Pressure Tuning of Magnetic Interactions in Layered $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ Manganite

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The effect of pressure of up to 9 GPa on the magnetic and structural properties of layered $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ manganite has been investigated. Pressure shifts the Mn atoms from the center of each bilayer towards the adjacent bilayer. The observed shift of the Mn atoms involves mainly a charge redistribution within the $d_{3z^2-r^2}$ axial orbital. The decrease in the interbilayer spacing and the shift of the Mn atoms away from the center of each bilayer result in increased magnetic and electronic coupling between the adjacent bilayers along the c axis.

The recent observation of "colossal" magnetoresistance (CMR) in the layered manganites $R_{2-2x}A_{1+2x}Mn_2O_7$ (R is a rare-earth ion and A is a divalent cation) has prompted a considerable effort aimed at understanding the electronic and structural properties of these materials [1]. The general mechanism of the CMR phenomena can be understood within the framework of the double-exchange (DE) theory originally developed to describe the electronic properties of manganites with perovskite-type structure [2]. The DE theory explains the conductivity of the manganite oxides as transport of polarized charge carriers in the local magnetic field generated by the manganese ions. DE theory predicts that the closer the alignment of magnetic moments on the Mn ions to parallel, the higher the conductivity.

The key property of the layered manganites, which makes them distinct from the perovskite-type materials, is the high degree of anisotropy. This anisotropy arises from the presence of $(R_{1-x}A_x)_2O_2$ NaCl-type blocks, which separate paired MnO_2 sheets forming bilayers. In the unit cell of the layered manganese oxide, manganese atoms occupy the positions in the centers of MnO_6 octahedra. The oxygen ions occupy three nonequivalent positions in the lattice. Oxygen O(1) occupies the corners of the unit cell. This ion is involved in the Mn-O-Mn bond along the fourfold c axis. Oxygen O(3) occupies the $(0, 1/2, z)$ position. Like O(1) it is involved in the Mn-O-Mn bonding but this time along the a axis in the basal plane. Oxygen O(2) is at the $(0, 0, z)$ position. It forms a covalent bond with a Mn ion at only one end of the bond along the c axis. The other end binds O(2) with the $R, A(2)$ ion, occupying a position between the two adjacent bilayers.

This type of stacking results in strong magnetic and electronic coupling within each bilayer and a much weaker coupling along the fourfold axis. It is, therefore, possible to view the layered manganites as natural spin-valve devices [3]. In such devices the application of external magnetic field along the c axis aligns the moments on the Mn sites parallel to the field and enhances the electron transport along the c axis. Another way to change the dimensionality of the magnetic interactions is to apply pressure.

Indeed, the transport and magnetic properties of layered manganites are very sensitive to applied pressure due to the anisotropic compressibility of these materials. Kimura *et al.* found that applied pressure suppresses the steep drops in resistivity accompanying the phase transition to the ferromagnetic phase in $La_{1.4}Sr_{1.6}Mn_2O_7$ [4]. A similar effect of pressure on another layered manganite— $La_{1.2}Sr_{1.8}Mn_2O_7$—has been described by Argyriou *et al.* [5]. It was found that at ambient temperature manganese atoms shift towards O(1) ions, making magnetic interactions in this material more two dimensional. The calculations of the Madelung potential for the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series has shown that the applied pressure stabilizes the in-plane $d_{x^2-y^2}$ orbital in comparison with the axial $d_{3z^2-r^2}$ orbital [6]. Pressure-induced charge transfer from the axial to the in-plane orbital weakens the interbilayer coupling and reduces the charge transport along the c axis.

We have recently studied the resistivity of the layered $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ manganite and found that applied pressure has the opposite effect on the transport properties of this material [7]. At ambient pressure $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ undergoes a phase transition from a paramagnetic state to a spin-glass-like state at about 40 K [8]. When the temperature is lowered below 40 K, the resistivity increases, reflecting the insulating state of the material. The application of pressure lowers the resistivity, making it more metallic [7]. In this Letter we report on the structural and magnetic properties of $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ and explain the observed enhancement in electrical conductivity. To our knowledge this is the first study of structure and magnetism of a layered manganite at pressures as high as 9 GPa.

