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Anomalous relaxation behavior in the resistivity and magnetization of $La_5Mo_4O_{16}$

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We found anomalous relaxation behaviors in a two-dimensional magnet, $La_5Mo_4O_{16}$, in a pure crystalline form in both the resistivity and magnetization, whose characteristics are similar to those of disordered materials. We also found that such anomalous relaxation behaviors disappear in the impurity-doped sample. We propose a possible scenario for the relaxation behavior that the charge rearrangement of Mo^{4+} and Mo^{5+} causes a change in the interlayer magnetic interaction in this compound.

I. INTRODUCTION

Relaxation behaviors are observed for various quantities in various materials, for example, magnetization and electric polarization.[1–16] In many cases, disorder in the material plays an important role in the relaxation behavior. Spin-glass compounds[1] and relaxor ferroelectrics[2] are typical examples exhibiting a relaxation characteristic of the disordered the materials, where the relaxation is dominated by a free energy landscape with a large number of minima. Relaxation is also known to occur in pure crystals, which is often caused by the competition between different phases. In these cases, the relaxation time usually has an activation-type temperature dependence, and the activation energy corresponds to the energy barrier between two competing phases. In the present paper, we demonstrate that the two-dimensional magnet $La_5Mo_4O_{16}$ in a pure crystalline form exhibits unusual relaxation behaviors in both the resistivity and magnetization with an applied magnetic field, whose characteristics are similar to those of disordered materials even in the absence of obvious disorder in the compound.

In $La_5Mo_4O_{16}$ [Fig. 1 (a)],[17,18] Mo ions in MoO_6 octahedra form a square lattice and Mo_2O_{10} pillars exist between neighboring square-lattice layers. There are two inequivalent Mo sites in the square lattice in a checkerboard configuration, one of which (Mo2) is connected to the Mo_2O_{10} pillars and the other of which (Mo1) is not. It is considered that the Mo2 site is occupied by Mo^{4+} ($4d^2$) whereas the Mo1 site is occupied by Mo^{5+} ($4d^1$), and the Mo site in the pillar (Mo3) is occupied by Mo^{4+}.[18] It is also considered that the Mo^{5+} ions at Mo1 and the Mo^{4+} ions at Mo2 are magnetic whereas the Mo^{4+} ions at Mo3 (in the pillar) are nonmagnetic, probably due to the singlet formation between the two Mo ions in the pillar.[19]

This compound exhibits antiferromagnetic ordering at $T_N = 200$ K,[19–23] where the Mo moments in the square lattice order antiferromagnetically, thus giving rise to a ferrimagnetic moment along the c axis at each layer, and the ferrimagnetic moment at each layer orders in an antiferromagnetic manner along the c axis [Fig. 1 (a)]. It

has been found that a metamagnetic transition occurs when a magnetic field (H) of ~ 0.5 T is applied along the c axis, where the antiferromagnetic configuration of the ferrimagnetic moment changes into the ferromagnetic configuration.[23] This indicates that, although the magnetic interaction within a layer is sufficiently strong for antiferromagnetic ordering to occur at $T_N = 200$ K, the interlayer antiferromagnetic interaction is extremely weak, three orders of magnitude smaller than the intralayer interaction, indicating the two-dimensional character of this compound.[24] Associated with this metamagnetic transition, the time dependence of the magnetization, i.e., relaxation behavior with a relatively long relaxation time, was observed.[24] This is likely caused by the facts that there is an energy barrier when the Mo moment flips (arising from its Ising anisotropy) and that the Mo moments are strongly coupled within each layer but are loosely coupled between the layers, and thus, the magnetic correlation length is much longer within the plane compared to that along the c axis. As a result, many spins within a layer have to go beyond the energy barrier simultaneously when the metamagnetic phase transition occurs.

So far, the studies on $La_5Mo_4O_{16}$ have been carried out on single crystals grown by the fused salt electrolysis (FSE) method. In the present paper, we studied a single crystal grown by the floating-zone (FZ) technique and found that it exhibits unusual relaxation behaviors in both the resistivity and magnetization, which were not observed in the FSE crystal. We also found that such unusual behaviors disappear in the crystal with a small amount of impurity doping at the Mo sites.

