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Oxygen isotope effects in $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$: Relevance of the electron-phonon interaction to the phase segregation

M. R. Ibarra
Departamento de Física de la Materia Condensada e Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza y Consejo Superior de Investigaciones Científicas, 50009-Zaragoza, Spain

Guo-meng Zhao
Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland

J. M. De Teresa and B. García-Landa
Departamento de Física de la Materia Condensada e Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza y Consejo Superior de Investigaciones Científicas, 50009-Zaragoza, Spain

Z. Arnold
Departamento de Física de la Materia Condensada e Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza y Consejo Superior de Investigaciones Científicas, 50009-Zaragoza, Spain and Institut of Physics, Academy of Sciences of Czech Republic, Cukrovarniká 10, 16200 Praha 6, Czech Republic

C. Marquina and P. A. Algarabel
Departamento de Física de la Materia Condensada e Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza y Consejo Superior de Investigationes Científicas, 50009-Zaragoza, Spain

H. Keller
Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland

C. Ritter
Institute Laue Langevin, BP 156, 38042 Grenoble Cédex 9, France

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We have studied the oxygen isotope effect on $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$. Both isotope samples ($^{16}O$ and ^{18}O) segregate into a charge-ordered (CO) and a paramagnetic phase below 210 K, but the relative percentage of both phases strongly depends on the isotope mass. At low temperatures, the CO phase orders antiferromagnetically, whereas the remaining phase orders ferromagnetically. Our results can be explained by a scenario where the increase of the oxygen mass weakens the ferromagnetic interaction but has no influence on the electronic correlations that may be responsible for the CO state. [S0163-1829(98)00814-5]

The ceramic orthomanganites were already studied in the past[1–3] and more recently they have been the subject of intensive investigations because they exhibit colossal magnetoresistance.[4–6] The compounds $LaMnO_3$ and $CaMnO_3$ only have one type of Mn ion, i.e., Mn^{+3} (with three localized t_{2g} electrons plus one e_g electron) or Mn^{+4} (with three t_{2g} electrons). The magnetic interaction between the local moments formed by the t_{2g} electrons of these ions is antiferromagnetic (AF) and takes place indirectly through the oxygen (superexchange). The compounds $La_xCa_{1-x}MnO_3$ have mixed valence at the manganese sites, i.e., Mn^{+4}/Mn^{+3}. This allows the electronic transfer of the e_g electrons between Mn ions due to the covalent character of the chemical bonding. The local magnetic moments tend to be aligned due to this charge-transfer process. This so-called double exchange (Zener interaction) provides the ferromagnetic (F) interaction between the local moments. For the $x=\frac{2}{3}$ concentration, i.e., $La_{2/3}Ca_{1/3}MnO_3$ (33% of Mn^{+4}), the ferromagnetic interaction is very strong and the system is ferromagnetic below $T_C \approx 260$ K.[1,2] This state is characterized by a dramatic decrease in the electrical resistivity [metallic state (M)] in contrast to the paramagnetic state [insulating state (I)] above T_C.

The intensity of the ferromagnetic interaction is closely correlated with the structural parameters as well as with the lattice dynamics through the electron-phonon (e-ph) interaction. The bare electronic e_g bandwidth is determined by the Mn-O-Mn bond angle, being maximum for Mn-O-Mn$=180°$. Consequently, the Zener interaction is reduced as the structure becomes more distorted.[7] Hwang *et al.*[7] and De Teresa *et al.*[8] found a phase diagram in which for the highly-distorted structures, the long-range F ordering is suppressed and a spin-glass (or cluster-glass) state can appear at low temperatures due to the competition between the F and AF interactions. An increase in the e-ph interaction has been found to weaken the F interaction.[9] Besides, the long-range Coulomb interaction between electrons give rise to Mn^{+4}/Mn^{+3} charge ordering (CO) in some mixed-valence manganites.[10]

The ground state of a manganite is a subtle balance of the F, AF, CO, and e-ph interactions, which can be easily modified by chemical substitution, isotopic exchange, external pressure and magnetic field. The series $(La_{1-x}Nd_x)_{2/3}Ca_{1/3}MnO_3$ is an example of this strong competition. For $x<0.5$ there are paraferromagnetic and M-I transitions[11] whereas for $x>0.5$ there is not M-I transition and the compound with $x=1$ has been characterised as CO.[12] The $x=0.5$ compound is just on the border and macroscopic measurements seem to indicate that its ground state at low temperature is ''anomalous''.[13] That is the reason why we have chosen such a composition for the isotopic exchange.

