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Pressure effect on the double-exchange ferromagnet $La_{1-x}Sr_xMnO_3$ ($0.15 \leq x \leq 0.5$)

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The effect of hydrostatic pressure on the magnetic and electronic properties has been investigated for prototypical double-exchange ferromagnets, $La_{1-x}Sr_xMnO_3$, with varying nominal hole concentration x ($0.15 \leq x \leq 0.5$). A pressure-enhanced transfer interaction is observed to stabilize the ferromagnetic metallic phase, i.e., increase the Curie temperature T_C, over the whole concentration range investigated. The pressure coefficient of T_C is found to be significantly x dependent and steeply decreases from $d \ln T_C/dP \approx +0.065$ GPa^{-1} at $x=0.15$ to a small value ($\approx +0.005$ GPa^{-1}) at $x=0.4$–0.5. This suggests a symptomatic change of the electronic nature from the strong- to weak-coupling region with increasing the hole-doping level.

High pressure, which effectively increases the electron (or hole) transfer interaction or the one-electron bandwidth W, may be a powerful tool for investigation of the electronic and magnetic properties of strongly correlated $3d$-electron systems. Application of pressure and hence enhancement of the transfer interaction (t) affects the electronic properties, especially near the insulator-to-metal (I-M) phase boundary.[1–5] In an extreme case, a pressure-induced metallic phase persists down to zero temperature, as demonstrated in $PrNiO_3$ (Refs. 1 and 2) and V_2O_3.[3] In this class of compounds, the pressure-increased itineracy of the carriers is expected to influence the magnetic properties as well. One of the demonstrative examples is the pressure effect on a prototypical Mott insulator $LaTiO_{3+\delta/2}$:[4] The application of pressure increases the Néel temperature T_N in a filling ($n=1-\delta$) dependent manner, suggesting a crossover behavior from localized to itinerant magnetism with increasing δ.

In this paper, we have investigated the pressure effect on the magnetic and electronic properties of prototypical double-exchange ferromagnets, $La_{1-x}Sr_xMnO_3$, by systematically varying the nominal hole concentration x ($0.15 \leq x \leq 0.5$). Important quantities that govern the magnetic as well as electronic properties are the one-electron bandwidth (W) of the e_g band and the on-site exchange interaction (Hund coupling; J) between the itinerant e_g electron and the local t_{2g} spin.[6,7] Another important parameter of strongly correlated $3d$-electron systems is the nominal hole concentration x (or the degree of band filling $n=1-x$) which measures kinetic energy of the spin-polarized charge carriers. It was found in this study that application of pressure increases the Curie temperature T_C and enlarges the ferromagnetic metal phase. The *positive* pressure coefficient of T_C is in sharp contrast with the case of the conventional itinerant ferromagnets,[8] in which the increase of W generally suppresses T_C.[9] Furthermore, we have observed a remarkable reduction in the pressure coefficient of T_C with increasing the hole-doping level, suggesting a crossover of the system from a strong- to a relatively weak-coupling region.

The nominal Mn^{3+} ion in the parent compound $LaMnO_3$ ($x=0.0$) has electron configuration of $t_{2g}^3 e_g^1$. Among the four $3d$ electrons, t_{2g} electrons are localized on the Mn site and give rise to a local spin ($S=\frac{3}{2}$), while the e_g state hybridized with the O $2p$ state is either itinerant or localized as the case may be. There is a strong exchange interaction (Hund coupling J) between the itinerant e_g electron and the localized t_{2g} spins. In this sense, the system can be viewed as a Kondo lattice system with ferromagnetic coupling $J \geq 0$.[10] With hole doping, an insulator-to-metal (I-M) transition takes place close to a critical concentration $x_c \approx 0.17$ (Refs. 6,11,12) and the itinerant e_g carriers ferromagnetically align the local spins by way of the so-called double-exchange interaction.[13–15] The manganese oxide system has begun to attract current interest because of its giant magnetoresistance (MR) effect[6,16–20] (see the lower panel of Fig. 1). Recently, Furukawa has derived an exact solution for the ferromagnetic Kondo lattice model in infinite dimensions ($D=\infty$) and with $S=\infty$ (classical spins).[7] The solution well reproduces the observed magnitude of the negative MR as a function of the field-induced magnetization.[6]