II. EXPERIMENT

Polycrystalline samples of $La_5Mo_4O_{16}$ cannot be synthesized by mixing, for example, La_2O_3, MoO_2, and MoO_3 with a stoichiometric ratio of La, Mo, O and sintered in a sealed quartz tube or in the flow of Ar gas. Thus, we employed a reducing technique inside a sealed quartz tube. La_2MoO_6 and MoO_3, in both of which Mo is 6+ (d^0), were mixed, pressed into a rod, and sealed in

a quartz tube with an appropriate amount of Mo powder pressed into a rod, which acts as reducing agent. It was heated at 1250 °C for 12 hours. We confirmed that the sintered rod is $La_5Mo_4O_{16}$ with no impurity phase. La_2MoO_6 was synthesized by sintering the mixture of La_2O_3 and MoO_6 in air at 1250 °C for 6 hours.

The sintered rod was melted in the floating-zone furnace with a flow of Ar gas. The feed speed of the rod was typically 5 mm/ hour. The grown rod was found to be a mixture of $La_5Mo_4O_{16}$ and $La_{2.4}Mo_{1.6}O_8$ with a disordered fluorite structure, but pieces of the $La_5Mo_4O_{16}$ single crystals with plate-like shapes can be easily obtained by crushing the rod. Mn-doped single crystals were grown by the same method, using Mn metal as a starting material.

Resistivity (ρ) was measured (1) by a two-probe technique with an electrometer up to $\sim 10^{12}$ Ωcm and (2) by a four-probe technique with a voltage source and a voltmeter up to $\sim 10^8$ Ωcm, with the current direction parallel and perpendicular to the c axis, ρ_c and ρ_{ab}. Magnetoresistance (M) was measured with applied magnetic field H between -5 and 5 T by a superconducting magnet. Magnetization was measured by a SQUID magnetometer. Magnetic field was applied always along the c axis, which is the easy axis of the $La_5Mo_4O_{16}$. When the dependences of ρ and M on H and the time t were measured, the temperature of the sample was increased above T_N every time before starting the measurement at each T and thus, the sample is in the initial magnetization process.

III.   RESULTS AND DISCUSSION

Figure 1 (b) shows the temperature (T) dependence of the resistivity for $La_5Mo_4O_{16}$ grown by the floating-zone technique. The values of ρ_c measured by a two-probe technique and those by a four-probe technique almost overlap between 250 and 60 K. This indicates that the contact resistance of the present sample is smaller than the bulk resistance. Furthermore, the values of ρ_c is one or two orders of magnitude larger than those of ρ_{ab} measured by a four-probe technique. This indicates a modest size of anisotropy in the electron transport of $La_5Mo_4O_{16}$ with a two-dimensional crystal structure.

Figure 1 (c) shows the T dependence of ρ_c measured by a two-probe technique in a cooling run for the FZ crystal of $La_5Mo_4O_{16}$ and $La_5Mo_{3.9}Mn_{0.1}O_{16}$, and the FSE crystal of $La_5Mo_4O_{16}$. In $\rho_c(T)$ of the $La_5Mo_4O_{16}$ crystal grown by the FZ technique, there are anomalies at $T_1 \sim 60$ K and at $T_2 \sim 95$ K, which do not exist in that of the $La_5Mo_{3.9}Mn_{0.1}O_{16}$ crystal and the $La_5Mo_4O_{16}$ crystal grown by the FSE method.[23]

Figure 2 (a) shows the T dependence of the magnetization (M) for the FZ crystal of $La_5Mo_4O_{16}$ in the field-cooling (FC) and field-warming (FW) process at $H = 0.1$ T. In addition to the peak at $T_N = 200$ K, an anomaly with a T hysteresis at $T_1 = 60$ K and a smaller anomaly
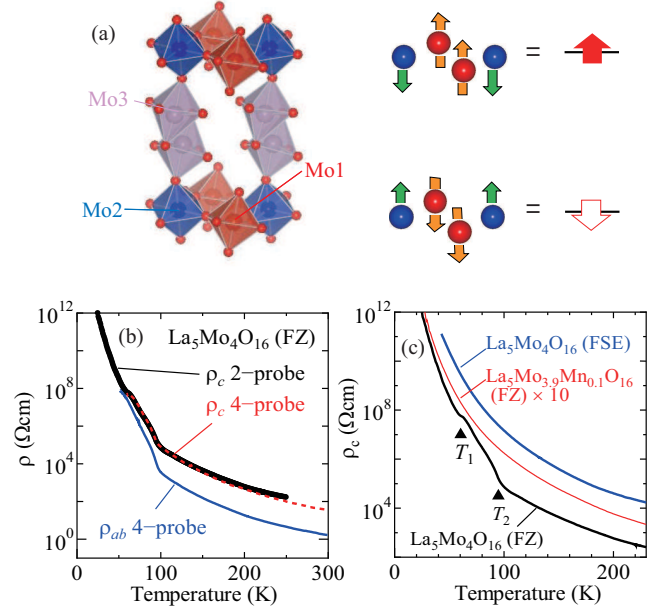

