PHYSICAL REVIEW B VOLUME 60, NUMBER 22 1 DECEMBER 1999-II

Effect of uniaxial pressure on orbital ordering in $Nd_{1-x}Sr_xMnO_3$

Taka-hisa Arima and Kenji Nakamura
Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan
(Received 3 September 1999)

We have investigated the uniaxial-pressure dependence of transition temperatures in perovskite-like manganese oxides $Nd_{1-x}Sr_xMnO_3$ ($x=0.50,0.55$) by means of electrical resistivity measurements. The uniaxial pressure along the *c* axis raises the charge- and orbital-ordering temperature in the $x=0.50$ compound at a rate of 0.19 K/MPa, in contrast to the case of hydrostatic pressure. The transition temperature from an orbitally disordered paramagnet to an orbital-ordered antiferromagnet in the $x=0.55$ compound also increases at a rate of 0.066 K/MPa. The changes in entropy at the phase transitions obtained from the modified Clausius-Clapeyron relation are found to be significantly smaller than expected by a simple estimation.
[S0163-1829(99)50546-8]

Perovskite-like manganese oxide compounds have attracted considerable attention owing to large negative magnetoresistance and other novel properties.[1–4] Many researchers have pointed out that such physical properties can be attributed to interplay among degrees of freedom of charge, spin, orbital, and lattice. The simultaneous ordering of the charge, spin, and orbital in $Nd_{1/2}Sr_{1/2}MnO_3$ (Refs. 5–7) is one of the typical phenomena originating from the strong coupling among them. With cooling from room temperature the compound first undergoes a ferromagnetic transition at $T_C \sim 250$ K. In the ferromagnetic phase it shows a metallic conduction. As further cooling beyond $T_{CO} \sim 150$ K, the ordering of Mn^{3+} and Mn^{4+} suddenly appears. The charge ordering is accompanied by complicated antiferromagnetic (AF) spin ordering which originates from orbital ordering: Mn^{3+} e_g electrons regularly occupy $3d_{3x^2-r^2}$ and $3d_{3y^2-r^2}$ orbitals. Here the *x*, *y*, and *z* axes are nearly parallel to the [110], [$\bar{1}$10], and *c* directions, respectively, in the *Pbnm* orthorhombically distorted perovskite with $a \sim \sqrt{2}a_p$, $b \sim \sqrt{2}a_p$, and $c \sim 2a_p$ (a_p denotes the lattice constant of a cubic perovskite). Making good use of the interaction among the charge, spin, and orbital degrees of freedom, one could control electrical resistivity in the $Nd_{1/2}Sr_{1/2}MnO_3$ compound through a change of the spin or orbital state. In fact, a magnetic field strong enough to align all the spins ferromagnetically melts the charge ordering away and makes the compound much more conductive, because the charge ordering and ferromagnetism cannot coexist in the perovskite manganite. This is a scenario for the giant negative magnetoresistance in $Nd_{1/2}Sr_{1/2}MnO_3$.[8]

The charge-ordering phase in the $Nd_{1-x}Sr_xMnO_3$ compound vanishes when the Sr content deviates a few percent from 1/2.[9] $Nd_{0.45}Sr_{0.55}MnO_3$ is fairly conductive even at low temperatures.[10,11] It is suggested that the itinerant nature of Mn 3*d* electrons are closely related to spin and orbital ordering of another type. A neutron study has clearly shown layered antiferromagnetism.[6] A model calculation has suggested that $3d_{x^2-y^2}$ orbitals are selectively occupied in the layered antiferromagnetic phase.[12]