Crystals of $La_{1-x}Sr_xMnO_3$ ($0.15 \leq x \leq 0.5$) were grown by the floating-zone method at a feeding speed of 5–10 mm/h. A stoichiometric mixture of La_2O_3, $SrCO_3$, and Mn_3O_4 was ground and calcined three times at 1050 °C for 24 h. Then, the resulting powder was pressed into a rod with a size of 5 mm$\phi \times$60 mm and sintered at 1350 °C for 24 h. Over the whole concentration range, the ingredient could be melted congruently in flowing air. To characterize the crystals, powder x-ray-diffraction measurement as well as electron probe microanalysis (EPMA) were carried out. The results indicated that the crystals are single phase and show a nearly identical composition with the nominal one in the composition range of $x \leq 0.4$. However, a slight deviation of the composition was observed for the $x=0.5$ sample ($x_{obs}=0.47$) though no trace of the impurity was detected in the diffraction pattern. With increasing x, the room-temperature struc-

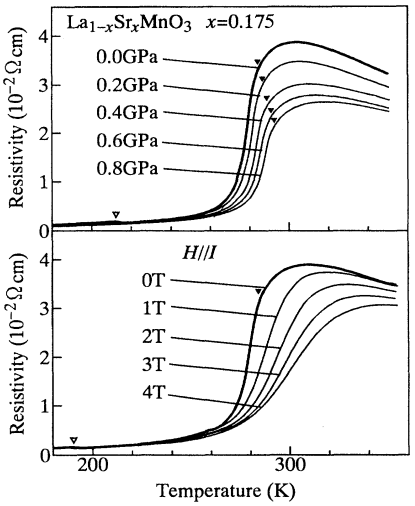

FIG. 1. (Top) Pressure dependence of resistivity for the $La_{1-x}Sr_xMnO_3$ ($x=0.175$) crystal. Filled triangles stand for the Curie temperatures determined by susceptibility measurements. An anomaly marked by an open triangle is due to a structural transition (see text). (Bottom) Magnetoresistance for the $x=0.175$ crystal with the current parallel to the magnetic field.

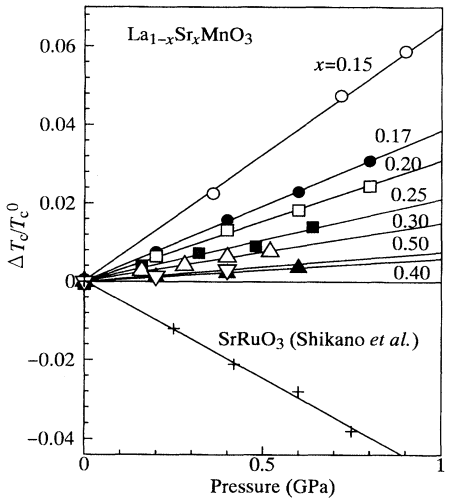

FIG. 3. Relative change of the Curie temperature T_C against pressure for $La_{1-x}Sr_xMnO_3$ crystals with various x values. The solid lines are the results of least-square fitting. Data for $SrRuO_3$ are cited from Ref. 22.

ture changes from orthorhombic ($Pbnm$; $Z=4$) to rhombohedral ($R\bar{3}c$; $Z=2$) at a critical concentration $x_s \sim 0.17$.[21]

The upper panel of Fig. 1 shows a prototypical example of the pressure dependence of resistivity (ρ) for the $La_{1-x}Sr_xMnO_3$ ($x=0.175$) crystal. A quasihydrostatic pressure was obtained with a cramp-type piston-cylinder cell using silicone oil as a pressure-transmitting medium. The sample was cut into a rectangular shape and electrical contact was made with a heat-treatment-type silver paint. The pressure-induced change of the ρ-T exhibited no hysteresis in repeated pressure cycles, and no indication of the sample deterioration was observed during the measurement. At ambient pressure ($P=0$ GPa, thick curve), the ρ-T curve gradually increases with decreasing temperature and then sharply drops around the Curie temperature (T_C indicated by a filled triangle), indicating a transition from the paramagnetic nonmetal to ferromagnetic metal. Application of pressure enlarges the ferromagnetic metal phase through the pressure-enhanced transfer interaction (t) of the holes generated by doping. T_C under pressure was determined by ac susceptibility measurements (*vide infra*) and is indicated in the figure by a filled triangle. The pressure-enhanced t value is also responsible for the reduction of ρ in the paramagnetic phase ($T \geq T_C$). Anomalies indicated by open triangles originate in the temperature-induced structural transition from the rhombohedral to the orthorhombic form.[6] (The difference in the transition temperature between the upper and lower panels is due to the thermal hysteresis effect.)