The small-angle neutron-scattering experiments have shown the existence of magnetic polarons in the paramagnetic phase in $La_{2/3}Ca_{1/3}MnO_3$.[14–16] They constitute a type of dynamic phase segregation, with an average life time larger than 10^{-5} s as evidenced from NMR experiments.[17] The existence of phase segregation is not related to the morphology of the sample but it is an intrinsic property. This seems to be a general feature shared by other ceramic oxides of great interest as the copper-oxides superconductors.[18] Ibarra *et al.*[19] have recently established that the temperature dependence of the volume thermal expansion in $A_{2/3}Ca_{1/3}MnO_3$ collapses into two universal curves. The metallic state is associated with a low-volume (LV) state, while the insulating state corresponds to a high-volume (HV) state.[17] When a M-I transition takes place, a LV-HV transition occurs simultaneously. However, when the M-I transition is not complete, a phase segregation takes place with an intermediate volume. Therefore, the volume of the sample gives information about the relative volume fraction occupied by the segregated phases. Zhao *et al.*[20] have shown a strong effect of the oxygen mass on the magnetic and transport properties in the compound $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$. The compound with the ^{18}O isotope is insulator over the whole temperature range, whereas the ^{16}O sample exhibits a M-I transition at ~ 150 K. This strong isotopic effect was first observed in $La_{2/3}Ca_{1/3}MnO_3$.[9] These results give strong evidence for the polaronic nature of the magnetotransport properties in these manganites. The formation of polarons in this system is due to a strong e-ph interaction that produces strong anharmonic effects.[21,22] In order to gain more insight into the role of the e-ph interaction to determine the ground state in the mixed-valence manganites and how it changes with various internal and external parameters, we have performed resistivity, thermal-expansion, magnetostriction, and neutron-diffraction measurements on the oxygen-isotope exchanged samples of $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$ under high magnetic fields and hydrostatic pressures. The results show that the strong e-ph interaction in this compound plays a relevant role in the weakening of the ferromagnetic interaction, but has no significant effect on the electronic correlations, which are responsible for the CO state.

The samples were prepared by conventional solid state reaction using La_2O_3, Nd_2O_3, $CaCO_3$ and MnO_2. The powders were mixed, ground, and calcined in air at 1100 °C for 15 h. The samples were then reground thoroughly, pressed and fired at 1250 °C for 60 h with two intermediate grindings. This oxygen-isotope diffusion was carried out for 48 h at 950 °C and oxygen pressure of 1 bar.[20] The ^{18}O sample showed $80\pm10\%$ ^{18}O.

The high-temperature thermal expansion was measured using a ''push rod'' method. The low-temperature thermal expansion (from 4–300 K) was measured with the strain-gage technique under steady magnetic fields up to 12 T. The magnetostrictions parallel ($\lambda_{\parallel}$) and perpendicular ($\lambda_{\perp}$) to the field were measured by applying a pulsed field up to 14 T. The temperature dependence of the resistivity was measured using the four points technique under a pressure up to 10 kbar, which was produced by a clamp copper-beryllium pressure cell. Neutron-diffraction experiments were performed at the D1B instrument at the high-flux reactor of the ILL in Grenoble ($\lambda=2.52$ Å).