Single crystals of $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ were grown by the floating-zone method. The precursor materials were

prepared by mixing stoichiometric amounts of La_2O_3, Nd_2O_3, $CaCO_3$, and MnO_2. A diamond anvil cell made of nonmagnetic alloy was used for the magnetic ac susceptibility measurements using an inductance method. The single crystal of $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ with the c axis along the magnetic field direction was loaded into the gasket hole. The pressure was determined at room temperature by the ruby fluorescence method. A part of the single crystal was ground into powder and mixed with the pressure transmitting liquid (Fluorinert) for high-pressure neutron diffraction. The neutron diffraction measurement at ambient temperature was performed using a Paris-Edinburgh cell at the PEARL high pressure facility (HiPr) at ISIS (Rutherford Appleton Laboratory, U.K.).

All diffraction patterns were analyzed with the Rietveld technique using the general structure analysis system package [9]. The refinement has confirmed that the structure is tetragonal with space group $I4/mmm$. The symmetry remains unchanged throughout the studied pressure region. A small amount ($\sim 3\%$) of rhombohedral phase was also found in the sample. This additional phase is most likely due to the presence of a $(La, Nd, Sr)MnO_3$ perovskite material in the grown crystal. Such a perovskite phase can originate from intergrowths which are common in crystals of layered $R_{2-2x}A_{1+2x}Mn_2O_7$ materials [10]. Scattering from the pressure cell resulted in the presence of low-intensity peaks from nickel and tungsten carbide.

The pressure dependence of the a and c lattice parameters of the main phase at $T = 300$ K is presented in Fig. 1. The compressibility along the a axis is 1.5 times larger than along the c axis. Such a "softness" of the ab basal plane in comparison with the c direction in the lattice plays a significant role in the behavior of the manganese atoms under pressure. The compressibility of the Mn-O(1) and Mn-O(2) bonds along the tetragonal c axis is shown in Fig. 2(a) and the pressure dependence of the O(3)-Mn-O(3) angle is presented in Fig. 2(b). At ambient pressure the Mn atoms lie closer to the center of each bilayer [Fig. 2(a)] and the O(3)-Mn-O(3) angle is close to 180° [Fig. 2(b)]. The MnO_6 octahedra are elongated towards the outer ends of each bilayer, as shown schematically in Fig. 2(b).
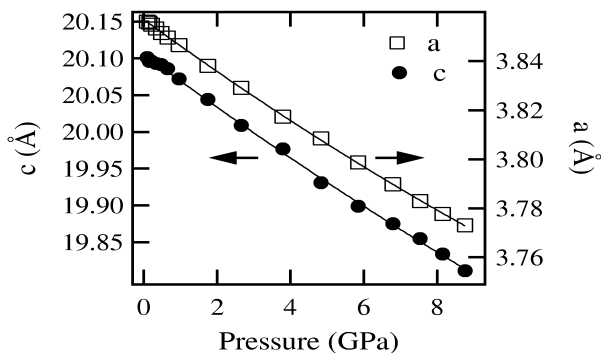
When pressure is applied, the length of the Mn-O(1) bond increases while the Mn-O(2) bond length decreases. This change is caused by the shift of the Mn atoms towards the outer edges of bilayers. The shift is continuous up to about 1.2 GPa. At this pressure we observe a discontinuous change in the bond lengths [Fig. 2(a)]. The interchange in the interatomic bonds is accompanied by a further distortion of the O(3)-Mn-O(3) angle [Fig. 2(b)] and by a decrease in the Mn-O(3) distance [Fig. 2(c)].

