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

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The thermoelectric effect and its systematic variation with doping level (x), temperature (T), and external magnetic field (H) have been investigated for crystals of double-exchange ferromagnets, $La_{1-x}Sr_xMnO_3$ ($0.15 \leqslant x \leqslant 0.50$). Large T- and H-dependent changes of the Seebeck coefficient S are observed around the Curie temperature T_C due to the corresponding changes of resistivity. S changes its sign from positive to negative around the insulator-metal phase boundary ($x=0.20$) above T_C for the paramagnetic phase, but around $x=0.30$ in the ferromagnetic metallic state far below T_C. A possibly anomalous change of the electronic structure with the spin-polarization is argued on the basis of the magnetothermoelectric data for the moderately doped ($x=0.20$–0.30) crystals.

Doping of charge carriers into antiferromagnetic correlated insulators such as 3*d* transition metal oxides often causes various insulator-metal (*I-M*) phenomena. Since there are strong correlations between the magnetism and the charge transport properties in such barely metallic phases, curious spin-charge coupled phenomena have been aroused, which is a recent subject of extensive studies in strongly correlated electron systems. Large magnetoresistance effect observed near a ferromagnetic transition temperature T_C in perovskite-type manganese oxides, $R_{1-x}A_xMnO_3$ (where R is a trivalent rare-earth ion and A a divalent ion such as Ca, Sr, Ba, or Pb), is one of the issues, which has attracted current interest in relation to possible applications to magnetoresistance (MR) devices.[1–9]

Among various manganese oxides with perovskite structure, $La_{1-x}Sr_xMnO_3$ is a prototypical double-exchange ferromagnet, in which the ferromagnetic interaction between localized t_{2g} spins (spin quantum number $S=\frac{3}{2}$) is meditated by itinerant e_g electrons (double-exchange interaction).[10–14] By the substitution of La^{3+} with Sr^{2+} ions, holes can be doped nominally into the e_g orbital band. A ferromagnetic metallic (FM) state appears below T_C for a critical composition of $x_C \approx 0.17$, and develops up to $T_C \approx 380$ K for $x=0.3$–0.5 crystals.[6,7] It is important to note that the spins of both t_{2g} and e_g electrons are fully polarized in the FM state because the intra-atomic exchange interaction between these spins ($J_H \approx 1.2$ eV,[9] Hund's-rule coupling) is sufficiently large compared with the e_g orbital bandwidth. Therefore the electronic band structure for the conduction e_g electrons completely splits by an order of J_H into, say, the up-spin band and the down-spin band in the FM state,[9] being much different situation from other conventional conducting ferromagnets.

In this paper we report systematic studies of the thermoelectric effect in $La_{1-x}Sr_xMnO_3$ with various doping levels ($0.15 \leqslant x \leqslant 0.50$), which gives us important information about the electronic nature of charge carriers in this system.[15] We discuss the observed results in terms of change of the electronic structure with band filling and spin-polarization in the present system.

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.[7,8] Measurements of x-ray powder diffraction patterns and electron-probe microanalysis confirmed that all the samples are homogeneous and of single phase. The samples were cut out to form a rectangular shape with a typical dimension of $1\times1\times7$ mm^3. Electrical resistivity (ρ) measurements were carried out in a conventional four-point probe configuration. Seebeck coefficient of the sample was measured in a vacuum by employing the constant-ΔT method.[16]

Figure 1 shows the temperature dependence of Seebeck coefficient $S(T)$ and electrical resistivity $\rho(T)$ under magnetic fields of 0 and 7 T for $La_{1-x}Sr_xMnO_3$ crystals with the FM ground state: low-doped ($x=0.18$), moderately doped ($x=0.25$), and high-doped ($x=0.40$) crystals. The T- and H-dependent behaviors of S are intimately related to those of ρ. For the low-doped ($x=0.18$) sample, the S above T_C is characteristic of insulators or semiconductors, namely, $|S|$ (the absolute value of S) increases with lowering T. For the moderately or the high-doped metallic samples ($x=0.25$ and 0.40), on the other hand, the S above T_C is characteristic of metals, i.e., $|S|$ decreases with lowering T. For all the samples, the rapid decrease in $|S|$ around T_C, irrespective to its sign, corresponds to that in ρ upon the phase transition to the FM state.