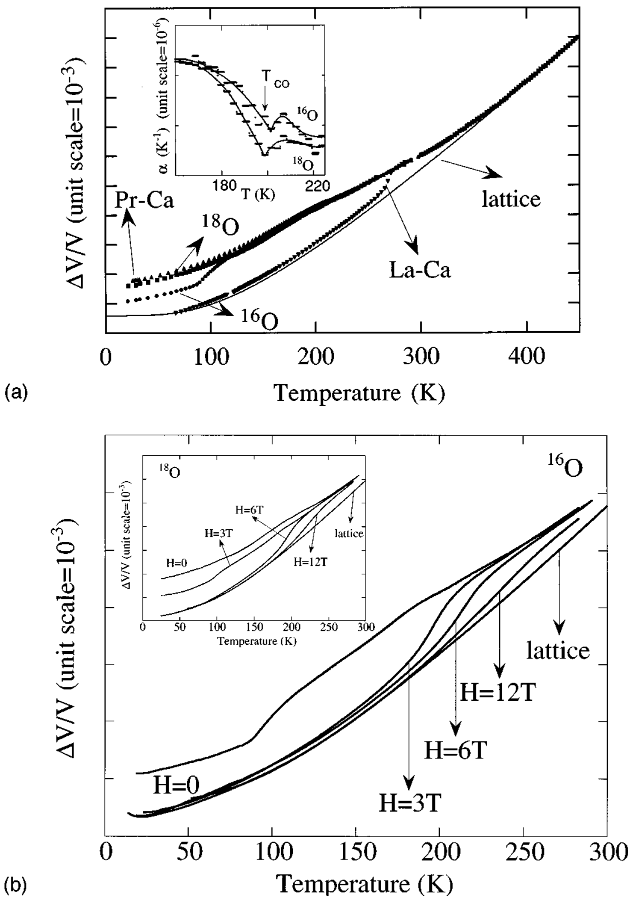

FIG. 1. Volume thermal expansion. (a) Comparison of the ^{16}O (dots) and ^{18}O (squares) volume thermal expansion with prototype insulating ($Pr_{2/3}Ca_{1/3}MnO_3$) (triangles) and metallic (low-temperature $La_{2/3}Ca_{1/3}MnO_3$) (inverted triangles) compounds. ''Lattice'' stands for the calculated phonon contribution using the Grüneisen law (line). The inset shows the linear thermal expansion coefficient for the ^{16}O and ^{18}O samples in the vicinity of T_{CO}. (b) Volume thermal expansion under several applied magnetic fields for ^{16}O. Inset: the same for ^{18}O.

The volume thermal expansion for the ^{16}O and ^{18}O samples of $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$ (denoted as ^{16}O and ^{18}O) is shown in Fig. 1(a). For comparison, we also include the results for the ^{16}O samples of $La_{2/3}Ca_{1/3}MnO_3$ and $Pr_{2/3}Ca_{1/3}MnO_3$. The solid line represents the phonon contribution calculated from the Grüneissen law using a Debye temperature (Θ_D) of 500 K. The extra anharmonic contribution with respect to the phonon contribution has been associated with the carrier localization due to polaronic effects.[19,21] We have choosen the volume thermal expansion curve of the compound $Pr_{2/3}Ca_{1/3}MnO_3$ (Ref. 23) as a prototype for the insulating state, whereas the result of $La_{2/3}Ca_{1/3}MnO_3$ at low temperatures is representative of the metallic state.[14] At $T\approx 200$ K, anomalies in the linear-

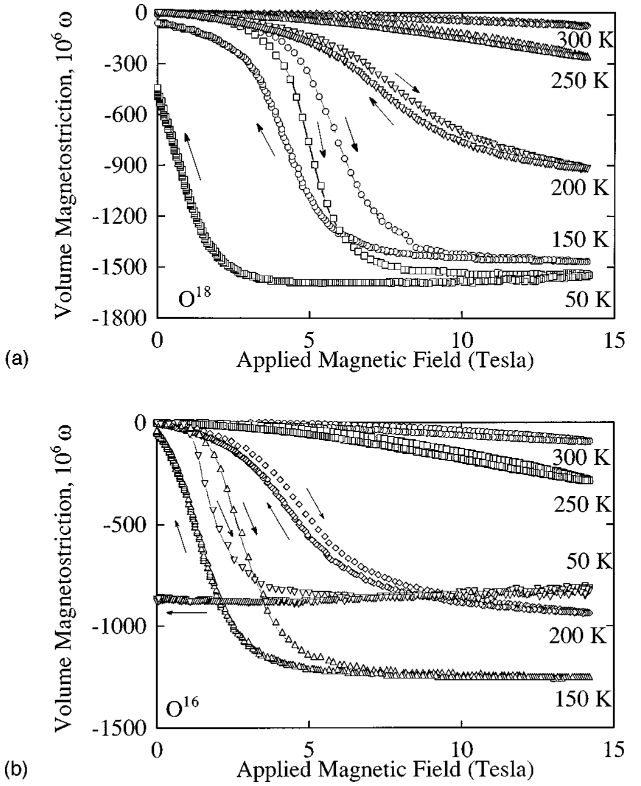

FIG. 2. Volume magnetostriction isotherms at selected temperatures. Arrows indicate increase or decrease of the applied magnetic field. (a) ^{18}O and (b) ^{16}O.

thermal-expansion coefficient of both ^{16}O and ^{18}O samples, which are characteristic of CO,[23] are present [see inset of Fig. 1(a)]. The CO temperature seems to be independent of the isotopic mass. The thermal expansion for the ^{18}O sample follows the insulating behavior over the whole temperature range, which indicates that the insulating CO state is stable down to the lowest temperature. There is no M-I transition, in good agreement with previous electrical resistivity measurements.[20] In contrast, the ^{16}O sample shows a different behavior. Above 150 K, the thermal expansion curve corresponds to the insulating behavior, and, below this temperature, the curve falls in between those for the insulating and metallic states. This result suggests that, at low temperature, insulating CO and metallic F regions coexist in the ^{16}O sample of $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$, whereas the ^{18}O sample has an homogeneous CO state.

