RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 61, NUMBER 14 1 APRIL 2000-II

Pressure-induced phase segregation in single-crystal $La_{2-2x}Sr_{1+2x}Mn_2O_7$ $(x=0.32)$

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(Received 16 November 1999)

The temperature dependence of resistivity $\rho(T)$ and of the thermoelectric power $\alpha(T)$ of a single crystal of the ferromagnetic Ruddlesden-Popper compound $La_{2-2x}Sr_{1+2x}Mn_2O_7$ $(x=0.32)$ have been measured under different hydrostatic pressures. Pressure induces segregation into antiferromagnetic electron-rich and ferromagnetic electron-poor Mn_2O_7 layers. With increasing pressure, the ferromagnetic majority phase exhibits contraction of the apical (Mn-O) bond and spin reorientation from the *c* axis to the basal plane at a critical pressure $P_c(6 \leqslant P_c \leqslant 7\ \text{kbar})$. The phase segregation appears to reflect a first-order inversion of the exchange coupling between ferromagnetic Mn_2O_7 layers.

The tetragonal Ruddlesden-Popper system $La_{2-2x}Sr_{1+2x}Mn_2O_7$ contains perovskite bilayers separated by a $La_{1-y}Sr_yO$ rocksalt layer, which makes its physical properties strongly anisotropic.[1,2] In an oxygen-stoichiometric sample, *x* is the fraction Mn(IV)/Mn and therefore represents the number of holes in the Mn(IV)/Mn(III) couple. Figure 1 illustrates some critical features of the ambient-pressure phase diagram. The spin orientations indicated were obtained at 20 K.[3] The Mn_2O_7 layers order ferromagnetically for all *x*, but the coupling between Mn_2O_7 layers changes from antiferromagnetic at $x=0.30$ to ferromagnetic at $x=0.32$. In the range $0.32<x<0.33$, the apical Mn-O bond lengths shorten and the ordered spins change their orientation from the *c* axis to the basal plane.[3,4] Whereas the Néel temperature T_N of the $x=0.30$ antiferromagnetic phase decreases with increasing pressure,[5] the Curie temperature of the ferromagnetic $x=0.40$ composition increases with pressure.[6] Over the range $0.30 \leqslant x \leqslant 0.40$, the magnetic-ordering temperature increases by about 40 K from a $T_N \approx 90\,\text{K}$ for $x=0.30$ to a maximum Curie temperature $T_c \approx 131\,\text{K}$ at $x \approx 0.36$.[7] Moreover, on cooling through T_c, the c/a ratio decreases in the range $0.32<x<0.36$ and increases in the range $0.36<x \leqslant 0.40$; there is no change at $x \approx 0.36$, where T_c is a maximum.[7] The $x=0.32$ composition is in a unique position between an exchange inversion at smaller *x* and a spin flop with changing apical Mn-O bond length at larger *x*. Therefore, we have studied the evolution with pressure of the transport properties of a single crystal of this composition. The data reveal a pressure-induced stabilization of a minority phase in which the Mn_2O_7 bilayers undergo an exchange inversion from ferromagnetic to antiferromagnetic coupling to their neighboring bilayers. The antiferromagnetic minority phase has a $T_N \approx 90\,\text{K}$ that decreases with increasing pressure as occurs for $x=0.30$; the ferromagnetic majority phase has a $T_c > 110\,\text{K}$ that increases with pressure as the fraction of minority phase increases, which is consistent with a transfer of electrons from the majority to the minority phase. At a critical pressure P_c, an abrupt change in dT_c/dP signals a change in the character of the majority phase.

A single-crystal sample of nominal composition $x=0.32$ was grown in an infrared (IR) image furnace at the Argonne National Laboratory. Inductively coupled plasma analysis of similar crystals grown by the same method have shown that the actual average composition is close to the nominal composition. Crystals with mirrorlike surfaces were cleaved from the as-grown boule, and the crystal orientation was verified by Laue back diffraction. The susceptibility measurement under $H=100\,\text{Oe}$ in a dc magnetometer (Quantum Design) shows a single ferromagnetic transition at $T_c \approx 110\,\text{K}$. A four-probe Montgomery configuration was used in the resistivity measurements. The resistivity tensors could be calculated at ambient pressure, but not under applied pressure because measurements under pressure were carried out separately with different current-to-crystal-axis configurations.