FIG. 1: (Color online) (a) (Left) crystal structure and (right) magnetic structure below T_N for $La_5Mo_4O_{16}$. (b) Temperature dependence of resistivity for $La_5Mo_4O_{16}$: ρ_{ab} by the four-probe technique, ρ_c by the four-probe technique, and ρ_c by the two-probe technique. (c) Temperature dependence of ρ_c by the two-probe technique for the FZ crystal of $La_5Mo_4O_{16}$, $La_5Mo_{3.9}Mn_{0.1}O_{16}$, and the FSE crystal of $La_5Mo_4O_{16}$.

at $T_2 = 95$ K (which is more clearly seen in the data multiplied by 20 times) exist. Fig. 2 (b) shows the $M(T)$ data for the same compound in the FC and FW process at 5 T and that in the FW at 0.1 T after cooling the sample at 5 T. The anomaly at T_1 is observed in all three curves, and the anomaly at T_2 is clearly observed in $M(T)$ at 5 T.

Figure 2 (c) shows the $M(T)$ data for the FZ crystal of $La_5Mo_{3.9}Mn_{0.1}O_{16}$ in the field cooling (FC) and field warming (FW) at $H = 0.1$ T. Though a peak at $T_N = 190$ K is clearly observed also in this compound, anomalies at T_1 and T_2 are barely observed, unlike the data for the pure compound shown in Fig. 2 (a). Fig. 2 (d) shows the $M(T)$ data for the same compound in the FC at 5 T and that in the FW at 0.1 T after cooling the sample at 5 T. Anomalies at T_1 and at T_2 disappear in the 5 T data. The decrease in $M(T)$ measured at 0.1 T at ~ 30 K corresponds to a relaxation of M from the ferromagnetic state (induced by the magnetic field of 5 T applied when decreasing T) to the antiferromagnetic state, whose relaxation time becomes shortened with increasing T.[24] This is the same behavior observed in the FSE crystal of $La_5Mo_4O_{16}$ shown in Figs. 2 (e) and (f).

To understand the anomalies observed in the FZ crystal of $La_5Mo_4O_{16}$, the $M(H)$ curves were measured at various T. A typical $M(H)$ curve above T_1 (at 150 K) is shown in Fig. 3 (a) There is an anomaly in $M(H)$ from $M = 0$ to $|M| \sim 3000$ Gcm^3/mol at $|H| \sim 0.5$ T with H hysteresis. This corresponds to a metamagnetic
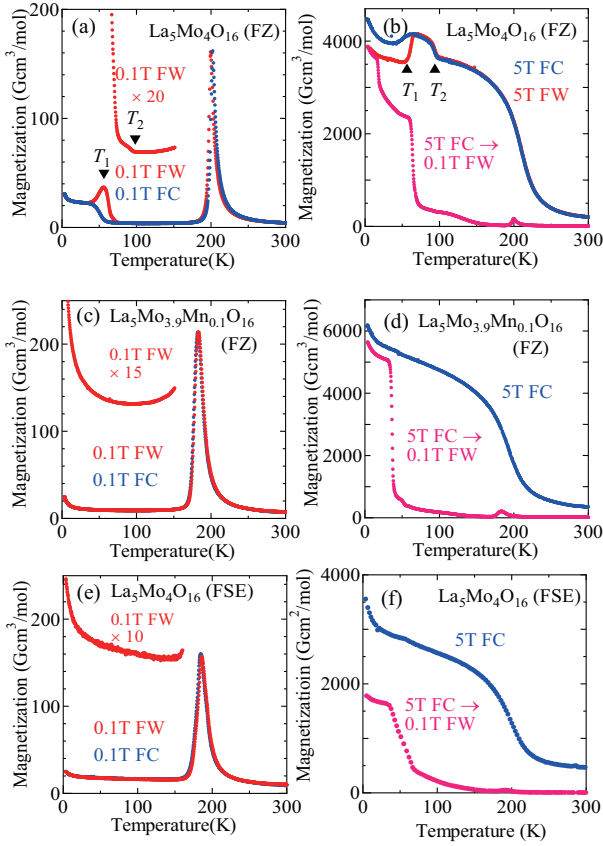
FIG. 2: (color online) Temperature dependence of magnetization for the FZ crystal of $La_5Mo_4O_{16}$ and $La_5Mo_{3.9}Mn_{0.1}O_{16}$ and the FSE crystal of $La_5Mo_4O_{16}$ at various conditions. For the details, see text.
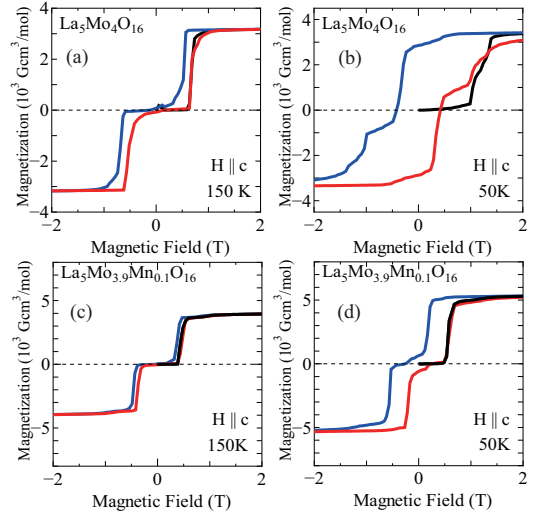

