Oxygen-isotope effects on local structure distortions and transport properties of epitaxial thin films of $Nd_{0.67}Sr_{0.33}MnO_3$

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Investigations of incoherent lattice fluctuations and electrical transport in oxygen isotope substituted $Nd_{0.67}Sr_{0.33}MnO_3$ thin films have shown an increase in the incoherent displacement of the Mn atoms as the sample goes from the ferromagnetic to paramagnetic state. The observed enhancement is about 15% larger and occurs over a ~12% narrower temperature range for ^{18}O than for ^{16}O. The peak in resistivity, which is close to the magnetic phase transition, is enhanced in intensity and shifted to lower temperatures by about 25 K for ^{18}O films as compared to the ^{16}O films. The different behavior for the two oxygen isotopes demonstrates the importance of quantum fluctuations of the O phonon on the magnetic phase transition in this system.

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During the past eight years the manganese-based perovskites $Ln_{1-x}A_xMnO_3$ (where Ln is a trivalent rare-earth element and A is a divalent), which exhibit very large magnetoresistance, have been the subject of intensive investigations.[1–3] The undoped parent compound $LaMnO_3$ with Mn^{3+} is an insulating antiferromagnet.[4,5] When Mn4+ ions are introduced by substituting divalent ions (e.g., Ca, Sr, Ba) for La^{3+}, the materials undergo a transition from a high-temperature paramagnetic insulating state to a ferromagnetic metallic ground state for $0.2<x<0.5$. A prominent feature of these materials is a large maximum in the resistivity[2,3] close to the ferromagnetic transition temperature (T_c). This resistivity peak decreases dramatically by a few orders of magnitude[3] by the application of magnetic field. This phenomenon is now known as colossal magnetoresistance (CMR). The physics of manganites has primarily been described by the double-exchange model.[6,7] This model accounts qualitatively for ferromagnetic ordering and carrier mobility that depends on the relative orientation of Mn moments, which near T_c are strongly dependent on the applied field. The observed large resistivities measured in these materials, significantly beyond the Mott limit, could not be explained by the double exchange mechanism. However, Millis, Littlewood, and Shraiman[8,9] have proposed that polaronic effects due to strong electron phonon coupling arising from a strong Jahn-Teller effect should be involved. Many experiments, including those showing strong isotope effects on the intrinsic resistivity of the ferromagnetic state, have provided strong evidence[10,11] of polaronic charge carriers in manganites.

We present here ion channeling and transport studies on high quality epitaxial thin films of $Nd_{0.67}Sr_{0.33}MnO_3$ made by laser ablation on $LaAlO_3$ substrates which are identically exchanged by the ^{16}O and ^{18}O isotopes. Three prominent features are observed in these films. (1) Across the ferromagnetic to paramagnetic phase transition, the ^{18}O samples have larger local lattice distortions than the ^{16}O samples. (2) In the paramagnetic state close to the ferromagnetic transition the peak in resistivity of the ^{18}O samples is much higher than that in the ^{16}O samples.[11] (3) The ^{18}O samples have a sharper resistivity drop below T_c than the ^{16}O samples, and accordingly the enhancement in lattice fluctuations is confined in a narrower temperature region.

The epitaxial thin films of $Nd_{0.67}Sr_{0.33}MnO_3$ were grown on $\langle 100 \rangle$ $LaAlO_3$ single crystal substrates by pulsed laser deposition using a KrF excimer laser. The deposition frequency is 10 Hz and the laser fluence is about 1.6 J/cm^2. The substrate temperature was 820 °C and the oxygen pressure was kept constant at 400 mTorr during the deposition. After deposition, the chamber was backfilled with oxygen to about 400 Torr. The film is then slowly (15 °C/min) cooled to room temperature. The film thickness was about 190 nm. Two pieces were cut from the same sample for oxygen-isotope diffusion. The diffusion for sample pair I was carried out for 10 h at about 900 °C and oxygen pressure of about 1 bar. The diffusion for sample pair II was performed for 10 h at 940 °C. The cooling rate was 300 °C/h. The ^{18}O-isotope gas is enriched with 95% ^{18}O, which can ensure 95% ^{18}O in $Nd_{0.67}Sr_{0.33}MnO_3$ thin films.