We define as ρ_c the resistivity measurement with current *I* parallel to the *c* axis, the measurement with current *I* parallel to the *a*-*b* plane as ρ_{ab}. The setup used for measuring the thermoelectric power $\alpha_c(T)$ and $\alpha_{ab}(T)$ can be found in a previous publication.[8] The results of measurements on different pieces of crystalline boule were found to be identical.

Figures 2 and 3 show the resistivities $\rho_c(T)$ and $\rho_{ab}(T)$ under different hydrostatic pressures. The resistivity scale is for the ambient-pressure data; the curves taken at high pressure are shifted along the resistivity axis for clarity of pre-

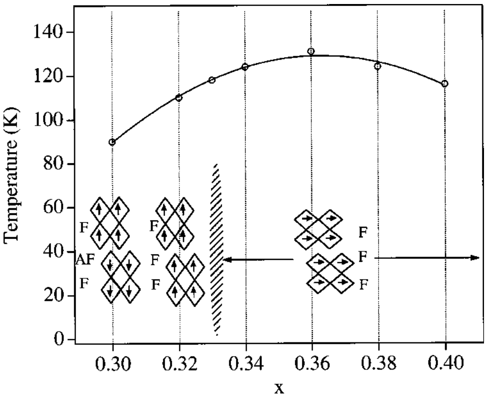

FIG. 1. A schematic phase diagram for $La_{2-2x}Sr_{1+2x}Mn_2O_7$.

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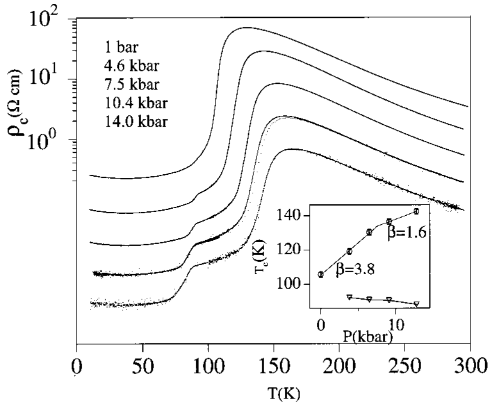

FIG. 2. The temperature dependence of ρ_c under different pressures. The inset shows the pressure dependence of T_c/T_N for majority phase and pressure-induced minority phase. Pressure coefficient dT_c/dP is labeled by a symbol β with unit K/kbar.

sentation. At ambient pressure, the resistivity is strongly anisotropic. The room-temperature ratio $\rho_c/\rho_{ab} \sim 10^2$ is close to that found[5] for an $x=0.30$ crystal, but it is an order of magnitude higher than that found for an $x=0.40$ crystal.[6] At room temperature, all the crystals were paramagnetic, and the change in the ratio ρ_c/ρ_{ab} therefore appears to reflect the change in the apical Mn-O bond length. Both $\rho_{ab}(T)$ and $\rho_c(T)$ show a change of slope on cooling to $T_c \approx 110$ K; a dramatic change in $d\rho/dT$ occurs at T_c, and we identify T_c with this change in the curves taken under pressure. The behavior of $\rho(T)$ on crossing T_c is similar to what is observed in the pseudocubic manganese-oxide perovskites exhibiting a colossal magnetoresistance (CMR).

With the application of a pressure $P \approx 4.6$ kbar, a second transition is already evident in $\rho_c(T)$ at 90 K, Fig. 2, which is the T_N of the antiferromagnetic $x=0.30$ phase, and the fraction of material undergoing the second transition clearly increases with P. Moreover, the lower transition temperature decreases with increasing P as does T_N for $x=0.30$.[5] Therefore, we identify the lower transition with a minority $x=0.30$ phase that develops progressively with increasing pressure. Evidence for the presence of the second phase does not appear in the $\rho_{ab}(T)$ data until pressures $P>10$ kbar. From the measurements of both ρ_{ab} and ρ_c, the insets of Figs. 2 and 3 show a large $dT_c/dP = 3.8$ K/kbar in the interval $0 \leqslant P \leqslant 7$ kbar with an abrupt decrease to 1.3–1.6 K/kbar at higher pressures.