FIG. 3: (Color online) Magnetic-field dependence of magnetization for $La_5Mo_4O_{16}$ at (a) 150 K and (b) 50 K and for $La_5Mo_{3.9}Mn_{0.1}O_{16}$ at (c) 150 K and (d) 50 K.
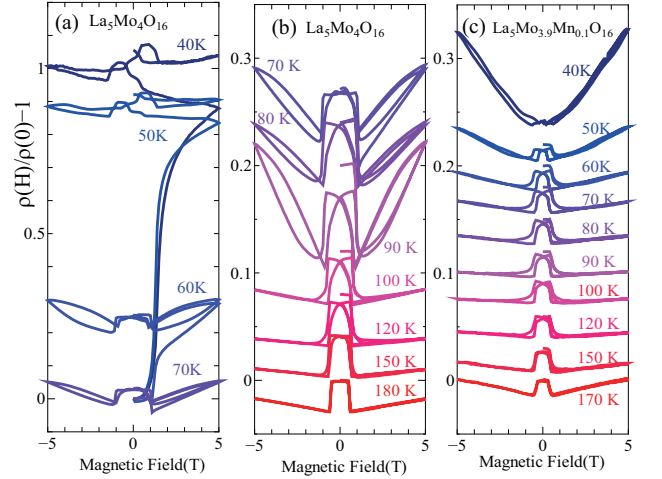

FIG. 4: (Color online) Magnetic-field dependence of resistivity for $La_5Mo_4O_{16}$ (a) below 70 K and (b) above 70 K, and (c) for $La_5Mo_{3.9}Mn_{0.1}O_{16}$.

transition from the antiferromagnetic alignment of the ferrimagnetic moment along the c axis (the AFM state) to the ferromagnetic alignment (the FM state), as also observed in the FSE crystal.[23] On the other hand, we found that the $M(H)$ curve below T_1 shows a hysteresis loop reminiscent of ferromagnets, in which M does not remain at zero after the initial magnetization, as shown in Fig. 3 (b). Such a marked change in the behavior of $M(H)$ with T was barely observed for the $La_5Mo_{3.9}Mn_{0.1}O_{16}$ FZ crystal [Figs. 3 (c), (d)] or for the previously reported[23] FSE crystal of $La_5Mo_4O_{16}$. The $M(H)$ curves at other temperatures are shown in the supplementary material.[25]