It can be seen in Fig. 1 that application of a magnetic field (7 T) also decreases $|S|$ considerably near T_C, suggesting that the decrease in $|S|$ should be compared with the MR effect. Figure 2 shows the correlation between the magnetothermoelectric and the MR effects in a field up to 7 T. Here the change of S in a magnetic field is normalized by the zero-field value $(-\Delta S/S(0))$ and plotted as a function of the normalized resistivity change $(-\Delta\rho/\rho(0))$ at various temperatures for the $x=0.18$ crystal that shows a nearly maximal

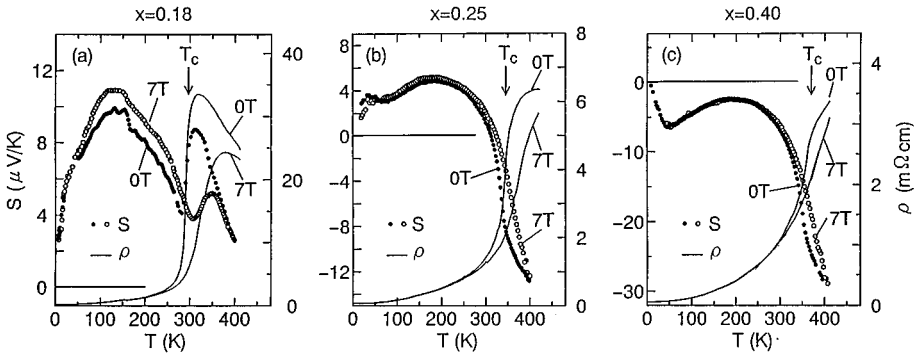

FIG. 1. Temperature dependence of Seebeck coefficient S and electrical resistivity ρ under magnetic fields of 0 and 7 T for $La_{1-x}Sr_xMnO_3$ crystals: (a) low-doped (x=0.18), (b) moderately doped (x=0.35), and (c) high-doped (x=0.40) crystals. Zero level of S is indicated in each figure.

MR phenomenon.[7] Although all the data are not scaled onto a single curve, we can see a tendency that $-\Delta S/S(0)$ is nearly proportional to $-\Delta\rho/\rho(0)$. However, the deviations from the linear relation are noticeable for the curves near T_C and in high-field regions. For example, $-\Delta S/S(0)$ below T_C once shows a maximum, as indicated by the arrows in Fig. 2, and then decreases with further increasing field. Such a positive change of S in the high-field region near T_C is characteristic of increasing spin polarization and is in accord with the increase in S with lowering T below T_C [see Fig. 1(a)], since both cases induce a rapid increase in the magnetization.

The global feature can be qualitatively understood in terms of Mott's formula for the charge contribution to the Seebeck coefficient in metals,

$$S=-\frac{\pi^2}{3}\frac{k_B^2T}{e}\frac{\sigma'(\epsilon_F)}{\sigma(\epsilon_F)}, \tag{1}$$

where e is the elementary charge, $\sigma(\epsilon_F)$ the conductivity at Fermi level and σ' stands for $(\partial/\partial\epsilon)\sigma(\epsilon)$.[17] The observed decrease in $|S|$ around T_C or by applying a magnetic field is attributed to the large increase in the conductivity due to the phase transition to the FM state or the MR effect that results from the field-reduced spin scattering, provided that the change of σ' or the phonon drag effect is regarded as a minor contribution. It is worth noting, however, that the Seebeck coefficient near T_C keeps on decreasing across zero level with doping and hence does not converge into a small positive or zero value. The S above T_C shows a sign change from positive to negative around $x\approx0.20$. For the x=0.25 crystal, the S changes again its sign from negative to positive below T_C with lowering T, as can be seen in Fig. 1(b). These behaviors cannot be interpreted simply in terms of a change of σ.