In Fig. 1(b), we show the low temperature thermal expansion under several steady magnetic fields for the ^{16}O and ^{18}O (inset) samples, respectively. On the basis of the two-volume-states model, it is clear that the ^{16}O sample reaches a complete metallic state above 3 T. However, for the ^{18}O sample, the ground state is not completely metallic but phase segregated at 3 T [see inset of Fig. 1(b)]. An applied magnetic field as high as 6 T is necessary to reach completely the F metallic state at low temperature.

In Fig. 2, we show the volume magnetostriction ($\omega = \lambda_{\parallel} + 2\lambda_{\perp}$) isotherms at selected temperatures for the ^{18}O sample [Fig. 2(a)] and the ^{16}O sample [Fig. 2(b)]. The results clearly indicate that there is a critical value of the applied magnetic field (H_C) and large hysteresis. We consider that the huge value of ω is related to the transformation of the insulating CO phase into the metallic F state at fields higher than H_C. Above the CO temperature (≈ 200 K), the values of the volume magnetostriction for the two isotopic samples are comparable, but below this temperature, they become different. This difference is more pronounced below ~ 100 K, which indicates that in absence of applied field the CO phase extends over a large volume fraction of the ^{18}O sample in comparison with the ^{16}O sample. As a consequence, at 50 K and at fields higher than 5 T, the magnetostriction in the ^{18}O sample is twice the value found under the same conditions in the ^{16}O sample. This gives rise to a huge isotopic effect on the volume magnetostriction, which constitutes a new effect never observed up to now. Furthermore, The H_C value obtained for the ^{18}O sample is larger than that for ^{16}O samples at the same temperature. These results indicate a higher stability of the CO state in the ^{18}O sample than in the ^{16}O sample.

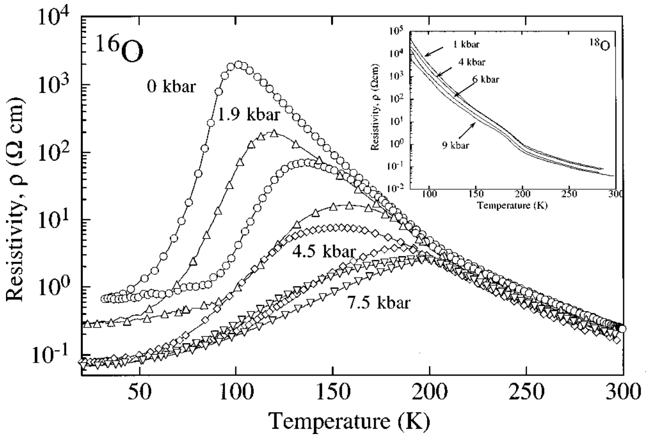

FIG. 3. Thermal dependence of the electrical resistivity at several selected pressures in ^{16}O. Inset: the same for ^{18}O.

The pressure effect on the electrical resistivity is shown in Fig. 3 for the two isotopic samples. For the ^{18}O sample (inset), there is no significant effect under pressures up to 9 kbar. There is a weak anomaly at T_{CO} and an insulating behavior over the whole temperature range. The absolute value of the resistivity depends weakly on the pressure. However, the sample ^{16}O displays a M-I insulator transition, as seen from the peaklike anomaly, and the pressure effect is very large. These results in the ^{16}O sample are in good agreement with those reported by Zhou *et al.*[13] The different behavior of the low-temperature resistivity under pressure in both isotope exchanged samples, as we will discuss later on, can be explained by the important role of the phase segregation in the ^{16}O sample.