We measured the magnetoresistance $\rho(H)$ along the c axis at various T. Figure 4 (b) shows the $\rho(H)$ curves from 180 to 70 K, where ρ decreases at $|H| \sim 0.5$ T with increasing $|H|$, corresponding to the metamagnetic transition shown in Fig. 3 (a). This is the same behavior as observed in the previously reported FSE crystal.[23] On the other hand, below $T_1 = 60$ K [Fig. 4 (a)], a large increase in ρ is observed only in the initial magnetization process, and $\Delta\rho/\rho$ amounts to ~ 100 % at 40 K. With further increasing and sweeping of H between ± 5 T below T_1, ρ remains at large values with a small structure

near $H = 0$ T. These results, together with the experimental result that M does not remain at zero after the initial magnetization process below T_1 [Fig. 3 (b)], imply that the magnetic state below T_1 without H is different from the AFM state observed above T_1. We also found that such an anomalous increase in $\rho(H)$ in the initial magnetization process disappears in the FSE crystal of $La_5Mo_4O_{16}$[23] and in the FZ crystal of $La_5Mo_{3.9}Mn_{0.1}O_{16}$ [shown in Fig. 4 (c)].

Associated with such an anomalous increase in ρ in the initial magnetization process, we found that the change in ρ and M with H exhibits a time dependence, namely, a relaxation behavior. Fig. 5 (a) shows the t dependence of $\rho(t)/\rho(t = 0) - 1$ when $H = 1$ T is applied between $t = -60$ s to 0 s. An increase in ρ with t after H is fixed
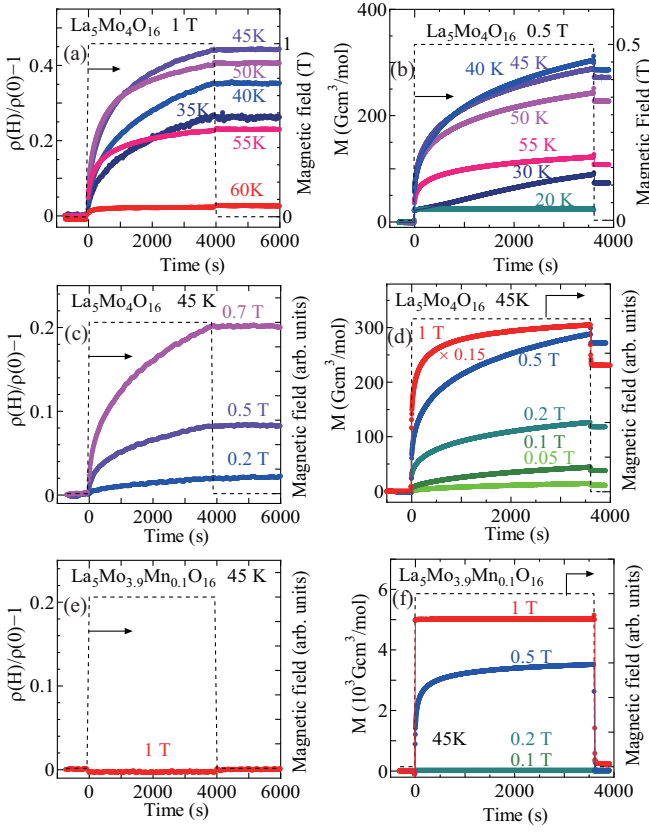
FIG. 5: (Color online) Time dependence of (a)(c)(e) resistivity and (b)(d)(f) magnetization for (a)(b)(c)(d) $La_5Mo_4O_{16}$ (a)(b) at a fixed magnetic field at various temperatures, and (c)(d) at 45 K at various magnetic fields, and for (e)(f) $La_5Mo_{3.9}Mn_{0.1}O_{16}$ at 45 K at various magnetic fields. The dashed lines in each panel indicate the t dependence of H.

to 1 T is observed over several thousand seconds for a wide range of T below $T_1 = 60$ K, and the change in ρ with t amounts to 40 % at around 50 K. Fig. 5 (b) shows the time (t) dependence of the magnetization M when $H = 0.5$ T is applied between $t = -20$ s to 0 s. The time evolution of M was also observed at various T.

It should be pointed out that the time evolution of M has been observed in an FSE crystal of the same compound[24] but not for ρ. The time evolution of ρ has been observed in several manganites exhibiting colossal magnetoresistance.[7–10] In these cases, there are two minima in the free energy corresponding to two magnetic states [antiferromagnetic (AFM) and ferromagnetic (FM)] states] with an energy barrier between them, and the magnetic field induces a transition from the AF state to the FM state, resulting in the time evolution of the FM state. In such a situation, there is a threshold of the magnetic field inducing the FM state.