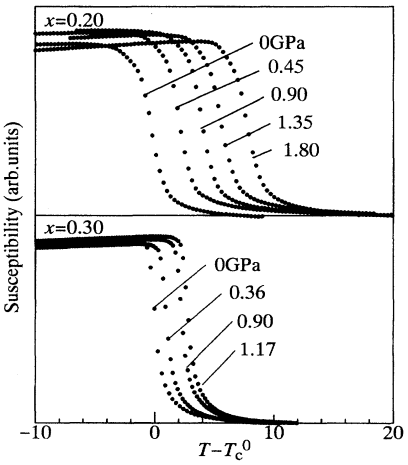

FIG. 2. Pressure dependence of susceptibility for $La_{1-x}Sr_xMnO_3$ crystals; the upper panel is for $x=0.20$ and the lower panel for $x=0.30$. T_C^0 is the Curie temperature at ambient pressure (0 GPa).

It is worth comparing the above pressure effect with the magnetoresistance (MR) effect. The MR effect for the $x=0.175$ crystal is shown in the lower panel of Fig. 1 with the current parallel to the field ($I \| H$). According to the double-exchange theory, the effective transfer interaction ($\tilde{t}$) is expressed as $\tilde{t}=t\cos(\Delta\theta/2)$, where $\Delta\theta$ is the relative angle of the local spins.[13] The external magnetic field forces alignment of the local t_{2g} spins ($\Delta\theta \rightarrow 0$) and hence reduces spin scattering. Thus, the application of an external magnetic field should be qualitatively analogous to the case of the pressure application, and enhances the transfer interaction t. However, the magnetic-field effect is more temperature dependent. The MR effect is prominent especially near T_C (a filled triangle), which apparently shifts the resistivity maximum toward the high-temperature side, as seen in the lower panel of Fig. 1.

To investigate the pressure dependence of the ferromagnetic Curie temperature, we have measured magnetic susceptibility (χ) under pressure. A small piece of crystal (~ 10 mg) was placed in a coil (2 mm in diameter and ≈ 10 mm in length) and χ was determined as a change in the coil induc-

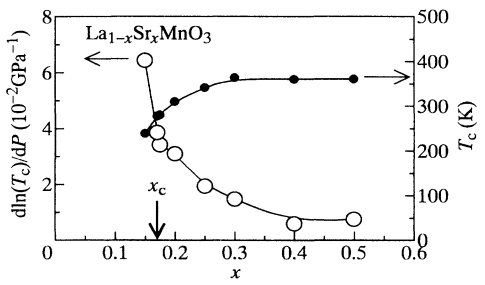

FIG. 4. Nominal hole concentration (x) dependence of T_C (filled circles) and its pressure coefficient (open circles) for $La_{1-x}Sr_xMnO_3$. A downward arrow indicates the critical concentration (x_c) for the insulator-to-metal transition. Solid curves are merely a guide to the eye.

tance at a frequency of 1 MHz. The sample temperature was monitored with a copper-constantan thermocouple placed in the coil. The change in χ was reversible in repeated pressure and thermal cycles. Figure 2 shows the χ-T curves for $La_{1-x}Sr_xMnO_3$ crystals under various pressures; the upper panel is for $x=0.20$ and the lower panel for $x=0.30$. Note that the abscissa is shifted by the ambient pressure value; $T_C^0=310.9$ K for $x=0.20$ and 364.4 K for $x=0.30$. Under pressure, the χ-T curve shifts rigidly to the high-temperature side. A striking feature is that the magnitude of the pressure shift is considerably suppressed at $x=0.30$ (lower panel) as compared with the $x=0.20$ sample (upper panel). We defined the inflection point of the χ-T curve as T_C and plotted values of $\Delta T_C/T_C^0$ against pressure in Fig. 3. The solid lines are the results of least-square fitting. The pressure coefficient ($\equiv d\ \ln T_C/dP$; slope of the lines) is fairly high (≈ 0.065 GPa^{-1}) in the relatively low-doping region, but steeply decreases to a small value (≈ 0.005 GPa^{-1}) at $x=0.4$–0.5.