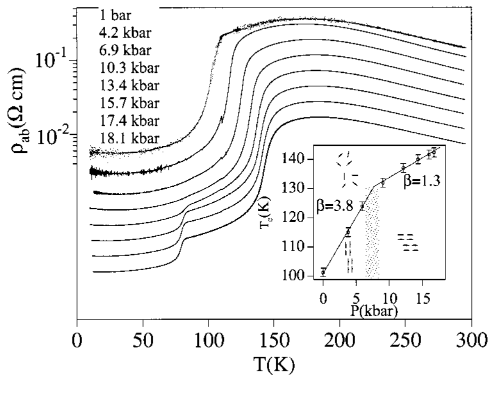

FIG. 3. The same as Fig. 2 for ρ_{ab}. The inset shows the pressure dependence of T_c and the schematic configurations of spin orientation for majority phase.

To interpret these results, we note that the perovskite bilayers are more conductive than the rocksalt layers. The perovskite bilayers are connected in parallel in the measurement of ρ_{ab} and in series with one another and with the rocksalt layers for ρ_c. Therefore we obtain a large anisotropy with $\rho_c/\rho_{ab} > 1$, and ρ_c should be more sensitive than ρ_{ab} to both an exchange inversion between adjacent Mn_2O_7 bilayers and a collapse of the elongated apical Mn-O bond length with reorientation of the spins into the basal planes. A $T_N \approx 90$ K is consistent with a transfer of electrons from the ferromagnetic to the antiferromagnetic layers to give them an electron occupancy like that in the $x=0.30$ compound with a $T_N \approx 90$ K. The exchange inversion between the perovskite bilayers clearly does not take place globally, but progressively with increasing pressure. In the ferromagnetic phase, a factor of 3 decrease in the pressure coefficient dT_c/dP at $P_c \approx 7$ kbar indicates a dramatic change in the sensitivity of T_c with pressure, even though the rate of increase in the fraction of antiferromagnetic phase is not diminished. We conclude that the pressure dependence of T_c changes at P_c without a diminution of the rate of any charge transfer with pressure from the ferromagnetic to the antiferromagnetic phase. Since the c-axis compressibility would be larger for the ferromagnetic phase with elongated apical Mn-O bonds, we identify the transition at $P_c \approx 7$ kbar with the onset of a collapse of the apical Mn-O bond lengths and an attendant flop of the spins from the c axis to the basal plane. The pressure coefficient for $P \geqslant 7$ kbar is similar to that in an $x=0.4$ crystal, which supports this argument. The appearance of an anomaly near 90 K in ρ_{ab} for pressures $P>10$ kbar suggests that electron scattering at the two-phase interfaces is responsible for increasing the resistivity of the majority-phase slabs. The concentration of these interfaces increases with the pressure.

The driving force for the pressure-induced spin flop and phase segregation is the greater compressibility of the apical Mn-O bonds. The spin-flopped phase has shorter apical Mn-O bonds, and we can expect a shorter c-axis Mn-O-O-Mn separation for antiferromagnetic versus ferromagnetic coupling between Mn_2O_7 layers having longer apical Mn-O bonds. Since electron transfer would be confined to a narrow, exchange-inverted hole-poor layer, the coulomb repulsion associated with a segregation into hole-rich and hole-poor layers is minimized. Hole ordering into layers is now well-documented for $La_{1-x}Sr_xMnO_3$ with $x=1/8$ (Ref. 9) and into stripes in the superconductive copper oxides.[10] The spin-flop transition would not require any charge transfer, but we can expect it to take place in stages; beyond the critical pressure P_c for the onset of shorter apical Mn-O bonds, the number of spin-flopped layers with shorter apical Mn-O bonds is predicted to increase progressively with increasing pressure. We also predict that exchange inversion occurs between Mn_2O_7 layers with longer apical Mn-O bonds as a result of an electron transfer to the layers to give them the ratio Mn(IV)/Mn≈0.30. If this interpretation is correct, we should find that phase segregation occurs below T_c. In order to test this prediction, we measured the thermoelectric power $\alpha_c(T)$ and $\alpha_{ab}(T)$ under pressure; the data are shown in Figs. 4 and 5.

