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Magnetoresistance in a doped Mott-Hubbard system: RTiO$_3$

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We studied the magnetoresistance of RTiO$_3$ ($R =$ Pr and Ce) with offstoichiometry as a doped Mott-Hubbard system and found positive magnetoresistance proportional to the absolute value of the magnetic field in the antiferromagnetic phase of both insulating and metallic samples. This result indicates that not only the coherent state that appears with doping and is responsible for the metallic conduction, but also the incoherent state of the Mott-Hubbard insulator is affected by the spin configuration.

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Magnetoresistance in strongly correlated electron systems often arises from the coupling between magnetic moments and itinerant carriers. A typical example is the large (colossal) magnetoresistance observed in perovskite manganites, in which three t_{2g} electrons acting as a localized magnetic moment and an e_g electron acting as an itinerant carrier, both in the Mn d state, are coupled by the so-called Hund coupling. The transfer of the itinerant electrons is favored by aligning the t_{2g} moments with an applied magnetic field, resulting in the suppression of electronic resistance, i.e., negative magnetoresistance [1].

On the other hand, magnetoresistance in Mott-Hubbard systems, in which only the transfer of electrons and the on-site Coulomb repulsion between two electrons are dominant, has been much less studied. Typically, a Mott-Hubbard system with an integer number of electrons per site becomes insulating (a Mott insulator) with magnetic ordering at low temperatures, whereas with hole/electron doping, it changes into a metallic state with suppression of the magnetic ordering. Characteristic properties, for example, enhanced effective mass and reduced Drude weight, are observed near the metal-insulator phase boundary in a doped Mott-Hubbard system [2]. It will be interesting to clarify how a magnetic field affects the electronic structure and charge dynamics of such a Mott-Hubbard system, although there have been few studies on this issue [3–7], presumably because a relatively large magnetic field is necessary to produce a detectable effect on such a system having a small magnetic susceptibility.

Perovskite RTiO$_3$ ($R =$ rare earth) [8–16] is a typical Mott-Hubbard system with a d^1 electron configuration on the Ti^{3+} site. When R is one of the rare earths between La and Sm, RTiO$_3$ becomes antiferromagnetic at low temperatures with a small ferromagnetic component arising from the Dzyaloshinskii-Moriya (D-M) interaction, and it becomes metallic with the substitution of Ca or Sr for the R site or the introduction of excess oxygen, which leads to hole doping into the Ti sites. It is known that the antiferromagnetic phase survives across the insulator-metal phase boundary, and thus, an antiferromagnetic metallic phase exists in the hole-doped RTiO$_3$ [17]. In this paper, we report the magnetoresistance of PrTiO$_3$ and CeTiO$_3$ with hole doping by offstoichiometry. We found positive magnetoresistance in the hole-doped RTiO$_3$, and its magnitude is proportional to the absolute value of the magnetic field $|H|$. Such an $|H|$-dependent positive magnetoresistance can be explained by assuming that the resistivity changes proportionally to the square of the magnetization and that the magnetization increases from a finite value at zero field (spontaneous magnetization) with increasing magnetic field. We also found that such an $|H|$-dependent positive magnetoresistance is observed in both an insulating sample and a metallic sample in a quantitatively similar manner, although the absolute values of the resistivity are different by several orders of magnitude.