In contrast to such magnetic relaxation behavior in "conventional" magnets, we found that both ρ and M for the FZ crystal of $La_5Mo_4O_{16}$ exhibit relaxation at low H without a threshold. Fig. 5 (c) shows the t dependence of ρ after various values of H are applied at 45 K. The

relaxation in ρ is observed down to 0.2 T, which is much smaller than the H value necessary for the relaxation behavior of ρ in various manganites. Fig. 5 (d) shows the t dependence of M after various values of H are applied at 45 K, where the time evolution of M is observed down to $H = 0.05$ T. Similar behaviors are observed between 55 and 30 K in the same compound (shown in the supplementary material.[25]) These results are not consistent with the relaxation behavior in compounds with a double-minimum structure in the free energy, but resemble the behavior of disordered systems (e.g., spin-glass compounds) with multivalley energy structures.

We also found that the relaxation in M for $La_5Mo_{3.9}Mn_{0.1}O_{16}$ exhibits a clear threshold in terms of H, similarly to the magnets with competing two phases, as shown in Fig. 5 (f). Namely, M is much less than 100 Gcm^3/mol for $H < 0.4$ T but immediately becomes 5000 Gcm^3/mol for $H > 0.7$ T and exhibits relaxation behavior only at $H \sim 0.5$ T. This suggests that the double-minimum-potential model can be applied to the Mn-doped compound, as is the case for the $La_5Mo_4O_{16}$ FSE crystal.[24] Furthermore, we barely observed the relaxation of ρ in $La_5Mo_{3.9}Mn_{0.1}O_{16}$, as shown in Fig. 5 (e). This is consistent with the absence of an anomalous increase in ρ in the initial magnetization process for this compound [shown in Fig. 4 (c)].

To show the overall features of the t dependence of M and ρ, we made 3D plots of $\log[M(t = 3600s)/M(t = 0s)]$ and $[\rho(t = 4000s) - \rho(t = 0s)]/\rho_0 H$, where $t = 0$ s is the time immediately after the magnetic field H is applied and ρ_0 is the resistivity without a magnetic field, as a function of H and T for $La_5Mo_4O_{16}$ [M in Fig. 6 (a) and ρ in Fig. 6 (b)] and $La_5Mo_{3.9}Mn_{0.1}O_{16}$ [M in Fig. 6 (c)]. As can be seen, large values of $\log[M(t)/M(0)]$ and $[\rho(t) - \rho(0)]/\rho_0 H$ are distributed over wide ranges of H (between 0 and 1 T) and T (between 60 and 30 K) for $La_5Mo_4O_{16}$ [Fig. 6 (a) (b)]. On the other hand, large values of $\log[M(t)/M(0)]$ are localized at around $H = 0.5$ T for $La_5Mo_{3.9}Mn_{0.1}O_{16}$ [Fig. 6 (c)].

Such anomalous behaviors in the initial magnetization process for the FZ crystal of $La_5Mo_4O_{16}$ suggest that the magnetic state below T_1 is a disordered state. When H is applied to a long-range AFM state, the transition to the FM state occurs when H exceeds a critical value H_c, where the ferrimagnetic moments originally aligned antiferromagnetically along the c axis are changed to the FM alignment. However, when H is applied to a magnetically disordered state, the flip of the ferrimagnetic moment to the direction of H can occur at various values of H, resulting in a gradual change to the FM state over a wide range of H. This is equivalent to stating that there are various magnetic states with local minima in the free energy with various values of the net magnetization M below T_1, and with applied magnetic field H, the magnetic state changes from that with $M = 0$ to that with a larger M by overcoming the energy barriers with various heights.