At ambient pressure, the $x=0.32$ composition remains

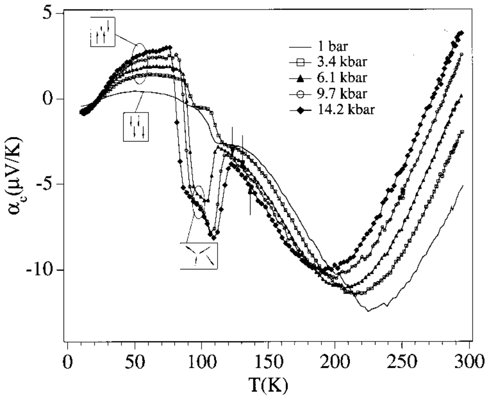

FIG. 4. The pressure dependence of α_c under different pressures. The schematic pictures shows the spin orientation for minority phase.

single-phase, so $\alpha_c(T)$ at $P=1$ bar provides a measure of the parent-phase contribution. On cooling at $P=1$ bar, $\alpha_c(T)$ has a minimum at 230 K and $T_c \approx 110$ K is marked by an abrupt increase (drop in magnitude) of $\alpha_c(T)$; below $T_c, \alpha_c(T)$ is small and featureless, so any features in $\alpha_c(T)$ that appear under pressure below T_c may be attributed to a minority phase. Above T_c, the crystal appears to remain single phase under all pressures. However, it is apparent from the data that $\alpha(T)$ varies systematically with the coherence length of the short-range fluctuations in the strongly coupled Mn_2O_7 layers; $|\alpha(T)|$ decreases as the spins become more aligned. Therefore, the change in $\alpha(T)$ at and below T_c can provide indirect information about the change in the c-axis coupling between Mn_2O_7 layers.

On the application of pressure to an $x=0.40$ crystal, we found no anomalous features in $\alpha_c(T)$ below T_c;[6] Figure 4 shows a quite different behavior for the $x=0.32$ crystal. Under $P=3.4$ kbar, the minimum pressure applied in our experiments, the jump in $\alpha_c(T)$ at T_c moves to a higher temperature and already a second feature appears at 90 K; it is a jump of 1.5 μV/K in $\alpha_c(T)$ on cooling. This second jump in $\alpha_c(T)$ appears at the T_N for $x=0.30$, and we attribute it to a stabilization of the minority phase only below $T_N=90$ K $<T_c$; it indicates that phase segregation at 3.4 kbar is driven by an inversion of the magnetic-exchange coupling between Mn_2O_7 bilayers. The jump at T_c lowers $|\alpha(T)|$ as long-range ferromagnetic order is established along the c axis; the jump at 90 K raises $|\alpha(T)|$ due to the introduction of antiferromagnetic coupling between some Mn_2O_7 layers. With increasing pressure, the temperature of the lower anomaly decreases as does T_N in $x=0.30$. Below T_N, the minority phase makes a positive contribution to $\alpha_c(T)$ that increases progressively with pressure as does the fraction of the minority phase seen in the $\rho(T)$ data. For $P \geqslant 6.1$ kbar, however, the jump in $\alpha_c(T)$ at T_c is no longer observed; the arrows in Fig. 4 mark T_c as determined from $\rho(T)$. Since $P=6.1$ kbar is close to the $P_c \approx 7$ kbar for the change of dT_c/dP, we conclude that the partial introduction of spin-flopped layers introduces multiple spin-orientation discontinuities between successive layers, but little within Mn_2O_7 layers. The transition from long-coherence-length short-range order to long-range order in the Mn_2O_7 layers gives a sharp change in $d\alpha_{ab}(T)/dT$ at T_c, Fig. 5, but it has little influence on $\alpha_c(T)$ if the degree of c-axis ferromagnetic order is not changed significantly. However, a charge-transfer phase segregation below T_{on} would introduce a paramagnetic minority layer in the range $T_N<T<T_{\mathrm{on}}$, which would increase $|\alpha(T)|$. Because the layers contribute to $\alpha_{ab}(T)$ as parallel circuits, the onset of some paramagnetic layers has little influence on $\alpha_{ab}(T)$ in Fig. 5. Below T_N, long-range magnetic order is restored to the minority-phase slabs, so $|\alpha(T)|$ decreases; but $\alpha_c(T)>0$ below T_N increases as the volume fraction of the minority phase increases with pressure. As predicted, a $T_{\mathrm{on}}<T_c$ is maintained for all pressures, and the data provide indirect evidence for a progressive introduction of the spin-flopped phase with increasing pressure.