We grew single crystals of PrTiO$_3$ (PTO) and CeTiO$_3$ (CTO) by the floating-zone technique as described elsewhere [11]. The composition of each sample was determined by the induction coupled plasma analysis and thermogravimetric analysis, and found that PTO with $T_N = 107$ K is Pr$_{0.932}$TiO$_{3.004}$ (nominal hole number $p = 0.21$), PTO with $T_N = 90$ K is Pr$_{0.926}$TiO$_{3.007}$ ($p = 0.24$), and CTO with $T_N = 77$ K is Ce$_{0.984}$TiO$_3$ ($p = 0.05$) [18]. The axes of the grown crystals were determined by the Laue method. We found that for the crystals of PTO, the c axis in the orthorhombic setting, which is along the [001] axis of the cubic perovskite structure, can be distinguished from the [100] and [010] axes (in the cubic setting), but the a and b axes, which are along the [110] and [1$\bar{1}$0] axes in the cubic setting, respectively, cannot be distinguished by our Laue measurement because of the small difference in the lattice constants. Thus, we defined the [110] axis as that along which the spontaneous magnetization is larger, which is presumably the a axis according to the discussion of symmetry for the D-M interaction [19], and the [1$\bar{1}$0] axis as that along which the spontaneous magnetization is smaller (b axis). On the other hand, for CTO, we found that the three principal axes of the perovskite structure in the cubic setting are mixed in the grown crystals. Resistivity was measured by a conventional four-probe technique with applied magnetic fields of up to 7 T. Magnetization was measured by a SQUID magnetometer [17].

Figure 1(a) shows the temperature (T) dependence of the magnetization (M), which was measured with an applied magnetic field (H) of 100 G while increasing the temperature after decreasing T to the lowest value with $H = 7$ T. The increase of $M(T)$ at low T corresponds to the antiferromagnetic ordering with a small ferromagnetic component cause by the D-M interaction. Figure 1(b) shows the T dependence of the resistivity (ρ) for PTO. ρ for the sample with $T_N = 90$ K is

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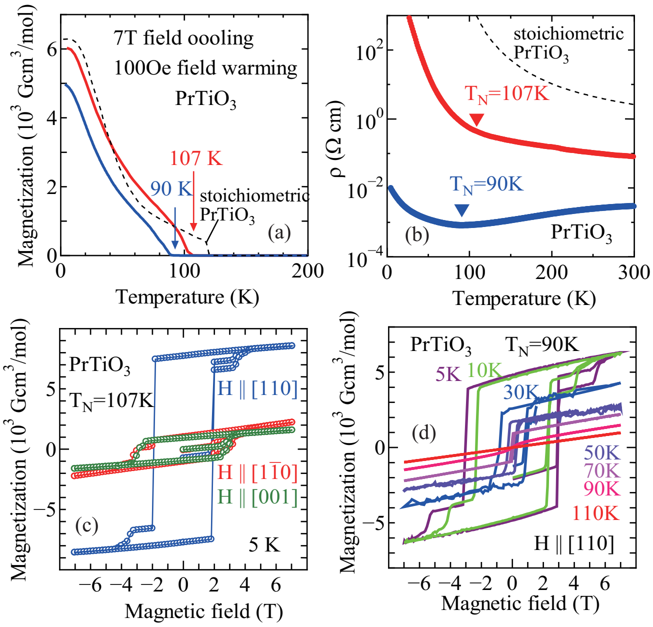

FIG. 1. (Color online) (a)(b) Temperature dependence of (a) magnetization and (b) resistivity for two $PrTiO_3$ single crystals (solid lines) and stoichiometric $PrTiO_3$ (dashed line, from Ref. 11). Note that 5585 Gcm^3/mol corresponds to 1 μ_B/f.u. (c) Magnetization vs magnetic field along various directions at 5 K for $PrTiO_3$ with $T_N = 107$ K. (d) Magnetization vs magnetic field along the [110] direction at various temperatures for $PrTiO_3$ with $T_N = 90$ K.

