from those origins. Nevertheless, it is expected that those intrinsic structures in $\sigma(\omega)$ are similar between $\mathrm{BaV_{10}O_{15}}$ and $\mathrm{SrV_{10}O_{15}}$ if there is no long-range ordering, and thus, by comparing the spectra of the two, one can obtain the evidence of a pseudogap formation without ambiguity.

Recent NMR measurement on $\mathrm{BaV_{10}O_{15}}$ has shown that the number of inequivalent V sites are larger than that expected in the high-T crystal structure (=3) between $T_c = 123$ and 220 K.[24] This result can be explained by assuming that V trimers are locally formed even above T_c. It is likely that the pseudogap formation observed in the optical spectra is correlated with such a local formation of V trimers.[25] The existence of V trimers without long-range ordering over a wide T range (130 ∼ 220 K) in $\mathrm{BaV_{10}O_{15}}$ gives us unique opportunity to study the dynamics of short-range orbital-ordered states in the future.

IV. SUMMARY

In summary, we studied the optical spectra of $\mathrm{SrV_{10}O_{15}}$, which becomes insulating without any long-range ordering. We found that a soft gap, whose magnitude is close to zero, opens in the optical conductivity spectra at low temperatures in $\mathrm{SrV_{10}O_{15}}$. This behavior is in contrast to $\mathrm{BaV_{10}O_{15}}$, which shows an orbital ordering below $T_c = 123$ K, where the gap magnitude of the optical conductivity amounts to ∼0.3 eV. We found that a peak at finite frequencies in the optical conductivity spectra dominates the temperature dependence of dc resistivity in $\mathrm{SrV_{10}O_{15}}$. We also found that the optical spectra of $\mathrm{BaV_{10}O_{15}}$ and $\mathrm{SrV_{10}O_{15}}$ are discernibly different even above T_c, suggesting that orbital fluctuation evolves and produces a pseudogap in $\mathrm{BaV_{10}O_{15}}$ above T_c.

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[25] The energy scale of NMR measurement (several hundred MHz) is quite low and thus, what NMR sees is a formation of quasistatic local trimers. The pseudogap in $\sigma(\omega)$ begins to open below 260 K [see Fig. 4(b)], and this indicates that trimers are fluctuating with time between 220 and 260 K, and the fluctuation slows down to zero, but still fluctuating in space, at 220 K.