Despite the dramatic change in the individual axial Mn-O bond lengths, the mean bond length [Mn-O(1) + Mn-O(2)]/2 is almost unchanged in the pressure range
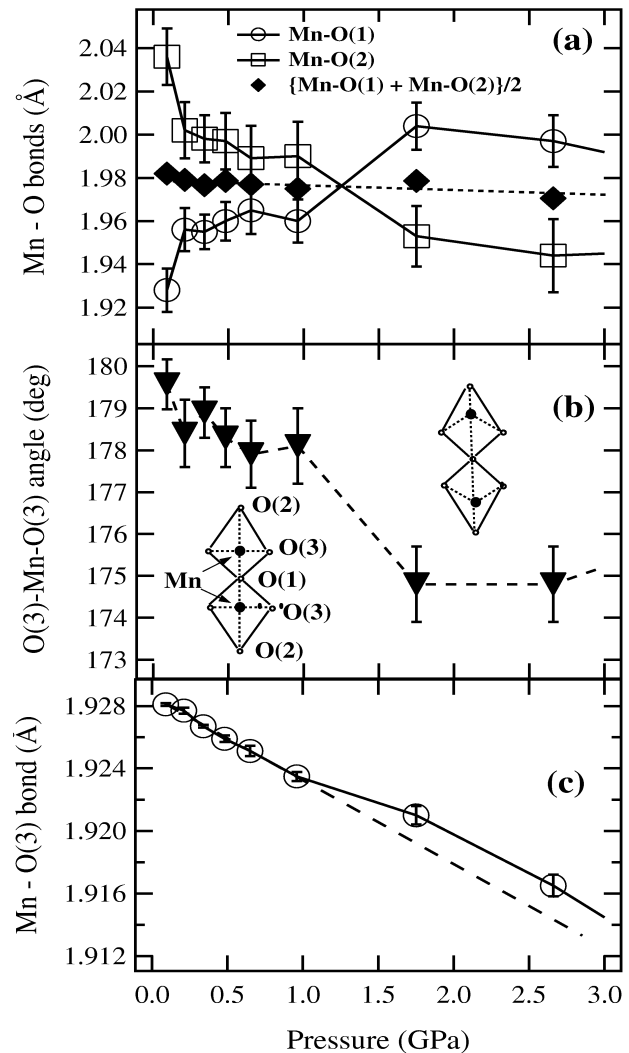

FIG. 2. The compressibility of Mn-O bond lengths and angles: (a) Mn-O(1), Mn-O(2), and the mean bond length (the error bars are omitted for clarity). At about 1.2 GPa the Mn-O(2) bond abruptly shortens to become equal in length to that of the Mn-O(1) bond below 1.2 GPa, while the Mn-O(1) increases in length by about the same amount; (b) O(3)-Mn-O(3) angle. The rhombs represent the bilayers of MnO_6 octahedra and show the position of the Mn atom above and below 1.2 GPa; (c) Mn-O(3) bond. The Mn-O(3) becomes slightly longer to compensate for the buckling of O(3)-Mn-O(3) at 1.2 GPa. This explains the observed deviation from the low-pressure linear approximation (dashed line).

FIG. 1. Pressure dependence of the a and c lattice parameters at $T = 300$ K (the error bars are smaller than the symbols).

from 1 bar to 3 GPa [Fig. 2(a)]. In other words, the spacing between O(1) and O(2) atoms, representing effectively the "thickness" of the bilayer, remains constant. The application of pressure results mainly in the shift of the manganese atom along the O(2)-Mn-O(1) linkage towards the O(2) atom, due to a rather high in-plane compressibility as discussed above. A similar effect has been observed in $(La_{1-z}Nd_z)_{1.2}Sr_{1.8}Mn_2O_7$ ($z = 0$) at pressures of up to 0.6 GPa [5]. Interestingly, in $La_{1.2}Sr_{1.8}Mn_2O_7$ the Mn-O(1) bond length decreases and Mn-O(2) bond length increases under pressure. However, generally the Mn-O(2) bond responds in the same way as we observe in $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$. Since the Mn-O(2) bond is not part of the Mn-O-Mn linkages, the Mn-O(2) bond adjusts to the changes in length of the Mn-O(1) and the Mn-O(3) bonds to conserve the mean equilibrium bond length sum for the Mn valences.