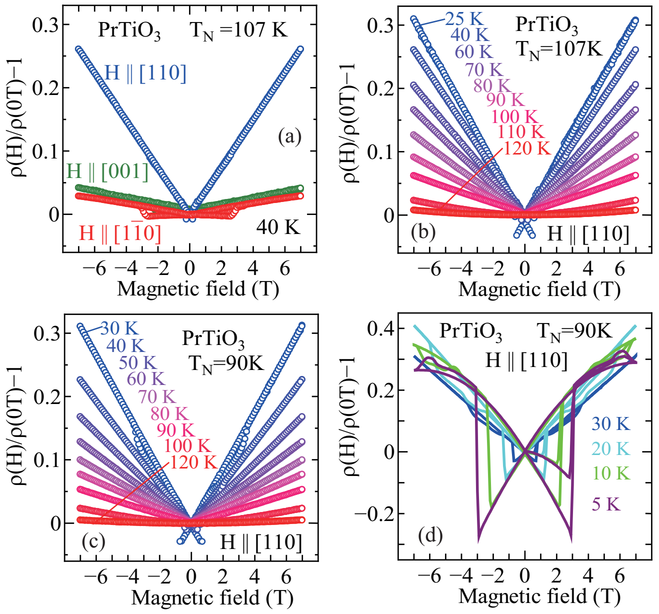

FIG. 2. (Color online) (a)(b) Magnetic field dependence of resistivity normalized to the value at zero magnetic field, $\rho(H)/\rho(0T) - 1$, for $PrTiO_3$ with $T_N = 107$ K (a) at 40 K with various directions of the magnetic field and (b) at various temperatures with the magnetic field along the [110] direction. (c)(d) $\rho(H)/\rho(0T) - 1$ for $PrTiO_3$ with $T_N = 90$ K with the magnetic field along the [110] direction (c) between 120 and 30 K and (d) between 30 and 5 K.

less than 10^{-2} Ωcm over the entire T range, whereas ρ for the sample with $T_N = 107$ K increases with decreasing T and diverges at the lowest T, even though the absolute values are still smaller than those of stoichiometric PTO, shown by a dashed line.

Figure 2(a) shows the changes in ρ with the applied magnetic field at 40 K, where ρ is normalized to the absolute value at $H = 0$, $\rho(H)/\rho(0T) - 1$, for the PTO sample with $T_N = 107$ K exhibiting insulating behavior. As can be seen, ρ increases with increasing H (positive magnetoresistance), and the rate of increase is the largest when H is applied along the [110] direction. Note that M is also the largest when H is applied along the [110] direction, as shown in Fig. 1 (c). Furthermore, $\rho(H)/\rho(0T) - 1$ shows an $|H|$-linear dependence, although in many compounds magnetoresistance scales with H^2. Figure 2(b) shows $\rho(H)/\rho(0T) - 1$ with the magnetic field along the [110] direction at various temperatures T. As can be seen, positive magnetoresistance appears below $T_N = 107$ K, and $\rho(H)/\rho(0T) - 1$ is proportional to H^2 near T_N [17]. However, it changes to an $|H|$-linear dependence at approximately 100 K and the coefficient of the $|H|$-linear term increases with decreasing T down to 25 K. Below 25 K, the resistivity of this sample is too high to be measured.

We also performed the same measurement on the PTO sample with $T_N = 90$ K exhibiting metallic behavior [Fig. 2(c)]. Surprisingly, $\rho(H)/\rho(0T) - 1$ exhibits almost the same behavior as that of the insulating PTO with $T_N = 107$ K down to 30 K, positive magnetoresistance below T_N and an $|H|$-linear dependence at low T. Upon further decreasing T to below 30 K, $\rho(H)/\rho(0T) - 1$ deviates from the $|H|$-linear dependence and an H^2 term with a negative coefficient is superposed [Fig. 2(d)]. Furthermore, the hysteresis of $\rho(H)/\rho(0T) - 1$ is observed upon sweeping H, and the range in which hysteresis is observed becomes wider with decreasing T. At 5 K, the hysteresis appears between 3 and −3 T, which corresponds to the range of the hysteresis in $M(T)$, as shown in Fig. 1(d). At both ends of the hysteresis range (at 3 and −3 T), $\rho(H)/\rho(0T) - 1$ jumps by ∼ 40%, indicating the correlation of the flip of the magnetization with H and resistivity.