The reported results, along with the previous resistivity and magnetization measurements,[20] clearly demonstrate a very strong influence of the change in the oxygen mass on the ground state of the system and can be explained as follows. The substitution of La by Nd results in a weakening of the Zener interaction as a consequence of the decrease in the Mn-O-Mn angle.[11] When the substitution is 50%, as in the present study, there exists a subtle energy balance between the F and CO interactions. In the ^{16}O sample we propose the existence of F regions coexisting with CO regions. The situation in the ^{18}O sample is different: the CO state extends over the whole sample in which the isotopic exchange took place ($\approx 80 \pm 10\%$). It is worth noticing that a CO state requires well-localized charge, whereas ferromagnetism in these compounds is based on mobile charges. This implies that each phase settles in different regions of the sample. At this stage, we must underline that sample inhomogeneity cannot be responsible for the electronic phase segregation, which is rather an intrinsic feature. If there were La-rich regions in the ^{16}O sample, the isotopic exchange would only produce a 10 K shift in T_C (Ref. 9) but never a CO state. The large isotopic effect can be explained considering the weakening of the Zener interaction with the increase of the oxygen mass.[9] This gives rise to the almost suppression of spontaneous phase segregation in the ^{18}O sample, the CO state being favored instead of the F state. The pressure experiments can be explained in a similar way. It is well established that pressure enhances the Zener interaction. As a consequence, the effect on the phase segregation is opposite to the effect by isotopic exchange. Under pressure the ferromagnetic phase is favored respect to the CO, resulting in a decrease of the resistivity under pressure. However, the effect is not large enough in the ^{18}O sample to produce an I-M transition.

In order to confirm these predictions and the possible existence of AF order in the CO region, we performed neutron-diffraction experiments in both isotopic samples. The detailed analysis of these data will be published elsewhere. Here we report the most significant results concerning the former explanation. Neutron-diffraction spectra taken at different temperatures showed the following relevant features:

(a) A small superstructure peak appears at $T_{\mathrm{CO}} \approx 210$ K (hereafter called CO peak), which coincides with the temperature at which the anomaly in thermal expansion and resistivity is found.

(b) An extra contribution over the Bragg nuclear peaks is observed, which reveals the presence of a F phase below $T_C \approx 200$ K.

(c) The existence of an extra peak of magnetic origin indicates the existence of an AF phase below $T_{\mathrm{AF}} \approx 170$ K. We consider that the long-range AF order occurs within the CO region.

In Fig. 4 we show the thermal dependence of the integrated intensity of selected CO, F, and AF peaks. The appearance of the CO peak indicates the transition from paramagnetism to CO in the ^{18}O sample. In the case of ^{16}O this transition takes place only in a small part of the sample, the CO peak being too small to be refined. The AF phase sets in at T_N. The intensity of the AF peak in the ^{18}O sample, where CO is the majority phase, is very large in comparison with the ^{16}O sample. This is consistent with the existence of a para-AF transition within the CO region. The results for the F peak, shown in the inset of Fig. 4, are an indication of the presence of a majority F phase in the ^{16}O sample, which is almost imperceptible in the ^{18}O sample. The small F contribution found in this sample can be associated with the ^{16}O-rich region in which the isotopic exchange was not achieved.

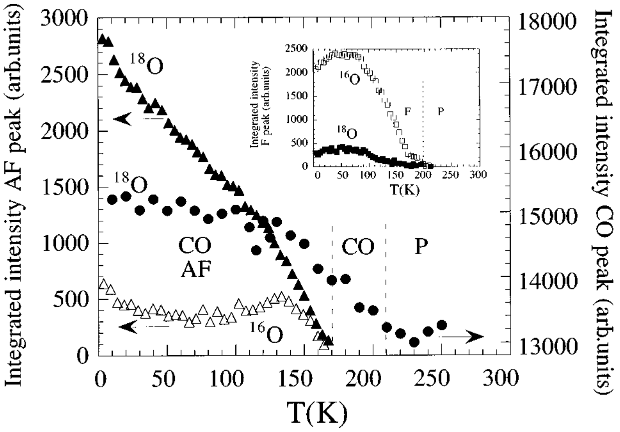

FIG. 4. Thermal dependence of the integrated intensity of the superstructure peak (CO) (dots) and $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$ antiferromagnetic (AF) peak (triangles), characteristic of the insulating CO region. Inset: thermal dependence of the ferromagnetic (F) contribution to the (0,0,1) and (1,1,0) Bragg peak, which characterises the metallic F region (squares). P means paramagnetic. Open symbols stand for the ^{16}O sample and closed symbols for the ^{18}O sample.

In summary, we have found a very large isotopic effect on the magnetic, magnetotransport, and magnetoelastic properties of the mixed-valence manganite $(\mathrm{La}_{0.5}\mathrm{Nd}_{0.5})_{2/3}\mathrm{Ca}_{1/3}\mathrm{MnO}_3$, where a subtle energy balance makes this compound phase segregated. We have found that the CO temperature does not change. As a consequence, we propose that the long-range Coulomb interaction, responsible for the CO, is not affected by the change in the oxygen isotopic mass. Considering the large effect of the isotopic change on the phase segregation, we conclude that the weakening of the Zener interaction due to a strong electron-phonon interaction existing in these compounds is responsible for the observed effects.

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