At 300 K there are no long-range magnetic correlations between the Mn atoms and any exchange striction effects can be excluded from the consideration. We should, therefore, seek an explanation for the observed discontinuity of the Mn-O(1) and Mn-O(2) linkages at about 1.2 GPa by considering the electrostatic interactions and the geometry of the chemical bonds. We suggest that the interchange is the manifestation of the electron transfer within the $d_{3z^2-r^2}$ orbital from the Mn-O(2) to the Mn-O(1) side of the O(1)-Mn-O(2) linkage. As the Mn atom is pushed away from the O(1) atom by the increased buckling of the O(3)-Mn-O(3) bond under pressure [Fig. 2(b)], it has to transfer the electron to maintain the Mn-O(1) bond and to allow the Mn atom to absorb the strain by getting closer to the O(2) atom. To undergo such a transfer the $d_{3z^2-r^2}$ electron in the Mn atom has to go through a potential barrier. This barrier is created by the difference in the electronegativities of the O(1) and O(2) atoms in Mn-O(1)-Mn and Mn-O(2)-La, Nd, Sr(2) linkages, respectively, which is due to the fact that La, Nd, and Sr all have smaller electronegativity values than Mn. Since during the interchange the mean bond length [Mn-O(1) + Mn-O(2)]/2 is conserved, we have omitted from this qualitative discussion the influence of any redistribution of electrons between the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals with pressure in the vicinity of the interchange.

If the applied pressure does not change the thickness of the bilayers, where does all the strain along the c axis (Fig. 1) go? Figure 3 shows the pressure dependence of the distance between the O(2) atoms and the ab plane formed by O(3) atoms in the adjacent bilayer. The applied pressure affects mainly the interbilayer spacings and brings rigid bilayers closer to each other. Summarizing the effect of pressure on the structure of the $(La_{0.6}-Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ manganite, we conclude that it has a twofold effect. At first, the manganese atoms are shifted from the center of each bilayer. Second, the bilayers themselves are brought closer together. Both of these pressure-induced changes should promote the coupling between the manganese atoms along the c axis and should enhance the
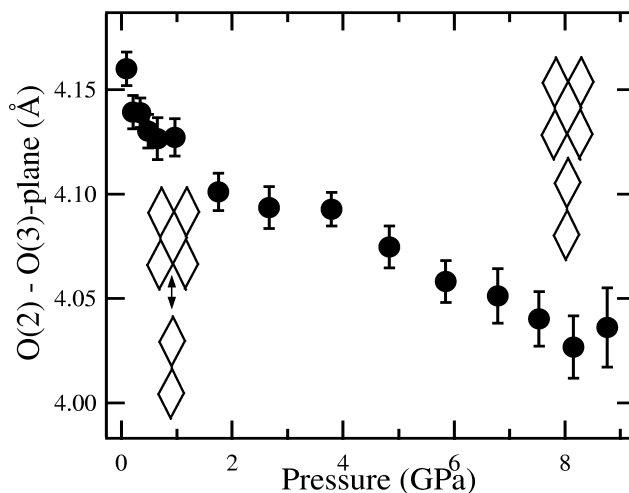
FIG. 3. Pressure dependence of the distance between a layer of O(2) in one bilayer and a layer of O(3) atoms in the adjacent bilayer. The paired octahedra represent the projection of two adjacent bilayers along the a direction. Note, the adjacent bilayers are shifted by $a/2$ with respect to each other.

electric conductivity and any three-dimensional magnetic interactions.

The set of curves presenting the temperature dependence of magnetic ac susceptibility along the c axis at several pressures is shown in Fig. 4. When pressure is applied, the amplitude of the susceptibility peak increases rapidly, reaching a maximum at 1.9 GPa. The large pressure-induced positive shift of about 5 K/GPa in the position of the peak indicates that the applied pressure enhances the coupling between the manganese ions. Our recent data on the electrical resistivity [7] collected at pressures up to 1.1 GPa show that the conductivity is also greatly enhanced by applied pressure below 40 K. In other words,
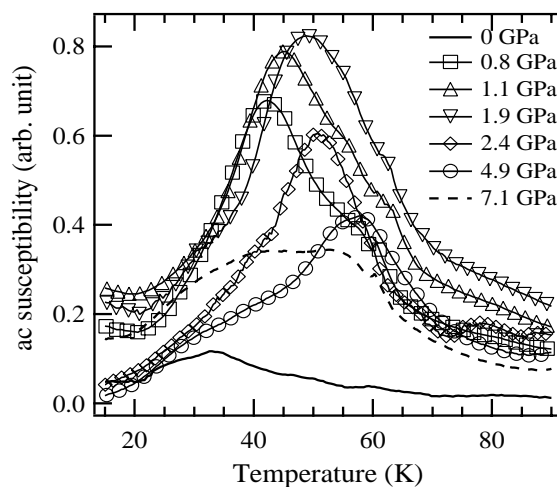

FIG. 4. The temperature dependence of the magnetic ac susceptibility measured along the c axis at several pressures. The small peak at about 40 K on the ambient pressure curve shows that $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$ undergoes a phase transition to a spin-glass-like state, which is in a good agreement with the observations reported by Y. Moritomo et al. [8].

the application of pressure up to the pressure of the interchange results in the enhancement of the 3D correlations in $(La_{0.6}Nd_{0.4})_{1.2}Sr_{1.8}Mn_2O_7$.