In this paper we report a uniaxial-pressure study in the $Nd_{1-x}Sr_xMnO_3$ compounds with $x=0.50$ and 0.55. The *c* parameter of the orthorhombic *Pbnm* cell in the $x=0.50$ compound shrinks about 1% at the charge-ordering temperature T_{CO} on account of the $3d_{3x^2-r^2}/3d_{3y^2-r^2}$-type orbital ordering accompanied by the cooperative Jahn-Teller distortion.[5] Also in the $x=0.55$ compound the *c* parameter suddenly shrinks about 2.7% at the Néel temperature T_N (~ 230 K) owing to the $3d_{x^2-y^2}$-type orbital ordering. Therefore, one can expect that the application of uniaxial pressure along the *c* axis would significantly affect the transition temperatures in these compounds. In this connection a large effect of anisotropic strain on the phase stability in an epitaxial film of a perovskite-like manganese oxide has already been pointed out.[13] A film sample usually shows different electrical and magnetic properties from bulk samples with the same composition. For example, the ferromagnetic transition temperature T_C significantly depends on the lattice parameters of a substrate. The present study of the uniaxial-pressure effect on manganese perovskites should provide an important information for the film fabrication.

Crystals of $Nd_{1-x}Sr_xMnO_3$ with $x=0.50$ and 0.55 were melt grown by using a floating zone furnace. No trace of impurities was found in x-ray powder-diffraction patterns. Thin samples with a rectangular surface perpendicular to a pseudofourfold axis (typically $2\times1\times0.5$ mm^3) were cut out from the crystal bars. Because of twin mosaics in an orthorhombically distorted perovskite structure, the [001] axis was perpendicular to the sample surface in some domains and the [110] axis in the others. We roughly estimated the ratio of the *c*-axis-oriented domains from the intensities of the x-ray (002) and (110) reflections. Well *c*-axis-oriented samples were selected for a uniaxial-pressure experiment.

Resistivity under uniaxial stress was measured by using an apparatus shown in Fig. 1. A KS steel coil spring with a spring constant of 6.2 kgf/mm was used to load pressure on a sample surface. The load was calculated from shrinkage of the spring at room temperature (typically a few millimeters). The pressure apparatus was set in a copper cylinder used as a heat sink. The cylinder was first slowly cooled to 77 K and then warmed to measure a resistivity-temperature curve under constant pressure. The change of pressure with temperature was estimated to be within 10%. Resistivity was mea-

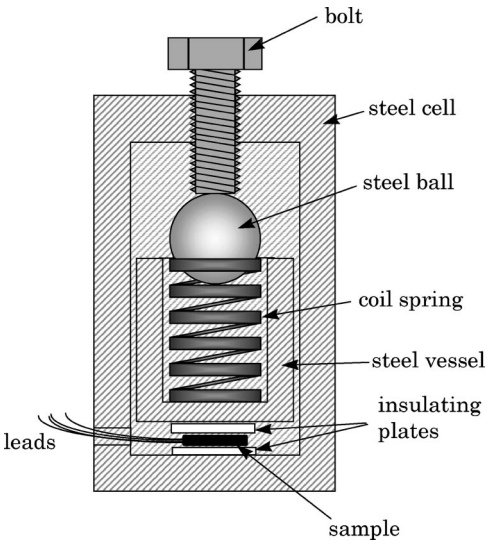

FIG. 1. Schematic drawing of a cell for resistivity measurements under uniaxial pressure.

sured by a conventional four-probe method. The current direction was perpendicular to the uniaxial stress. Temperature was monitored with a silicon diode thermometer attached to the pressure apparatus.

Large effects of uniaxial pressure are observed in the $x=0.50$ compound as shown in Fig. 2. In this sample pressure was loaded on a 78% *c*-axis-oriented surface. The charge-ordering transition can be clearly detected as a critical point of a resistivity curve at around 160 K. A kink at around 250 K is caused by the ferromagnetic transition. The application of uniaxial pressure clearly raises the charge-ordering temperature T_{CO} and lowers the Curie temperature T_C. The transition temperatures are plotted against uniaxial pressure, shown by solid lines in Fig. 3. In this pressure range, T_{CO} and T_C change linearly with uniaxial pressure at rates of 0.19 K/MPa and -0.06 K/MPa, respectively. While there is a large hysteresis in the charge-ordering transition, T_{CO}'s on cooling and warming increase almost at the same rate.