Note that such an $|H|$-linear dependence of the magnetoresistance in the magnetically ordered phase with spontaneous magnetization has been observed in $Fe_{1-x}Co_xSi$ with helical magnetic ordering [20,21]. Regarding this behavior, Onose *et al.* proposed that if the magnitude of the electrical resistivity ρ scales with M^2 and the increase in M with H in the phase with spontaneous magnetization M_0 is given by $M = M_0 + \alpha H$, a seemingly H-linear dependence of ρ appears as $M^2 - M_0^2 \sim 2\alpha M_0 H$ [21]. On the basis of this idea, we calculated the magnetization under various applied magnetic fields and the possible magnetoresistance for PTO. In the calculation, we assumed the antiferromagnetic interaction between neighboring Ti spins (J), the D-M interaction between neighboring Ti spins (D), and the ferromagnetic interaction between Ti spins and neighboring Pr moments (J'), and solved the problem by performing a mean-field approximation. The D-M interaction leads to the appearance of spontaneous magnetization below T_N, and the ferromagnetic Ti-Pr interaction leads to an increase in the spontaneous magnetization below ∼ 50 K, as shown in Figs. 3(a) and 3(b). Furthermore, the ferromagnetic Ti-Pr interaction is critically important in enhancing the increase in the ferromagnetic component of the Ti magnetization with

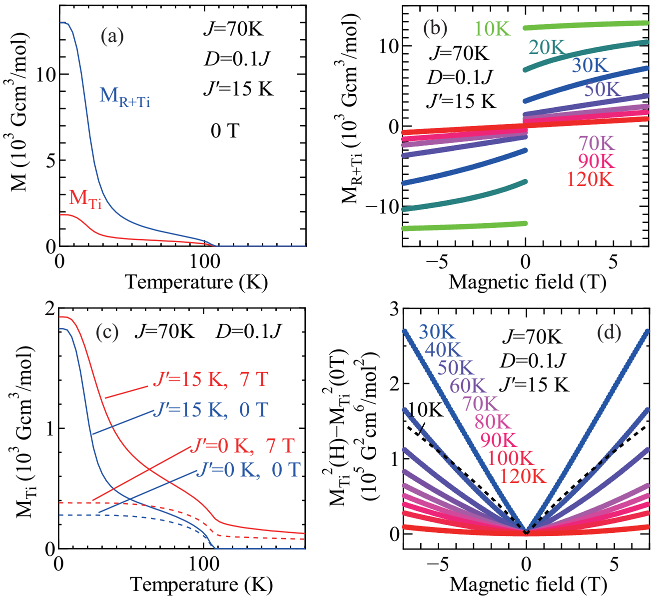

FIG. 3. (Color online) (a) Calculated magnetization for the Ti spin and the total magnetization (the sum of the R and Ti magnetizations) at 0 T. (b) Calculated total magnetization vs magnetic field at various temperatures. (c) Calculated Ti magnetization at 0 and 7 T with (solid lines) and without (dashed lines) the Ti-Pr ferromagnetic interaction J'. (d) Calculated square of the ferromagnetic component in the Ti magnetization (M_{Ti}^2) at H minus that at $H = 0$ T as a function of the magnetic field at various temperatures.