The observed *positive* pressure coefficient is in sharp contrast with the *negative* value observed in the conventional itinerant ferromagnets.[8,22] Crosses in the lower part of Fig. 3 show the pressure shift of T_C for a prototypical band ferromagnet $SrRuO_3$ with a similar perovskite structure (cited from Ref. 22). With increasing pressure, T_C decreases at a rate of $d\ \ln T_C/dP=-0.048$ GPa^{-1} in $SrRuO_3$. By contrast, the magnetic interaction in the present system is governed by the double-exchange mechanism mediated by the itinerant e_g holes.[13–15] In this case, the application of pressure enhances the t value and strengthens the ferromagnetic interaction.

The x dependence of the observed pressure coefficient of T_C is shown as open circles in Fig. 4, together with the respective T_C value (filled circles). Except for $x=0.15$ (orthorhombic lattice), the crystal has a rhombohedral structure ($R\bar{3}c$; $Z=2$).[23] The double-exchange model[13] predicts that the magnitude of the intersite-exchange (double-exchange) interaction between the neighboring t_{2g} spins is proportional to W in the strong-coupling limit ($J \gg W$), but varies as $\sim J$ in the limit $J \ll W$. In the case of $La_{1-x}Sr_xMnO_3$, the exchange interaction energy between the e_g electron and t_{2g} spins ($S=\frac{3}{2}$) is estimated as $\frac{3}{2}J \sim 2$ eV,[24] and is even larger than the one-electron (bare) bandwidth of the e_g electron ($W \sim 1$ eV).[25] The large pressure coefficient near the I-M phase boundary ($x_c \approx 0.17$; a downward arrow) suggests that the system remains in the strong-coupling region. However, further hole doping (or the deviation of the band filling from unity) appears to drive the system effectively towards the weak-coupling region, where the system is less sensitive to pressure or to change in W. Thus, the degree of filling $n(=1-x)$ of the conduction (e_g) band is another important parameter that governs the electronic nature in the perovskite manganese oxide. In addition, the change of the lattice parameter induced by substitution of the La site by Sr (Ref. 11) is expected to increase W, which also tends to drive the system toward the weak-coupling region.

Changes in the electronic nature with hole doping also show up in magnetotransport.[6] The magnitude of the negative MR in the $La_{1-x}Sr_xMnO_3$ system is proportional to the square of the magnetization (M) in the low-M region and is well described[6] using the scaling function

$$[\rho(0)-\rho(M)]/\rho(0)=C(M/M_s)^2, \tag{1}$$

where M_s is the saturated magnetization ($\approx 4\mu_B$). The coefficient C is about 4 nearby the I-M phase boundary, but decreases with x down to ~ 1 ($x=0.4$). On the basis of the ferromagnetic Kondo lattice model in the limit of $S=\infty$ and infinite dimension ($D=\infty$), Furukawa[7] showed that the C value depends critically on both parameters, the exchange interaction J/W, and the band filling $n(=1-x)$. C is enhanced (~ 4) near half-filling ($x \sim 0$) in the case of strong coupling ($J \gg W$) but decreases with decreasing J/W and/or n. Thus, the x dependence of C again suggests that hole doping drives the system effectively toward the weak-coupling region, in accord with the present conclusion from the pressure effects.

In summary, we have systematically investigated the pressure coefficient of the Curie temperature ($d\ \ln T_C/dP$) for the prototypical double-exchange ferromagnet, $La_{1-x}Sr_xMnO_3$ ($0.15 \leq x \leq 0.5$). Over the whole x range, we observed a *positive* pressure coefficient, reflecting a pressure-enhanced double-exchange interaction. The magnitude of the coefficient steeply decreases with x, indicating that the degree of filling $n(1-x)$ is the another important parameter that governs the electronic nature of the system. The hole-doping procedure drives the the system effectively toward the weak-coupling region.

Note added in proof. Recently, we became aware that the pressure effect of T_C was investigated for a ceramics sample of $La_{0.8}Ca_{0.2}MnO_3$ by S. Tamura [J. Magn. Magn. Mater. **31-34**, 675 (1982)].

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