To see clearly this sign change of S induced by doping or lowering T, we show in Fig. 3 the Seebeck coefficient at T_C (upper panel) and at T=30 K$\ll T_C$ (lower panel) plotted against x. The Seebeck coefficient at T_C sharply decreases with x, crosses zero around x=0.20, and then becomes negative but less x dependent for $x\geq0.20$ than for $x\leq0.20$. At sufficiently low temperature (e.g., 30 K) below T_C, on the other hand, the behavior of S is anomalous as seen in the lower panel of Fig. 3. The sign of S abruptly changes from negative to positive at $x\approx0.17$, which exactly corresponds to the compositional phase boundary of the *I-M* transition in the ferromagnetic phase. Then S reaches a positive maximum at x=0.20. Above x=0.20, S decreases gradually with doping and crosses zero around $x\approx0.3$. Thus the metallic phases in

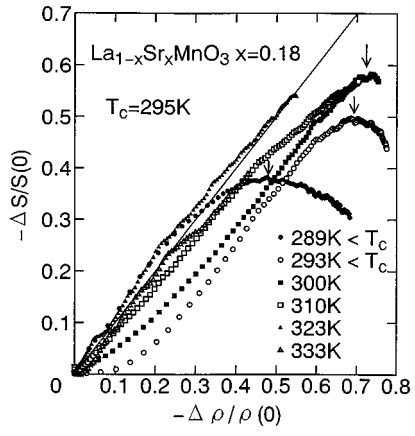

FIG. 2. Correlation between magnetothermoelectric and magnetoresistance effects at various temperatures in the x=0.18 crystal. The change of S in a magnetic-field normalized by the zero-field value $[-\Delta S/S(0)]$ is plotted as a function of the normalized resistivity change $[-\Delta\rho/\rho(0)]$. A solid line represents a linear relation that $-\Delta S/S(0)=-\Delta\rho/\rho(0)$. Arrows indicate maxima of $-\Delta S/S(0)$ (see text).

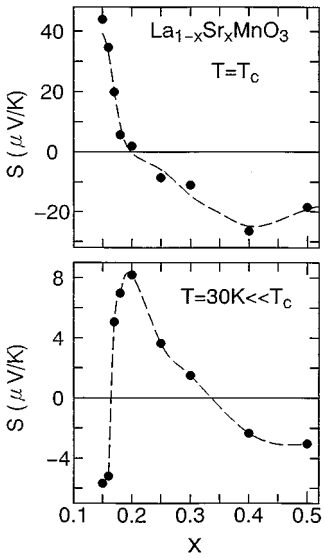

FIG. 3. Seebeck coefficient at T_C (upper panel) and at T=30 K ($\ll T_C$, lower panel) as a function of doping level x. Broken lines are a guide to the eye.

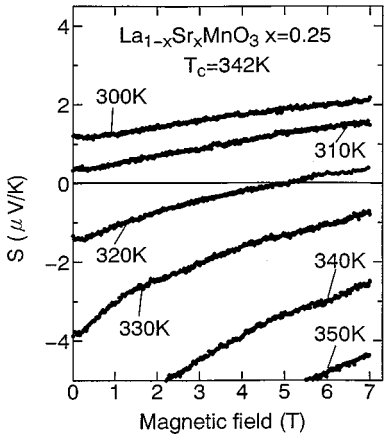

FIG. 4. Magnetic field dependence of the Seebeck coefficient at various temperatures for the $x=0.25$ crystal. At temperatures (e.g., $T=320$ K) slightly below T_C, S changes its sign from negative to positive by applying a magnetic field.

the present system can be classified into three regions. For the low-doped region ($x=0.17$–0.20), the S is positive over the whole temperature range. For the moderately doped region ($x=0.20$–0.30), the S is negative above T_C but changes its sign to positive below T_C. For the high-doped region ($x=0.30$–0.50), the S is negative over the whole temperature range. Provided that the sign of S reflects a type of charge carriers, the sign change of S suggests that the electronic state of $La_{1-x}Sr_xMnO_3$ crystal has been altered between holelike and electronlike charge carriers by doping and also by lowering T for the moderately doped region.

The thermally induced sign change of S observed for the moderately doped crystals implies that an evolution of the spin polarization changes the electronic nature of charge carriers. If this is the case, it is expected that the sign change of S can be induced also by applying a magnetic field. In Fig. 4 we show the magnetic field dependence of S for the $x=0.25$ crystal at various temperatures: the S increases with a field or with a spin polarization near T_C, but tends to saturate at lower temperatures away from T_C [see also Fig. 1(b)]. In particular, at $T=320$ K slightly below T_C, the S starts from a negative but changes its sign as the field is increased. Therefore, application of a magnetic field tends not only to *decrease* the $|S|$ value in relation to the negative MR, but also to *increase* the S value itself with an evolution of the spin polarization for the crystals with $x=0.17$–0.30. Such a tendency also shows up as maxima of the $-\Delta S/S(0)$ vs $-\Delta\rho/\rho(0)$ curves indicated by the arrows in Fig. 2.