This is in contrast with results reported for $La_{1.4}Sr_{1.6}Mn_2O_7$ [4], in which electrical resistivity increases and magnetic ac susceptibility decreases under pressure. To find the explanation for this we will compare the effects of the external hydrostatic pressure, presented in this Letter, and of chemical pressure introduced on Nd doping, as reported by Akimoto *et al.* for the $(La_{1-z}Nd_z)_{1.2}Sr_{1.8}Mn_2O_7$ family of compounds [11]. According to the latter study, Nd doping results in a longer Mn-O(1) and shorter Mn-O(2) bonds, while the Mn-O(3) bond length remains the same. At the doping level of $z = 0.4$ the Mn-O(1) and Mn-O(2) become very similar in length. Akimoto *et al.* [11] do not report structural data for compounds with $z > 0.4$, but it is possible to assume that a further increase in the Nd content above $z = 0.4$ would result in the interchange of the Mn-O(1) and the Mn-O(2) bond lengths which is similar to the changes induced by the application of external pressure observed in this study [Fig. 2(a)]. However, the results reported by Moritomo *et al.* [8] for the $(La_{1-z}Nd_z)_{1.2}Sr_{1.8}Mn_2O_7$ series do not show any enhancement of the magnetic correlations for materials with $z = 0.6$ and 1.0, i.e., with $z > 0.4$. We suggest that this is due to the narrow pressure and composition range near the interchange of Mn-O(1) and Mn-O(2) bonds in which such an enhancement can be observed. When Mn-O(1) becomes longer than Mn-O(2) under applied chemical or external pressure, the separation distance between MnO_2 sheets forming each bilayer increases. The coupling of magnetic moments on the manganese sites within each bilayer become even weaker, resulting in the collapse of the long-range magnetic order.

When the pressure is increased further above 1.9 GPa, the amplitude of the susceptibility peak starts to decrease (Fig. 4). However, this effect is different from what has been observed recently in $La_{1.4}Sr_{1.6}Mn_2O_7$ [4] and does not indicate a crossover from 3D- to 2D-type magnetism. In $La_{1.4}Sr_{1.6}Mn_2O_7$ the Mn-O(2) bond is longer than the Mn-O(1) bond [12], which indicates that 3D-type interactions between the bilayers are already weakened at ambient pressure. In $(La_{1-z}Nd_z)_{1.2}Sr_{1.8}Mn_2O_7$ the Mn-O(2) bond is shorter than the Mn-O(1) bond at pressures $P > 1.2$ GPa, promoting 3D-type electronic and magnetic interbilayer interactions. The weak pressure dependence (the peak on susceptibility is still present at 7.1 GPa) suggests that the observed decrease in the amplitude and the broadening of the peak are due to the pressure-induced "freezing" of spin disorder in the Mn sublattice at very high pressures.

In conclusion, we have studied the effect of high pressure on structural and magnetic properties of the $(La_{1-z}Nd_z)_{1.2}Sr_{1.8}Mn_2O_7$ ($z = 0.4$) layered manganite. The application of pressure leads to a buckling of the Mn-O(3)-Mn linkages in the *ab* plane. The compressibility along the *c* axis is "absorbed" by the interbilayer spacing. At an atomic level the application of pressure leads to an increase of the Mn-O(1) and a decrease of the Mn-O(2) bond lengths, which results in the interchange of these two axial bonds at about 1.2 GPa. The pressure-induced shift of the Mn atom away from the center of the bilayers leads to enhanced 3D-type electronic and magnetic interactions between the adjacent bilayers. Such a pressure-induced 2D to 3D crossover has been shown for the first time.

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