The temperature-dependent incoherent lattice fluctuations are measured by ion channeling which is an ultrafast unique method, providing a direct real space probe of extremely small (<picometer) uncorrelated displacements (static and dynamic) of atoms in single crystalline materials.[12] Ion channeling occurs when energetic ions incident along a major crystallographic direction, are steered by a series of glancing collisions with the atoms of close packed atomic rows or planes. The critical angle for channeling to occur, or the full width at half maximum (FWHM) of the channeling angular scan, depends on the incident ion energy, the atomic numbers of the projectile and target, the interatomic spacing, electron screening potential, and most importantly, any displacement (dynamic or static) of the atoms from their regular lattice sites. The FWHM is affected dramatically by incoherent atomic displacements (both static and dynamic), as opposed to an equivalent coherent change in lattice parameter (e.g., thermal expansion). The magnitude of the atomic displacement u is extracted from the measured FWHM using

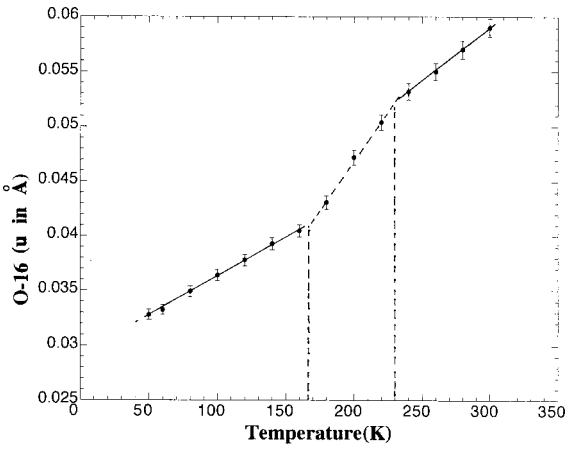

FIG. 1. The incoherent atomic displacement u as determined by ion channeling as a function of temperature in $Nd_{0.67}Sr_{0.33}Mn_{16}O_3$ thin films is plotted as a function of temperature. A large change ($\sim$20%) in u is seen across the ferromagnetic phase transition in the temperature range 168 to 230 K. The T_c of the sample is at 231 K.

Lindhard's continuum model[13] for channeling, with appropriate corrections based upon the Monte Carlo computer simulation of Barrett[14] and using average atomic numbers and lattice spacing. More details regarding ion-channeling studies are given in our earlier work.[15]

These measurements have been carried out using a very well collimated beam (0.5 mm diameter and $<0.01°$ divergence) of 1.5 MeV He ions. The sample was mounted on a precision four-axis goniometer having an angular resolution of 0.01°. Suitable arrangements were made to vary the temperature of the sample from room temperature down to 40 K with the help of close cycle refrigeration system. The backscattered particles were detected in an annular surface barrier detector of 300 mm^2 active area with a 4 mm diameter central hole and mounted along the beam axis at a distance of 7 cm from the target. For the channeling studies, the [001] $Nd_{0.67}Sr_{0.33}MnO_3$ film grown on $LaAlO_3$ substrate was first aligned parallel to the incident beam direction. Angular channeling scans were made across the [001] axis at different temperatures in the range 40 to 300 K for both the samples, one containing ^{16}O and the other ^{18}O, respectively, under identical conditions. The atomic displacement (u_1) values were extracted from the measured FWHM of these angular scans and are plotted in Figs. 1 and 2. We find that, in the film containing ^{16}O there is a nonphononic enhancement in the u_1 value in the temperature range 168–230 K, while that in ^{18}O sample it is in the range 130–185 K, consistent with the observed shift in the temperature of the magnetic phase transition. The magnitude of the total change in the later case is seen to be larger by about 15% and narrower by approximately 12% as compared to that in the former one.

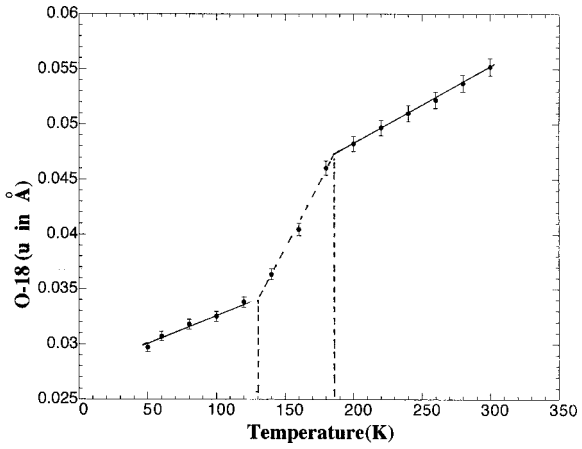

FIG. 2. Same as in Fig. 1 except that ^{16}O is replaced by ^{18}O. The ferromagnetic phase transition is shifted to lower temperature (T_c=186 K). The large change in u is now seen at a lower and narrower temperature region between 130 and 186 K. Also the effect is about 15% larger as compared to that shown in Fig. 1.

