Oxygen-isotope effect on the charge-ordering transition of La$_{1-x}$Ca$_x$MnO$_3$

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The colossal-magnetoresistance compound La$_{1-x}$Ca$_x$MnO$_3$ shows a transition to commensurate charge ordering (Mn^{3+}–Mn^{4+}) for $x=50\%$. In the range $x=42–50\%$, the high-temperature paramagnetic insulating phase transforms first into a conducting ferromagnetic phase at the Curie temperature T_C, and at somewhat lower temperature T_{CO} into the charge-ordered phase. The oxygen isotope effect on T_C is small in this range, $\alpha_O = -d\ln T_C/d\ln m_O \approx 0.14$. In contrast to this, the charge-ordering transition shows a large and negative isotope effect, i.e., the heavier mass (^{18}O) favors charge ordering. At the border of the existence of the charge-ordered phase, ^{18}O substitution can induce this transition in an ^{16}O sample that does not show this transition. The effect can be reversed by back exchange. These results show the extreme mass dependence of the charge-ordering transition in this system. [S0163-1829(98)51510-X]

The perovskites of the series La$_{1-x}$Ca$_x$MnO$_3$ exhibit a rich magnetic phase diagram.[1] At high temperatures, they are paramagnetic. At low temperatures, both antiferromagnetic and ferromagnetic phases have been observed. The ferromagnetic phase can be both insulating (for $x<20\%$), or metallic ($20\% < x < 45\%$). At higher calcium concentration, $0.5 < x < 1$, the ground state is antiferromagnetic (AF) and nonmetallic. Measurement of specific heat and sound velocity as a function of temperature and calcium concentration showed that, for a certain range below $x=50\%$, approximately in the range 42–50 %, both the paramagnetic to ferromagnetic conducting transition and, at lower temperature, the charge-ordering transition occur.[2,3] TEM electron diffraction spectra indicated the appearance of superlattices as an evidence of charge ordering in the AF phase,[3] i.e., the real-space ordering of the 1:1 Mn^{3+}/Mn^{4+} species. The exact extent of this region depends on making conditions and is very sensitive to the Mn^{4+} concentration.

Strong lattice effects have been observed in this (and other related) compounds, e.g., in the transport properties. A very large isotope effect has been observed[4] for $x=10\%$ and 20%, i.e., in the ferromagnetic insulating phase, and at the border towards conducting ferromagnetism. In the present work we present results of a study of the isotope effect in the system La$_{1-x}$Ca$_x$MnO$_3$ in the calcium concentration range where both the ferromagnetic conducting and the charge-ordered phases are present.

Powder samples of La$_{1-x}$Ca$_x$MnO$_3$ were prepared following the method of standard solid-state reaction, using high-purity metal oxides and carbonates that were preheated and dried. Lanthanum oxide (La$_2$O$_3$, purity 99.999%) was preheated at 800 °C, calcium carbonate (CaCO$_3$, purity 99.99%) at 125 °C, and manganese oxide (MnO$_2$, purity 99.999%) at 350 °C. Such a low preheating temperature for manganese oxide ensured the absence of Mn$_3$O$_4$, which exists at elevated preheating temperatures (>1000 °C).

The stoichiometric mixture for each concentration x was fired in air at 1200 °C for 38 h with two intermediate grindings. X-ray-diffraction analysis was carried out at room temperature after each firing stage and did not show any foreign phases. The resulting powder was ground again and packed inside two identical gold tubes (height 5 mm, diameter 3 mm). Typical samples had masses of about 100 mg. The samples were then gas exchanged at 950 °C for 60 h in either ^{16}O$_2$ or ^{18}O$_2$. The ^{18}O concentration was determined from the weight change to be near 90% ($\pm5\%$). Back exchanging ^{16}O was also carried out at 950 °C and was effective in restoring the ^{16}O concentration in 60 h.