The large effect on T_{CO} can be interpreted in terms of the interplay among charge, orbital, and lattice. The compression along the *c* axis should assist the cooperative Jahn-Teller distortion and stabilize the orbital-ordering phase, but not the orbitally disordered ferromagnetic metallic phase. Therefore

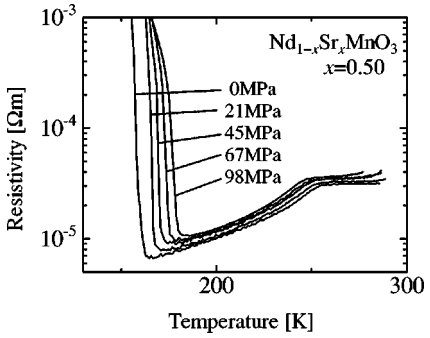

FIG. 2. Semilog plot of the resistivity of $Nd_{1/2}Sr_{1/2}MnO_3$ as a function of temperature under various uniaxial pressures measured on warming. Uniaxial pressure was loaded on the sample surface 78% *c* axis oriented.

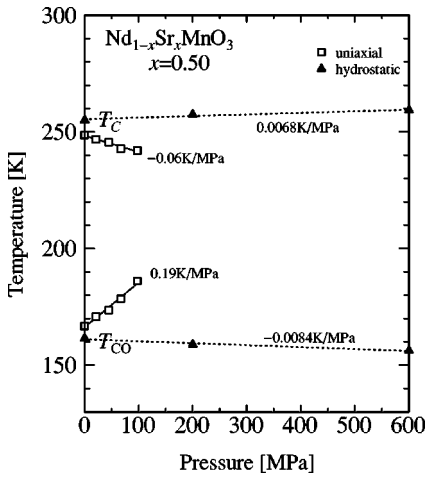

FIG. 3. Squares and solid lines: the ferromagnetic transition temperature, T_C, and charge-ordering temperature, T_{CO}, as a function of applied uniaxial pressure for $Nd_{1/2}Sr_{1/2}MnO_3$ measured on warming. Triangles and dotted lines: dependence of T_C and T_{CO} on hydrostatic pressure from Ref. 17. The difference in T_C and T_{CO} under ambient pressure between the uniaxial-pressure study and the hydrostatic-pressure study may be due to a small difference of the composition or oxygen nonstoichiometry.

it raises T_{CO}. The reason for the decrease in T_C is not yet clear on the other hand. The application of anisotropic pressure along the *c* axis would affect the electron transfer in the *a*-*b* plane and along the *c* axis in the opposite way. The decrease in T_C with uniaxial pressure may be related to the variation of the transfer energies. Studies of the crystal structure under uniaxial pressure are necessary for a further discussion. Next let us compare the effect of uniaxial pressure with the case of hydrostatic pressure, given by the dotted lines in Fig. 3. It is clearly shown that the variation of the transition temperatures with hydrostatic pressure is much less drastic than with uniaxial pressure. Moreover hydrostatic pressure affects the transition temperature in the opposite way to the uniaxial pressure along the *c* axis: it raises T_C and lowers T_{CO}.[17] Here the small difference in T_C and T_{CO} under ambient pressure between the previous report and the present study may be due to a small difference of the composition or oxygen nonstoichiometry. Isotropic pressure usually increases the electron transfer between $3d$ orbitals in perovskite-like transition-metal oxide compounds.[14,15] As the transfer increases, the double-exchange interaction is enhanced and hence the itinerant ferromagnetic phase is stabilized.[16]

