Hall effect in $La_{1-x}Sr_xMnO_3$

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The Hall effect and its systematic variation with doping level (x) and temperature have been investigated for crystals of $La_{1-x}Sr_xMnO_3$ ($0.18 \leqslant x \leqslant 0.50$) with perovskite structure. The ordinary Hall coefficient (R_H) at 4.2 K indicates that the carrier is a hole, and that its density (n) is nearly x independent ($R_H \approx 0.4$ cm^3/C or $n \approx 1$ hole/Mn site) even near the compositional insulator-metal phase boundary. The anomalous part of the Hall effect, which originates from the asymmetric scattering of charge carriers by local spin moments, is negative and strongly x and T dependent. The anomalous Hall coefficient was found to scale with 3/2 power of the change of magnetization irrespective of x. [S0163-1829(98)03326-8]

The carrier-doped perovskite manganese oxide $La_{1-x}Sr_xMnO_3$ shows a ferromagnetic metallic (FM) state below a Curie temperature T_C above the critical composition of $x_c \approx 0.17$.[1,2] The substitution of La^{3+} by Sr^{2+} ions produces holes in the e_g orbitals which are strongly hybridized with oxygen $2p$ states. In the FM state, the ferromagnetic interaction between localized t_{2g} spins (spin quantum number $S=3/2$) is mediated by itinerant e_g electrons (double-exchange interaction).[3–7] The intra-atomic exchange interaction (i.e., Hund's coupling J_H) is much larger than the e_g electron transfer integral (t_{ij}) and hence the e_g conduction band completely splits into, say, an empty upper and a partially filled lower band by an order of J_H even above T_C.[8] Below T_C, the population of up-spin electrons in the lower band grows corresponding to the evolution of the magnetization while that of down-spin electrons decreases. At $T=0$ K, therefore, the e_g carriers are expected to be 100% spin polarized and thus $La_{1-x}Sr_xMnO_3$ is a half-metallic ferromagnet. In the FM state, no static Jahn-Teller distortion of MnO_6 octahedron has been observed[9] and hence there remains the orbital degree of freedom, namely, the double degeneracy of e_g orbitals ($d_{3z^2-r^2}$ and $d_{x^2-y^2}$, or their linear combinations).

In this paper we report on the Hall effect in crystals of $La_{1-x}Sr_xMnO_3$ and its systematic variation with doping level ($0.18 \leqslant x \leqslant 0.50$) and temperature, which tell us not only the character of doped charge carriers but also the nature of the magnetic scattering in the FM state. In particular, x-dependent variation of the ordinary Hall coefficient would be of considerable interest in light of the doping-induced insulator-metal transition in the correlated electron system. Furthermore, the half-metallic nature of $La_{1-x}Sr_xMnO_3$, as a prototypical double-exchange system, may provide us a unique opportunity of quantifying anomalous Hall effect in the ferromagnetic state whose microscopic origin is well understood.

Crystals of $La_{1-x}Sr_xMnO_3$ were prepared by the floating-zone method. The details of growth conditions as well as structural and chemical characterizations of the crystals have been published in previous papers.[2] Measurements of x-ray powder diffraction patterns and electron-probe microanalysis have confirmed that all the crystals are homogeneous and single phase. The crystals were cut into thin rectangular shapes with a typical dimension of 7 mm in length, 2 mm in width, and 0.3 mm in thickness. Electrodes for electrical measurements were made with silver paint, and copper leads are indium-soldered on them. Two Hall voltages were measured either by rotating the crystal by 180° in a fixed field or by reversing the field direction at a fixed temperature to remove the offset voltage due to the asymmetric Hall terminals.

Figure 1 shows the ordinary Hall coefficient R_H, which is defined as a proportional constant of Hall resistivity (ρ_{xy})

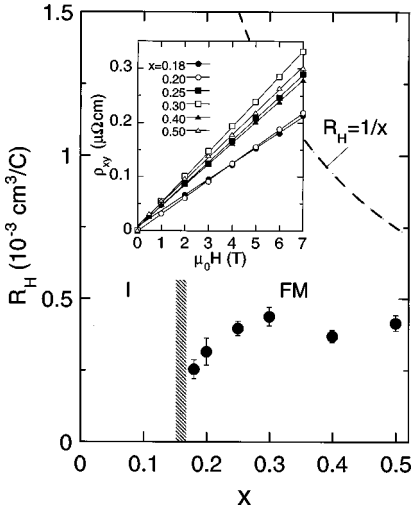

FIG. 1. Ordinary Hall coefficient R_H of $La_{1-x}Sr_xMnO_3$ crystals with $x=0.18-0.50$ at 4.2 K. The nominal carrier number (n) calculated from R_H using $R_H=1/en$ is about $1.5–2.0\times10^{22}$ cm^{-3} or ≈ 1 hole/Mn site. The Hall resistivity ρ_{xy} at 4.2 K as a function of applied field is shown in the inset. I and FM denote insulating and ferromagnetic metallic states, respectively.