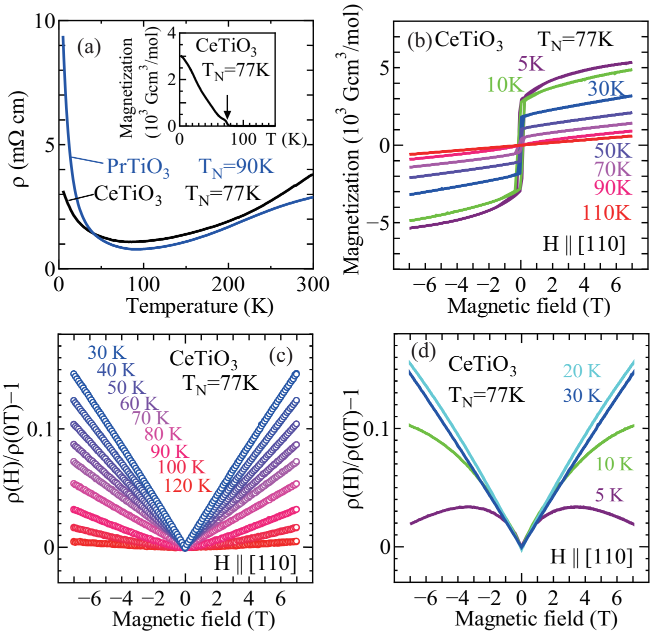

FIG. 4. (Color online) (a) Temperature dependence of resistivity for $\mathrm{CeTiO_3}$ with $T_{\mathrm{N}} = 77$ K and $\mathrm{PrTiO_3}$ with $T_{\mathrm{N}} = 90$ K. The inset shows the magnetization as a function of the temperature for $\mathrm{CeTiO_3}$. (b) Magnetization vs magnetic field for the $\mathrm{CeTiO_3}$ crystal. (c)(d) $\rho(H)/\rho(0\mathrm{T}) - 1$ for the $\mathrm{CeTiO_3}$ crystal (c) between 120 and 30 K and (d) between 30 and 5 K.

the applied magnetic field. Figure 3(c) shows the calculated ferromagnetic component of the Ti spins (M_{Ti}) with (solid lines) and without (dashed lines) the Ti-Pr interaction at 0 and 7 T. As can be seen, not only the spontaneous magnetization M_{Ti} at 0 T, but also the difference between M_{Ti} at 7 T and that at 0 T is enhanced with a finite-magnitude Ti-Pr interaction. This means that the Ti-Pr interaction effectively enhances the magnetic field on the Ti spins [17].

Figure 3(d) shows the square of the ferromagnetic component in the Ti magnetization (M_{Ti}^2) at H minus that at $H = 0$ T, which should be proportional to the magnetoresistance, $\rho(H)/\rho(0\mathrm{T}) - 1$, assuming that the change in resistivity is proportional to the square of the ferromagnetic component in the Ti magnetization. An $|H|$-linear dependence is clearly seen, and the coefficient of the $|H|$-linear coefficient increases with decreasing T down to 30 K, but is suppressed at 10 K. These results are qualitatively consistent with the experimental results shown in Figs. 2(b) and 2(c).

The hysteresis observed in ρ upon sweeping H and the large jump in ρ at the ends of the hysteresis (3 or −3 T) can be explained as follows. If a sufficiently large magnetic field is applied to the crystal in the positive direction, the ferromagnetic component arising from the canting of the antiferromagnetically ordered Ti spins (caused by the D-M interaction) is oriented in the positive direction, and the canting angle is increased from that at zero magnetic field. If the magnetic field is decreased to zero and then increased in the negative direction, the canting angle of the Ti spins is decreased to the value at zero magnetic field and continues to decrease as long as the ferromagnetic component is still oriented in the positive direction and the magnetic field in the negative direction acts as a backward field. However, when the magnitude of the magnetic field exceeds the coercive field and the ferromagnetic component flips in the negative direction, the magnetic field in the negative direction acts as a forward field, resulting in a sudden increase in the canting angle of the Ti spins [17].