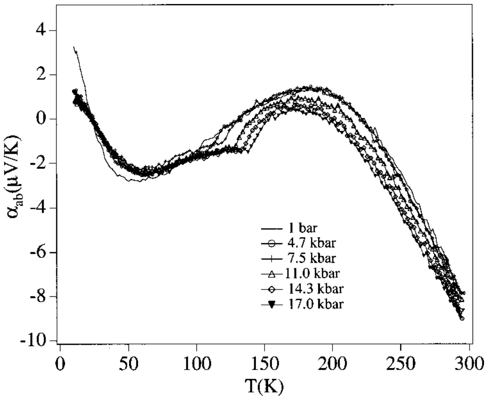

FIG. 5. The same as Fig. 4 for α_{ab}.

In conclusion, a complete set of structural and magnetic data from neutron-diffraction studies[3,7,11] have allowed us to select for high-pressure transport measurements a crystal of composition lying between a magnetic-exchange inversion on one side and a spin flop with collapsing apical Mn-O bond length in the other side. Our measurements clearly show a pressure-induced phase segregation between an antiferromagnetic and a ferromagnetic phase as a result of a progressive transition from ferromagnetic to antiferromagnetic coupling between Mn_2O_7 bilayers having larger Mn-O bonds. From the magnitude and pressure dependence of T_N of the antiferromagnetic phase, we conclude that the antiferromagnetic phase has a composition close to $x=0.30$ and therefore that there is an electron transfer from the ferromagnetic to the antiferromagnetic phase. Moreover, the majority phase exhibits a transition at a critical pressure $P_c(6 \leqslant P_c \leqslant 7$ kbar) that we interpret to mark a partial collapse of the elongated apical Mn-O bond lengths; a spin flop from the c axis to the basal plane can be expected to accompany locally this collapse. The thermoelectric power $\alpha_c(T)$ below T_c indicates that the electron-rich minority phase appears at a $T_{\mathrm{on}}<T_c$; the minority phase would be paramagnetic in the interval $T_N<T<T_{\mathrm{on}}$. The data are consistent with a larger compressibility of the apical Mn-O bonds forming the spin-flopped ferromagnetic phase on one side and antiferromagnetic coupling between Mn_2O_7 bilayers on the other side with electron transfer occurring to a minority phase that is in the form of a narrow (001) slab.

The NSF, the Robert A. Welch Foundation, Houston, TX, and HTSUH, Houston, TX are thanked for financial support.

[1] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).

[2] T. Kimura *et al.*, Science **274**, 1698 (1996).

[3] J. F. Mitchell *et al.*, J. Appl. Phys. **85**, 4352 (1999).

[4] T. Kimura, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. Lett. **81**, 5920 (1998).

[5] T. Kimura, A. Asamitsu, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **79**, 3720 (1997).

[6] J.-S. Zhou, J. B. Goodenough, and J. F. Mitchell, Phys. Rev. B **58**, R579 (1998).

[7] M. Medarde, J. F. Mitchell, J. E. Millburn, S. Short, and J. D. Jorgensen, Phys. Rev. Lett. **83**, 1223 (1999).

[8] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **54**, 13 393 (1996).

[9] Y. Endoh *et al.*, Phys. Rev. Lett. **82**, 4328 (1999).

[10] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).

[11] D. N. Argyriou *et al.*, Phys. Rev. B **59**, 8695 (1999).