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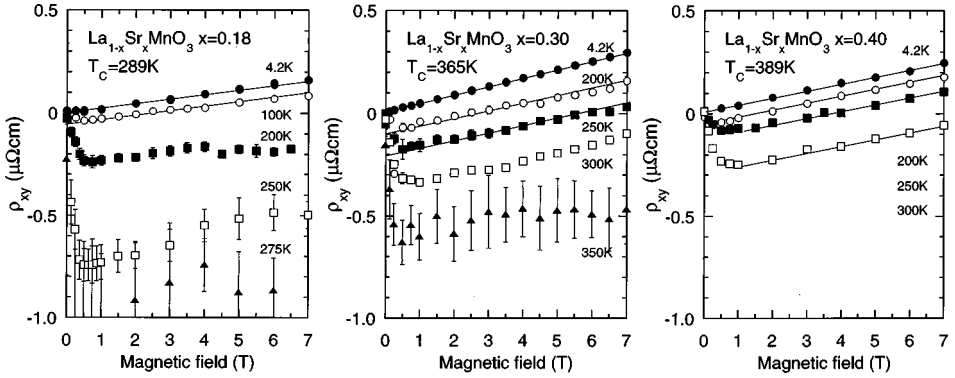

FIG. 2. The Hall resistivity ρ_{xy} as a function of applied field at various temperatures for $x=0.18$ (left panel), 0.30 (middle panel), and 0.40 (right panel).

with an external field, for the metallic crystals of $x=0.18-0.50$ at the lowest temperature (4.2 K) of the present study. At this temperature, no anomalous part in ρ_{xy} is observed as shown in the inset of Fig. 1. In insulating crystals with $x \leqslant 0.17$, it was difficult to estimate R_H because of the large offset of the Hall voltages and subsisting large magnetoresistance even at low temperatures. For the FM crystals, one can see that R_H is positive and nearly constant irrespective of x, or rather tends to decrease slightly towards the compositional insulator-metal (IM) phase boundary ($x_c \approx 0.17$, a hatched bar in the figure). It should be noted that R_H does not follow the relation $R_H=1/x$ which is intuitively expected from the nominal hole concentration $\delta=x$. This simple relation is also expected to hold approximately when the e_g conduction band is fully spin polarized (as it is) and completely splits due, for example, to the collective Jahn-Teller distortion of MnO_6 octahedra. The experimentally observed value of R_H is suggestive of orbital pseudo-degeneracy in the conduction band. Assuming the relation that $R_H=1/en$, we would obtain the carrier number $n=1.5-2.0\times10^{22}$ cm^{-3} or, equivalently, $n \approx 1$ hole/Mn site. No conspicuous critical behavior in R_H has been observed near the IM phase boundary. Such a small Hall coefficient as observed indicates that a large Fermi surface being typical of a metal is maintained down to $x=0.18$, namely, close to the MI phase boundary.

We now focus on the anomalous Hall effect in the manganites. In Fig. 2 is shown the field dependence of ρ_{xy} for $x=0.18$ (left panel), 0.30 (middle panel), and 0.40 (right panel) at various temperatures below T_C. Corresponding to the growth of the magnetization with field due to the domain rotation effect, ρ_{xy} decreases sharply towards the negative side at first and then increases with nearly constant positive slope due to the ordinary Hall effect. Note that the M-H curve of $La_{1-x}Sr_xMnO_3$ crystal is nonremanent without hysteresis and the saturation field is about 0.5 T, consistent with the saturation field of the anomalous part of ρ_{xy}.

In ferromagnets, ρ_{xy} is expressed in terms of an external field H as follows:[10]

$$\rho_{xy}=R_H H+R_1 M, \tag{1}$$

where $R_1=(1-N)R_H+R_s$, N being a demagnetizing factor determined from the sample shape ($N \approx 0.9$ in this study) and R_s an anomalous Hall coefficient. We can estimate R_s at each temperature from the intercept of ρ_{xy} curve to zero field by assuming R_H to be nearly T independent.