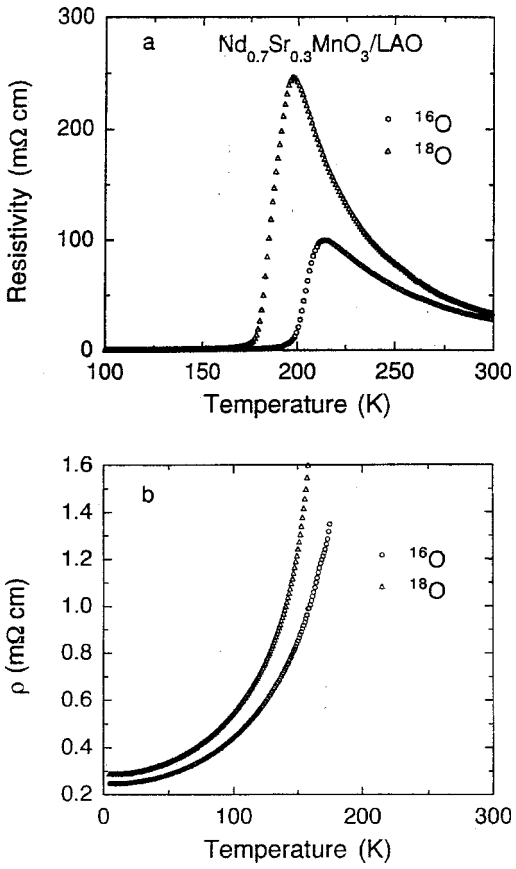

FIG. 3. (a) The resistivity (r) of the oxygen isotope exchanged films of $Nd_{0.67}Sr_{0.33}MnO_3$, with ^{16}O and ^{18}O respectively. The sudden drop in the r value at the magnetic phase transition is much larger and shifted to lower temperature for the sample with ^{18}O as compared to that containing ^{16}O. (b) The low temperature resistivity of O-isotope exchanged films. It is higher for the ^{18}O case.

The monotonic increase in u due to thermal vibration component is calculated using Debye and Einstein models relations taking into account both the acoustic and optic modes. The change in variation of u due to the acoustic and optic modes in the two cases of ^{18}O and ^{16}O is $\sim$2%.

The resistivity was measured by the van der Pauw technique and the contacts were made by silver paste. A small contact area makes it possible to accurately determine the absolute resistivity. In Fig. 3 we show the resistivity for the ^{16}O and ^{18}O samples of $Nd_{0.67}Sr_{0.33}MnO_3$ as a function of

temperature from 100–300 K [Fig. 3(a)] and from 10–150 K [Fig. 3(b)].[16] From Fig. 3(a), one can see that the temperature T_p (where the resistivity has a maximum) is different for the two isotope films, i.e., $T_p = 215$ K for the ^{16}O film and $T_p = 195$ K for the ^{18}O film. The oxygen isotope shift of T_p is 20 K. Since the ferromagnetic transition temperature T_c is near T_p,[2] the oxygen-isotope shift of T_c is also about 20 K. Similar shift is seen in ion channeling measurement (Figs. 1 and 2). At temperatures below T_p, the resistivity of the ^{18}O film has stronger temperature dependence than the ^{16}O film as seen in Fig. 3(b). Similarly the change in u_1 value across T_c is larger and narrower in the case of films containing ^{18}O (Fig. 2).

The r.m.s. displacement u_1 of ions in the ab plane, determined by ion channeling, as described above, has contributions from thermal vibrations of atoms due to acoustic and optical phonons, those arising from any defects and strain fields and, most importantly, any incoherent displacement of atoms at the ferromagnetic phase transition in the system. These are shown in Figs. 1 and 2 in the $Nd_{0.67}Sr_{0.33}MnO_3$ films of thickness ~190 nm made on $LaAlO_3$ substrate, one with ^{16}O and the other with ^{18}O, respectively. The low-temperature behavior in both the plots shows an approximate linear temperature dependence of u_1, which is consistent with thermal vibrations. However, in this temperature region there is significant difference (at least 10%) in the magnitude and slopes of the two curves for the ^{16}O and ^{18}O samples, which cannot be ascribed to the isotope effect on the phonons. The effect due to the isotope masses is only ~2%. It appears that there is more order in the case of ^{18}O sample as compared to the ^{16}O one. Since this does not follow from the conventional electron-phonon interaction in the metallic-ferromagnetic state we ascribe it possibly to the effect of the isotope mass on the character of the large polarons in this material. More rigorous theoretical study is required to calculate the isotope effect on the transport property of these materials.