In order to elucidate these thermoelectric properties, we propose the possibility that the orbital degree of freedom of the e_g band may play an important role. The e_g band is built up with degenerate $3d$ orbitals ($d_{3z^2-r^2}$ and $d_{x^2-y^2}$), and is split into the upper and the lower band by an order of J_H.[9] If the orbital degeneracy is not lifted in crystals, the filling (n) of the lower e_g band in $La_{1-x}Sr_xMnO_3$ is $n=1-x$ against the full filling of $n=2$. In this case, it is rather natural to suppose that the character of charge carriers is seen to be of electron type. By contrast, if the lower (up-spin) band built up with the two orbitals is split further into two bands in the FM state for some reason, then the lowest band is fulfilled when $n=1$ and hence the Sr substitution may literally introduce holes into the system.

By adopting the above scenario, we come to a conclusion that for $x\lesssim 0.3$ where S is positive at low temperatures, the e_g band in the fully spin-polarized FM state is nondegenerate or subject to a further splitting. For the high-doped ($x\gtrsim 0.3$) metallic phase, on the other hand, the e_g band is essentially degenerate and the S appears to be negative. For the moderately doped region ($0.2\lesssim x\lesssim 0.3$), the degeneracy of the e_g band seems to be gradually lifted as temperature is lowered below T_C and the S changes its sign from negative to positive with the increase of the spin-polarization.

At present, we have no definite assignment what is a driving force for the effective splitting of the fully spin-polarized e_g band or for the effective lifting of the degenerate e_g band. One of the possible origins may be some structural distortion of MnO_6 octahedra or the Jahn-Teller (J-T) effect. The importance of (dynamic) J-T distortion has been recently suggested theoretically[18] and experimentally[19] to explain the transport properties in Mn-based oxide perovskites. We can expect that the local distortion of the MnO_6 octahedron has in fact such an effect that lifts the degenerate e_g band. If this were the case, however, the thermally induced and/or the field-induced sign change of the Seebeck coefficient below T_C would be difficult to be explained since the J-T effect should become less prominent or disappear in the FM state.[18] Furthermore, a recent neutron diffraction study on a single crystal of $La_{1-x}Sr_xMnO_3$ ($x=0.3$) (Ref. 20) have showed no indication of the J-T distortion over the whole temperature range, although the Seebeck coefficient shows a similar sign-change anomaly with the increase of the spin-polarization.

Another possible origin we propose here is the ''antiferromagnetic'' orbital ordering or its dynamical correlation in the FM ground state. We may expect a strongly alternating tendency of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals in the pseudocubic lattice due to the ''antiferromagnetic'' exchange interaction between the orbital degree of freedom[21,22] (or so-called τ spins in the orbital-spin analogy) on the adjacent Mn site. What is most characteristic of the FM ground state in $La_{1-x}Sr_xMnO_3$ is that the spin degree of freedom is lost due to the full spin polarization of the e_g electrons and hence that only the orbital degree of freedom (τ spin) survives in the FM ground state. Therefore, we may have to consider that the dynamics of the spin-less fermions in the strong antiferromagnetic τ-spin fluctuation for the charge dynamics in the FM state of $La_{1-x}Sr_xMnO_3$ ($x\lesssim 0.3$).

In summary we have investigated the systematic variation of thermoelectric properties with doping level, temperature, and magnetic field in $La_{1-x}Sr_xMnO_3$ crystals. The experimental results indicate that the nature of charge carriers changes from holelike to electronlike around $x=0.20$ in the paramagnetic phase above T_C and around $x=0.30$ in the ferromagnetic metallic phase at $T\ll T_C$. For the moderately doped region ($0.2\lesssim x\lesssim 0.3$), the sign of S changes from negative to positive with the increase of the spin-polarization by lowering temperature or by applying a magnetic field. We have interpreted these behaviors in terms of a change of electronic structure relating to the orbital degree of freedom of the e_g carriers.

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