Figure 3 shows R_s below T_C for $x=0.18$, 0.30, and 0.40 as a function of reduced temperature $\tau=T/T_C$. Over the whole temperature range, R_s is negative and its absolute value monotonically increases with temperature. Three curves for $x=0.18$, 0.30, and 0.40 nearly scale with τ, suggesting that the origin of anomalous Hall effect is essentially the same for these crystals. It should be pointed out, however, that the temperature dependence of R_s is not simply described with a power law of τ. If we analyze the data in terms of the relation that $R_s \propto \tau^{\xi}$, ξ changes from ~ 2 for $T/T_C<0.5$ to ~ 5 near T_C. In the inset is shown the relation between R_s and longitudinal resistivity ρ_{xx}. One can see that R_s as a function of ρ_{xx} is better scaled in terms of the relation $R_s \propto \rho_{xx}^{\alpha}$: $\alpha \approx 2$ for $\rho_{xx}<1\times10^{-3}$ Ω cm and $\alpha \approx 1.2$ for $\rho_{xx}>1\times10^{-3}$ Ω cm for $x=0.18$, while for $x=0.30$ and 0.40, $\alpha=1.2-1.6$. The relation with $\alpha=2$ may simply come from the definition of ρ_{xy} ($\approx \sigma_{xy}/\sigma_{xx}^2$) when the scattering process responsible for the anomalous part is not relevant to that for the longitudinal resistivity. In this context, the low-

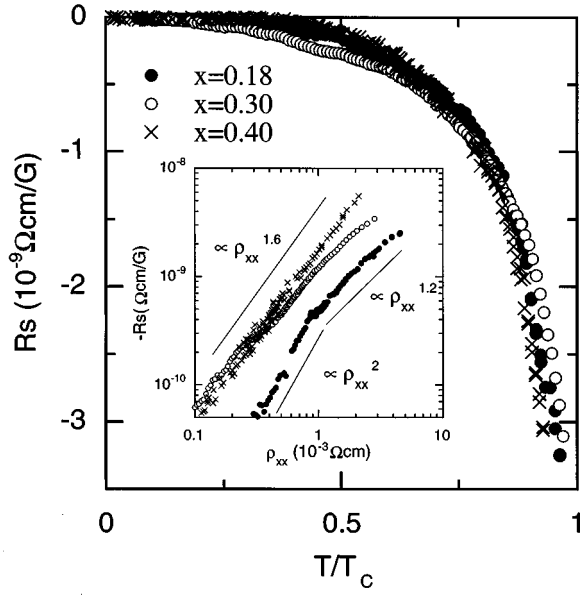

FIG. 3. Temperature dependence of the anomalous Hall coefficient R_s for $x=0.18$, 0.30, and 0.40. The inset shows $-R_s$ as a function of longitudinal resistivity ρ_{xx}.

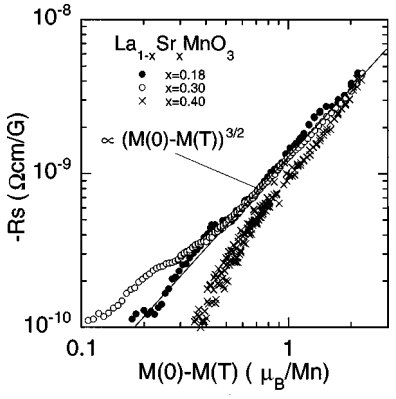

FIG. 4. $-R_s$ is plotted for $x=0.18$, 0.30, and 0.40 with the change of magnetization $[M(0)-M(T)]$, where $M(0)$ denotes the saturated magnetization at zero temperature. A solid line represents the empirical relation $R_s=-1.3\times10^{-9}[M(0)-M(T)]^{3/2}$, R_s and M being in units of Ω cm/G and μ_B/Mn site, respectively.

temperature resistivity (i.e., $\rho_{xx}<1\times10^{-3}$ Ω cm) for $x=0.18$, that obeys the T^2 law,[2] may be dominated by other mechanisms (e.g., electron-electron scattering) than thermal spin fluctuations. Incidentally, the magnitude of R_s in $La_{1-x}Sr_xMnO_3$ at the identical value of ρ_{xx} (e.g., 100 $\mu\Omega$ cm) is an order of magnitude smaller than in a conventional itinerant ferromagnet Ni.[11] This is due partly to the quenching of orbital moment ($\vec{L}=0$) in the $3d$ e_g state in the manganite, where the small spin-orbit interaction of conduction carriers arises from the hybridized O $2p$ component.