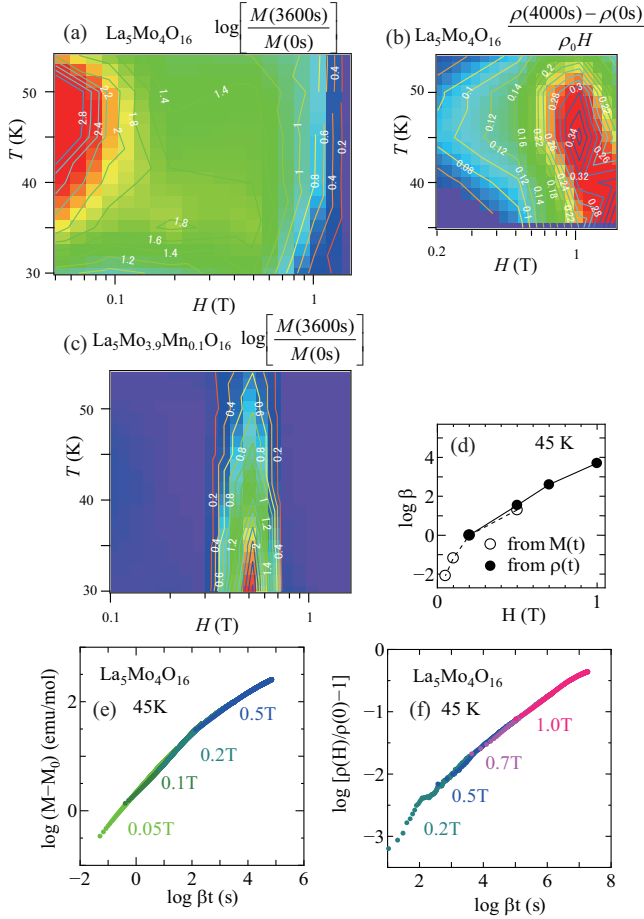We assume that the t dependence of M is given by the

FIG. 6: (Color online) (a)(b)(c) 3D plots of (a)(c) $\log[M(t = 3600\text{s})/M(t = 0\text{s})]$ and (b) $[\rho(t = 4000\text{s}) - \rho(t = 0\text{s})]/\rho_0 H$ for (a)(b) $La_5Mo_4O_{16}$ and (c) $La_5Mo_{3.9}Mn_{0.1}O_{16}$. (d) Parameter β for the scaling plot. (e)(f) Scaling plots of (e) magnetization and (f) resistivity vs time for $La_5Mo_4O_{16}$. β is unity for the data of $H = 0.02$ T.

sum of the relaxation functions with different relaxation times,

$$M = M_0 + \sum_i M_i \left\{ 1 - \exp\left(-\frac{t}{\tau_i}\right) \right\}, \qquad (1)$$

where M_0 gives the immediate response of M to H. We also assume that the relaxation time for the ith component, τ_i, has an activation-type T dependence with an activation energy of Δ_i, which decreases linearly with increasing magnetic field H.

$$\tau_i = \tau_i^0 \exp\left(\frac{\Delta_i - \alpha H}{k_B T}\right) \qquad (2)$$

Here, if α does not depend on i (although it may depend on H and T), then

$$M = M_0 + \sum_i M_i \left[1 - \exp\left\{ -\frac{\beta t}{\tau_i^0 \exp\left(\Delta_i / k_B T\right)} \right\} \right] \qquad (3)$$

where

$$\beta = \exp\left(\alpha H / k_B T\right) \qquad (4)$$

Note that in the formula for M given by eq. (3), H appears only in β. This means that if t is normalized appropriately by a factor of β determined by both H and T, all the $M(t)$ curves at each T at various values of H merge to a single curve. Figure 6 (e) shows such a scaling plot of the data at 45 K. We found that not only M but also ρ exhibits such scaling behavior, as shown in Fig. 6 (f). The parameter β is plotted as a function of H in Fig. 6 (d). We also confirmed that such scaling behavior holds between 55 and 40 K for both M and ρ (shown in the supplementary material.[25]) This result implies that the relaxation behavior in this compound is dominated by bulk properties and not by domain boundaries.

How does a magnetically disordered state appear below T_1? A possible scenario is that there is a change in the pattern of charge ordering that causes a change in the sign of the interlayer magnetic interaction. As described in the introduction, there are two inequivalent Mo sites on the square lattice in a checkerboard pattern, and along the c axis, the Mo^{4+} ion exists next to the Mo^{4+} ion and Mo^{5+} exists next to Mo^{5+}. However, the compound can save its long-range Coulomb repulsion energy by placing Mo^{4+} next to Mo^{5+}, even along the c axis. This causes a change in the occupation pattern of Mo1 and Mo2. Namely, Mo1 is occupied by Mo^{4+} and Mo2 is occupied by Mo^{5+} every two layers.[26] Associated with such a change in the charge-ordering pattern (charge rearrangement) possibly occurring at T_1, a connection between the Mo^{4+} ion and the Mo^{5+} ion via the Mo_2O_{10} pillar appears. Interestingly, in this charge-ordered state, the *antiferromagnetic* alignment of the two moments along the c axis results in the *ferromagnetic* alignment of the ferrimagnetic moment at each layer along the c axis. Namely, the effective interlayer magnetic interaction changes from AFM to FM with the charge rearrangement.