At higher temperatures, i.e., above $T = 170$ K, in the ^{16}O sample and above $T = 130$ K in the ^{18}O case as T approaches T_c, a more rapid increase in u_1 is observed which persists up to T_c. As mentioned above, T_c shifts to a lower value by about 20 K in the case of the sample with ^{18}O. The observed increase in the u_1 value near T_c in the two cases is too large to be attributed to thermal phonons. In addition, the increase in u_1 is found to be larger in the ^{18}O sample, which has the lower T_c. Also the increase occurs in a narrower temperature range in ^{18}O as compared to that in ^{16}O, which is consistent with the sharper and larger drop in resistivity in the ^{18}O case (Fig. 3). Finally above T_c the slope of u_1 is larger for the ^{16}O sample showing the stronger temperature dependence.

The increase in u_1 and its association with T_c suggests that the observed behavior is related to distortions of the lattice due to the formation of Jahn-Teller small polarons as the system approaches the paramagnetic state. The existence of polarons, imply rearrangement of the oxygen of the perovskite cage around the Mn^{3+} ions. While this oxygen motion would not displace the Mn ions within an isolated perovskite cage, the oxygen motion implies lattice distortions that would extend beyond the local perovskite cage and it is these distortions that would lead to Mn, Nd, and Sr motion. However, we have not observed any appreciable displacement of Nd and Sr in the channeling measurements, only the Mn atoms are affected. The observation that the rise in u_1 begins well below T_c implies that polarons persist into the ferromagnetic state. This observation is consistent with other experiments on the manganites.[17,18]

In the CMR manganites polaron formation competes with the double exchange process and lowers T_c from the value expected from double exchange alone.[8] Therefore, the lower T_c and larger step observed in the ^{18}O sample suggests a stronger Jahn-Teller effect than in the case of ^{16}O. Since the only difference is the oxygen mass it can be concluded that the lower frequency phonons in the ^{18}O case produces a stronger Jahn-Teller effect. Therefore the experiment demonstrates the importance of phonon dynamics in the competition for the thermodynamic phase. This may be understood in terms of the increased entropy of the polaron state for the ^{18}O ions. In the low-temperature limit the Jahn-Teller energy only involves the force constant of the oxygen ions. However, the low lying excited vibrational and vibronic states of the polaron are at lower energies for the ^{18}O ions so that the system acquires more entropy as the temperature is increased in the heavier isotopic oxygen case. The increased entropy lowers the free energy of the polaron state so that the ferromagnetic to paramagnetic phase transition occurs at a lower temperature. Above T_c the u_1, the manganese displacement, for the ^{18}O sample is seen to exhibit weaker temperature dependence than the ^{16}O case. This too is evidence that the Jahn-Teller effect is stronger for ^{18}O. At very high temperatures thermal agitation will wash out the Jahn-Teller polaron and there should be no difference in u_1 between the two samples. Therefore, thermal vibrations suppress the Jahn-Teller polaron as the temperature is raised above T_c. Consequently, above T_c the temperature dependence of u_1, which is the sum of the (rising) thermal phonon contribution and the (falling) Jahn-Teller contributions, will be weaker when the Jahn-Teller is stronger. From this argument a weaker temperature dependence of u_1 is expected for the ^{18}O sample above T_c as observed.

In summary an enhancement of incoherent lattice fluctuations is directly seen in the ferromagnetic to paramagnetic phase transition in the CMR manganite, $Nd_{0.67}Sr_{0.33}MnO_3$. It is shown that the changes in incoherent atomic displacements or lattice fluctuations is closely correlated with the transport properties at this phase transition. We conclude that channeling data for isotope oxygen substitution demonstrates the importance of the dynamics of the oxygen phonons, and therefore the oxygen mass, in the Jahn-Teller effect in the CMR managanites.

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