We also performed the same measurement on a CTO crystal ($T_{\mathrm{N}} = 77$ K) with twinned structures in terms of the orthorhombic distortion. As shown in Fig. 4(a), the behavior of $\rho(T)$ for the CTO crystal is similar to that for PTO with $T_{\mathrm{N}} = 90$ K; both exhibit metallic behavior. Spontaneous magnetization appears below $T_{\mathrm{N}} = 90$ K, as shown in Fig. 4(b). $|H|$-linear dependence with a positive sign of $\rho(H)/\rho(0\mathrm{T}) - 1$ and deviation from the $|H|$-linear dependence below 20 K are clearly observed in CTO, as shown in Figs. 4(c) and 4(d), similarly to the behaviors of PTO. The absence of the hysteresis in $\rho(H)/\rho(0\mathrm{T}) - 1$ as a function of H is consistent with the small coercive field observed in the $M(H)$ curve even at the lowest T for CTO [Fig. 4(b)]. The negative coefficient of the H^2 component in $\rho(H)/\rho(0\mathrm{T}) - 1$ for CTO, which results in the deviation from its $|H|$-linear dependence, seems comparable to that for PTO shown in Fig. 2(d).

The M^2 dependence of the magnetoresistance, which is likely to cause the seemingly $|H|$-linear dependence in the presence of spontaneous magnetization in $R\mathrm{TiO_3}$, is commonly observed in various metallic compounds such as perovskite manganites [1]. A possible origin of this M^2-dependent magnetoresistance is the splitting of the conduction band by spin polarization. Issues unique to the present system are (1) there is no obvious distinction between the itinerant carriers and the localized magnetic moments because of the d^1 electron configuration, and (2) the magnetic order below T_N is noncollinear and the canting of the magnetic moment with an applied magnetic field results in a large magnetoresistance in the magnetically ordered phase. It will be challenging to establish how such a noncollinear spin structure can be constructed from itinerant d^1 electrons and how the spin-polarized band can be described theoretically in such a case.

The present experimental results and the analysis indicate that the magnetoresistance does not depend on the detailed electronic structure of the doped Mott insulators. Theoretically, it has been proposed that upon doping into a Mott insulator, a quasiparticle peak, which is responsible for the metallic conduction and called a coherent state, appears between the upper Hubbard band and the lower Hubbard band (called incoherent states) in the density of states [22–24]. Experimentally, however, the system often remains insulating (with no coherent state) with a small amount of doping [11]. Such an insulating phase in doped Mott insulators has been attributed to Anderson localization caused by the disorder arising from the dopant (excess oxygen in the present case), or the formation of small polarons, i.e., the coupling between doped carriers and the local lattice distortion [2], although there have been no experimental results to confirm these ideas.

In the present system, the ground state of PTO with $T_N = 107$ K is insulating, whereas PTO with $T_N = 90$ K and CTO with $T_N = 77$ K are metallic. In spite of this critical difference, the behaviors of magnetoresistance are similar for these samples. This cannot be reconciled with the picture that only the coherent state responsible for the metallic conduction, which is absent in the insulating PTO, is affected by the spin configuration. However, we need to assume that both the coherent and incoherent states in the doped Mott insulator are affected by the spin configuration in almost the same manner [25].

In summary, we measured the magnetoresistance of a doped Mott-Hubbard system, $R\text{TiO}_3$ (R = Pr and Ce), and found an $|H|$-linear dependence of the positive magnetoresistance, whose magnitude hardly depends on whether the ground state of the compounds is insulating or metallic, in the antiferromagnetic phase with a small spontaneous magnetization. This $|H|$-linear dependence can be explained by assuming that the magnetoresistance is proportional to the square of the Ti magnetization (M_{Ti}^2) and that M_{Ti} increases with H from the value at $H = 0$. We calculated a model in which the antiferromagnetic interaction between Ti spins, the D-M interaction between neighboring Ti spins and the ferromagnetic interaction between the Ti spin and Pr moment are taken into account, and found that it can qualitatively reproduce the experimental results. The fact that the behavior hardly depends on the ground state indicates that not only the coherent state that is responsible for the metallic conduction, but also the incoherent state of the doped Mott-Hubbard system is affected by the spin configuration.

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[18] We cannot perform the thermogravimetric analysis for CeTiO_3 because of the unstable final state of the Ce ions (3+ or 4+) when oxidized, and thus, $\text{Ce}_{1-x}\text{TiO}_3$ was assumed in the analysis.

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