Figure 4 shows the resistivity in an $x=0.55$ sample under constant uniaxial pressures measured on warming. The sample was estimated to be 96% *c* axis oriented from x-ray data. A kink at around 220–240 K in each resistivity curve corresponds to the antiferromagnetic transition.[10,11] Here it is noteworthy that the resistivity data are dominated by the electrical conduction in the *a*-*b* plane which is reported to be metallic.[11] The gradual increase of the resistivity value at room temperature with pressure may be due to some cracks since the sample did not show the initial resistivity value even after the uniaxial pressure was released. The change in the transition temperature with uniaxial pressure, however, is intrinsic because the value of T_N at ambient pressure before

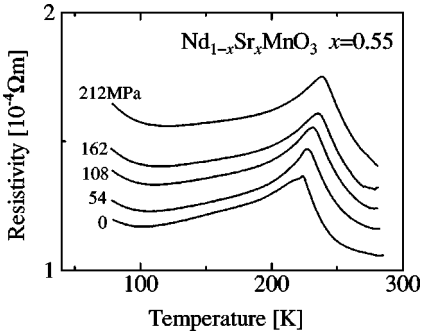

FIG. 4. Resistivity curves of $Nd_{0.45}Sr_{0.55}MnO_3$ under various uniaxial pressures measured on warming. Uniaxial pressure was loaded on the sample surface 96% *c* axis oriented. The shift of the resistivity well above T_N with pressure would not be intrinsic (see text).

and after the experiment was identical. Uniaxial pressure linearly raises T_N at a rate of 0.066 K/MPa. The rate of change of T_N on cooling is the same within an error. The compression along the *c* axis should stabilize the $d_{x^2-y^2}$ orbital configuration associated with the layered antiferromagnetic phase of $Nd_{0.45}Sr_{0.55}MnO_3$.

The pressure dependence of the temperature of a first-order transition between two phases is related to differences in entropy and volume. Let us first focus on the $x=0.50$ case. The Clausius-Clapeyron relation can be modified as,

$$\frac{dT_{CO}}{dP}=\frac{ab\Delta c}{\Delta\sigma}, \tag{1}$$

for the present measurements. Here σ denotes entropy per unit cell, i.e., four manganese ions, and *a*, *b*, and *c* are the cell parameters. Using the observed rate of 0.19 K/MPa and the reported Δc of 0.065 Å, the entropy difference $\Delta\sigma$ at T_{CO} is calculated to be $\sim 1.1k_B$. Here one should note that the order parameters just below T_{CO} are reported to reach 80–100% of the low-temperature value.[7] Assuming that the ferromagnetic phase above T_{CO} would be the disordered-polaron phase, the contribution of the charge distribution to $\Delta\sigma$ would be $\sim 4k_B\ln 2=2.8k_B$ per unit cell. One should also take account of the orbital degree of freedom in the ferromagnetic phase ($\sim 2k_B\ln 2=1.4k_B$). The total of $4.2k_B$ is nearly four times as large as the above-mentioned experimental value. In our opinion, the small $\Delta\sigma$ demonstrates that the electronic state in the ferromagnetic phase should rather be considered as a band metal, in which the contribution of the charge and orbital degrees of freedom to entropy should roughly be reduced by the factor of k_BT/E_F. If we adopt a realistic value, $E_F\sim 0.05$ eV, the result could be explained.

In the case of the $x=0.55$ sample, $\Delta\sigma$ at T_N is calculated to be $\sim 4k_B$ from the modified Clausius-Clapeyron relation. Assuming the perfect ordering of spin and orbital just below T_N, the loss of the spin entropy at T_N would be $2k_B(\ln 4+\ln 5)=6.0k_B$. The orbital contribution to $\Delta\sigma$, $2k_B\ln 2=1.4k_B$, should also be taken into account. As a result, one can expect $\Delta\sigma\sim 7.4k_B$, which is nearly twice as large as the experimental value. This discrepancy is probably due to the gradual growing of the antiferromagnetic order parameter below T_N.[6] A short-range correlation of spin and orbital in the paramagnetic phase is another possible reason.