We measured the dc magnetization of the samples using a superconducting quantum interference device magnetometer. A magnetic field of 50 G was applied at room temperature and the sample was cooled down to 5 K. Measurements were taken while warming up to room temperature. In some cases where hysteretic behavior is expected, measurements were taken on both cooling and warming. Higher magnetic fields were also used to study the antiferromagnetic behavior.

In Fig. 1(a) we show the results for $x=41\%$. In this case only the transition to the ferromagnetic conducting phase is seen. We observe an isotope shift of the Curie temperature T_C of 6.1 K. This shift gives an oxygen isotope exponent $\alpha_O = -\Delta\ln T_C/\Delta\ln m_O$ of 0.191. The ^{18}O sample has the lower T_C, so the α_O is positive.

For $x=42\%$, Fig. 1(b), we see in the ^{16}O sample only a very minute indication of the charge-ordering transition. Substitution of ^{16}O by ^{18}O produces a very pronounced peak at the transition to the antiferromagnetic charge-ordered state near $T=212$ K, followed by the ferromagnetic transition at higher temperatures. The results show the quite surprising fact that the charge-ordered phase can be produced by simple isotopic substitution. Back exchange with ^{16}O completely restored the original ^{16}O result, i.e., the charge-ordered phase is eliminated. Since charge ordering occurs at higher temperatures, we see that the isotope effect on this transition is negative, i.e., the heavier oxygen mass favors charge ordering.

At higher temperatures we see the ferromagnetic transition. The isotope effect in this transition was estimated by comparing normalized magnetization for the ^{16}O and the ^{18}O samples. Since the maximum magnitude of the magnetization for the ^{18}O sample can be assumed to be close to the saturation value, we use this as the normalization level for the ^{18}O sample. This is shown in Fig. 1(b). We find a shift
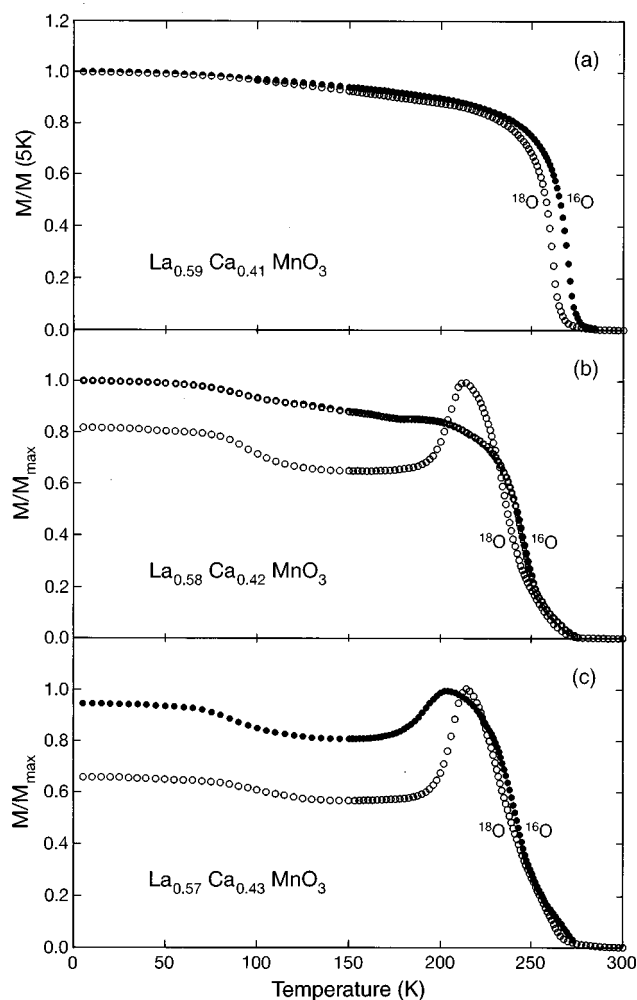
FIG. 1. Normalized magnetic moment in 50 G for $La_{1-x}Ca_xMnO_3$. (a) $x=0.41$, (b) $x=0.42$, (c) $x=0.43$.