Such a possible sign change in the interlayer magnetic interaction occurs far below the ferrimagnetic ordering temperature (~ 200 K), where the Mo spins are strongly coupled within a layer and behave as one spin. We speculate that the charge rearrangement at T_1 requires the reorientation of such a spin, which is composed of many spins strongly coupled within a layer, but they eventually fail to fall into a regular FM arrangement and remain in a disordered state along the c axis because of the difficulty in simultaneously flipping many spins. This disordered state can lead to the anomalous relaxation behaviors when the magnetic field is applied. It is known that such charge ordering is fragile against disorder,[27,28] and we speculate that the charge rearrangement disappears in the Mn-doped sample and the FSE crystal, where the high-T arrangement of Mo^{4+} and Mo^{5+} and the AF configuration of the ferrimagnetic moment along the c axis survive down to the lowest T. We also point out that the anomaly at $T_2 = 95$ K may be caused by another type of charge ordering (charge rearrangement), where

the number of the d electrons on the Mo2 ion (nominally Mo^{4+}) is enhanced whereas that on the Mo1 ion (nominally Mo^{5+}) is suppressed. Namely, the number of the d electrons is $1.5 + \delta$ and $1.5 - \delta$ on the Mo2 and the Mo1 ion, respectively, with the δ value of less than 0.5 above T_2, but the δ value increases and approaches 0.5 below T_2, inducing the localization of the d electrons. This can explain the increase in ρ [Fig. 1 (c)] and M at 5 T [Fig. 2 (b)] at T_2 with decreasing T.

Finally, let us discuss the possible mechanism of magnetoresistance in the present compound. In Ref. 23, the magnetoresistance of the $La_5Mo_4O_{16}$ crystal grown by the FSE method was measured only along the c axis, and was interpreted as the tunneling-type magnetoresistance based on the smaller resistance in the ferromagnetic configuration of the ferrimagnetic moment along the c axis. In the present study, we measured the magnetoresistance also along the ab plane, and found that the behaviors are similar to those along the c axis, as shown in the supplementary material.[25] This indicates that the origin of the magnetoresistance is not a tunneling-type but the three-dimensional electronic structure changes with the change in the configuration of the ferrimagnetic moment along the c axis. Another issue that should be considered is the positive magnetoresistance in the initial magnetization process; the resistivity becomes higher with the ferromagnetic configuration compared with the random configuration along the c axis. A possible idea to explain this result is that the random configuration of the magnetic moment along the c axis induces disorder in the potential for electrons and yields impurity states, which causes the hopping conduction in the impurity band.

IV. SUMMARY

We studied the resistivity and magnetization of $La_5Mo_4O_{16}$ and $La_5Mo_{3.9}Mn_{0.1}O_{16}$ grown by the float-

ing zone (FZ)technique. We found that, in addition to the antiferromagnetic ordering at $T_N \sim 200$ K, anomalies appear at $T_1 \sim 60$ K and $T_2 \sim 95$ K in the temperature (T) dependence of both resistivity (ρ) and magnetization (M) for the FZ crystal of $La_5Mo_4O_{16}$, though these anomalies disappear for the Mn-doped crystal or that grown by the fused-salt electrolysis method. We also found that a large positive magnetoresistance appears below T_1 only in the initial magnetization process for the FZ crystal of $La_5Mo_4O_{16}$. Furthermore, both ρ and M exhibit a time (t) dependence, $i.e.$, a relaxation behavior, when the magnetic field (H) is applied. In contrast to the magnetic relaxation behavior in conventional magnets, it occurs down to low H without any threshold. We found that the curves of both ρ and M vs t at various values of H merge to a single curve if t is normalized at each T. These experimental results indicate that the magnetic state below T_1 is a disordered one, and with the applied H, the magnetic state changes to that with a larger M by overcoming energy barriers with various heights. We propose a possible scenario that the charge rearrangement of Mo^{4+} and Mo^{5+} occurs below T_1 and it causes a change in the sign of the effective interlayer magnetic interaction from antiferromagnetic to ferromagnetic, resulting in the random configuration of the ferrimagnetic moment along the c axis.

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