In summary, the effects of uniaxial pressure on phase transitions in $Nd_{1-x}Sr_xMnO_3$ ($x=0.50$ and 0.55) were studied. The charge- and orbital-ordering phase in the $x=1/2$ compound is stabilized under uniaxial pressure along the *c* axis. The rate of change in the charge-ordering temperature is much larger than the hydrostatic-pressure case. For $x=0.55$, uniaxial pressure along the *c* axis raises the antiferromagnetic transition temperature. These results demonstrate that the orbital state can be well controlled by anisotropic pressure. The loss of entropy at the orbital-ordering temperature is obtained based on the Clausius-Clapeyron relation. The value is significantly lower than a simple estimation predicts.

The authors acknowledge the Chemical Analysis Center, University of Tsukuba for chemical analysis, and Joint Research Center for Atom Technology (JRCAT) for use of a Laue camera. This research was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture.

[1] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993).

[2] E.O. Wallan and W.C. Koehlar, Phys. Rev. **100**, 545 (1955); J.B. Goodenough, *ibid.* **100**, 564 (1955); K. Knizek, Z. Jirak, E. Pollert, F. Zounova, and S. Vratislav, J. Solid State Chem. **100**, 292 (1992).

[3] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature (London) **373**, 407 (1995).

[4] V. Kiryukhin, D. Casa, J.P. Hill, B. Keimer, A. Vigliante, Y. Tomioka, and Y. Tokura, Nature (London) **386**, 813 (1997).

[5] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science **270**, 961 (1995).

[6] H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **78**, 4253 (1997).

[7] K. Nakamura, T. Arima, A. Nakazawa, Y. Wakabayashi, and Y. Murakami, Phys. Rev. B **60**, 2425 (1999).

[8] Y. Tokura, H. Kuwahara, Y. Moritomo, Y. Tomioka, and A. Asamitsu, Phys. Rev. Lett. **76**, 3184 (1996).

[9] Y. Moritomo, T. Akimoto, A. Nakamura, K. Ohoyama, and M. Ohashi, Phys. Rev. B **58**, 5544 (1998).

[10] H. Yoshizawa, H. Kawano, J.A. Fernandez-Baca, H. Kuwahara, and Y. Tokura, Phys. Rev. B **58**, R571 (1998).

[11] H. Kuwahara, T. Okuda, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. Lett. **82**, 4316 (1999).

[12] R. Maezono, S. Ishihara, and N. Nagaosa, Phys. Rev. B **57**, R13 993 (1998).

[13] N.-C. Yeh, R.P. Vasquez, D.A. Beam, C.-C. Fu, J. Huynh, and G. Beach, J. Phys.: Condens. Matter **9**, 3713 (1997); T.Y. Koo, S.H. Park, K.-B. Lee, and Y.H. Jeong, Appl. Phys. Lett. **71**, 977 (1997); A.J. Millis, T. Darling, and A. Migliori, J. Appl. Phys. **83**, 1588 (1998); H.L. Ju, Kannan M. Krishnan, and D. Lederman, *ibid.* **83**, 7073 (1998).

[14] Y. Moritomo, H. Kuwahara, Y. Tomioka, and Y. Tokura, Phys. Rev. B **55**, 7549 (1997).

[15] X. Obradors, L.M. Paulius, M.B. Maple, J.B. Torrance, A.I. Nazzal, J. Fontcuberta, and X. Granados, Phys. Rev. B **47**, 12 353 (1993); P.C. Canfield, J.D. Thompson, S.-W. Cheong, and L.W. Rupp, *ibid.* **47**, 12 355 (1993).

[16] C. Zener, Phys. Rev. **82**, 403 (1951); P.W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).

[17] Y. Moritomo, H. Kuwahara, and Y. Tokura, J. Phys. Soc. Jpn. **66**, 556 (1997).