Karplus and Luttinger[12] first treated the anomalous Hall effect in itinerant ferromagnets from the viewpoint of band theory taking into account spin-orbit interaction of d electrons. They showed that $R_s=A\rho_{xx}^2$ in electrically isotropic system. The contribution from phonon scattering also gives a similar relation as shown by Irkhin and Shavrov.[13] In the $La_{1-x}Sr_xMnO_3$ system, however, the behavior of $R_s\propto\rho_{xx}^{\alpha}$ with 1.2–1.3 seems to be dominant, and ρ_{xx}^2 behavior is only observed at low temperatures for $x=0.18$. Since phonon scattering should be pronounced at high temperatures, it is not likely the main scattering process. As expected from the magnetoresistance behavior, the magnetic scattering or the spin-disorder scattering should govern the transport properties below T_C in this compound.

In Fig. 4 we show R_s as a function of magnetization M which was measured under field of 0.5 T. One can see that the change of R_s for all the crystals is well described in terms of the relation that $R_s\propto[M(0)-M(T)]^{\eta}$, where $M(0)$ stands for the saturated magnetization at zero temperature (3.80, 3.48, and $3.38\mu_B$/Mn ion for $x=0.18$, 0.30, and 0.40, respectively). We have found an empirical relation with $\eta=3/2$ (a solid line in Fig. 4), $R_s=-1.3\times10^{-9}[M(0)-M(T)]^{3/2}$, R_s and M being in units of Ω cm/G and μ_B/Mn site, respectively. Below $-R_s<5\times10^{-10}$ Ω cm/G, deviation of the data from the above relation is slightly pronounced, although this may be due partly to the experimental error in the estimation of a small R_s value.

In $La_{1-x}Sr_xMnO_3$ with the maximal conduction bandwidth, the assumption that conduction e_g electrons are magnetically scattered only by local $t_{2g}(S=3/2)$ spin moments holds. Thus a variety of transport as well as magnetic properties are well described by the so-called double-exchange model,[2,7]

$$H=-t\sum_{\langle i,j\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})-J_H\sum_i\vec{\sigma}_i\cdot\vec{S}_i, \qquad (2)$$

where the first term represents the hopping process of the e_g carriers and the second term the Hund's-rule coupling between the spin of the e_g carrier ($\vec{\sigma}_i$) and the localized t_{2g} spin ($\vec{S}_i$) on the same Mn site. It is therefore natural to suppose that the anomalous Hall effect also originates from the interaction between these.

According to Kondo's theory of s-d interaction,[14] the anomalous Hall effect arising from the spin-orbit coupling of a local d electron is governed by the process that a s electron is scattered from its momentum state $\vec{k}$ to $\vec{k}'$ while the local d electron changes its orbital state from $\vec{m}$ to $\vec{m}'$. He showed that R_s is proportional to $\langle[M_n-\langle M\rangle]^3\rangle=\langle\delta M^3\rangle$ where M_n denotes the magnetization of nth atom. The temperature dependence of R_s in conventional itinerant ferromagnets such as Fe and Ni (Ref. 11) is in good agreement with the theoretical curve, especially near T_C where R_s has a maximum around $T=0.9T_C$. Although some analogy such as $s\leftrightarrow e_g$ and $d\leftrightarrow t_{2g}$ may hold between Ni (Fe) and $La_{1-x}Sr_xMnO_3$, we have observed no such peak near T_C. With such an analogy between the s-d model and the double-exchange model, the above Kondo's relation may read as $R_s\propto[M(0)-M(T)]^3$ ($\eta=3$) for the manganites, which differs from the observation $\eta=3/2$. Maranzana[15] treated the mixed spin-orbit interaction between the local spin moment $\vec{S}$ and the angular orbital moment $\vec{L}$ of conduction electrons. Also in this case the theory gives the relation $R_s\propto\langle\delta M^3\rangle$, and the sign of R_s is the same as that of R_H. Thus, no existing theory can, to the best of our knowledge, quantitatively explain the presently observed scaling relation as well as the sign of R_s. The scaling behavior with $\eta=3/2$ observed for the manganites is thus left to be theoretically elucidated.

In summary we have studied the Hall effect in $La_{1-x}Sr_xMnO_3$. The ordinary Hall coefficient in the ferromagnetic metallic ground state indicates that the carrier is a hole, and that its density is nearly x and T independent, signaling that a large Fermi surface being typical of a metal subsists close to the compositional boundary ($x_c\approx0.17$) for the insulator-metal transition. The anomalous part of the Hall effect arising from the asymmetric scattering of charge carriers by local spin moments is, on the other hand, negative and strongly x and T dependent. The change of the anomalous part is attributed to the change of magnetization irrespective of x, which is described in terms of an empirical relation that $R_s=\text{const}[M(0)-M(T)]^{\eta}$ with $\eta\approx3/2$ (const $=-1.3\times10^9$ for R_s and M is in units of Ω cm/G and μ_B/Mn site, respectively).

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