ΔT_C of about 5.7 K giving an α_O for T_C of 0.189. The exponent is positive, i.e., the ^{18}O sample has the lower Curie temperature.

Figure 1(c) presents the results for a calcium concentration of 43%. In this case, both the antiferromagnetic charge-ordering transition and the ferromagnetic transition are present in the ^{16}O and the ^{18}O samples. The charge-ordering transition is near 203 K for the ^{16}O sample, and at 213 K for the ^{18}O sample. The effect is, therefore, again negative, i.e., the heavier mass induces charge ordering at a higher temperature. If one expresses this also as an isotope exponent, i.e., $\alpha_{CO} = -\Delta \ln T_{CO}/\Delta \ln m_O$, one finds $\alpha_{CO} = -0.41$. The ferromagnetic Curie temperature, on the other hand, shows only a small temperature shift, $\Delta T_C \approx 4.4$ K, leading to a positive α_O of about 0.14.

We estimated the molar susceptibility, in the case of calcium concentration $x=42\%$, for the three different oxygen situations: ^{16}O, ^{18}O, and back exchanged ^{18}O to ^{16}O, at a temperature of 5 K. In the first case, for which the sample has ^{16}O, the molar susceptibility was about 15 emu/(gauss/mole). A much smaller value was obtained for the ^{18}O sample; about 7.8 emu/(gauss/mole). Back exchanging the heavy oxygen isotope, ^{18}O to ^{16}O, restored not only the functional temperature dependence of the susceptibility, but also increased its value at 5 K to match the value for the ^{16}O
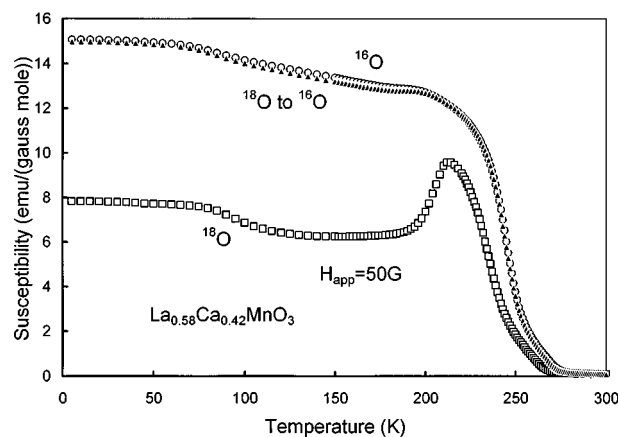

FIG. 2. Molar susceptibility for $x=0.42$, measured in a magnetic field $H_{app}=50$ G for samples with different isotopic oxygen. The sample with ^{18}O showed lower susceptibility at all temperatures. Higher values of the susceptibility were recovered by back exchange ^{18}O to ^{16}O (solid triangles).

sample. This matching was observed at all temperatures between 5 and 300 K, as indicated in Fig. 2.

In order to investigate the nature of the dual transition observed in the calcium concentration range $x>41\%$, we measured the magnetization in a field of 50 G on cooling and warming int he $x=42\%$ sample. The measurements were carried out for both the ^{16}O and the ^{18}O samples and the results are shown in Fig. 3. Both isotopic samples experienced hysteresis, but it is more pronounced for the ^{18}O sample. Figure 3(a) presents the results for the ^{18}O sample. We first see that the paramagnetic to ferromagnetic transition is second order. This is inferred from the fact that the cooling and warming curves merge together before the transition is completed, at about 230 K. Then we see a large difference in the magnitude of the magnetization and the transition temperature, between the cooling and warming cases. In the warming case, the charge-ordering transition takes place at 215 K, and the maximum value for the magnetization in this case is 0.52 emu. On the other hand, if the sample is measured on cooling, the charge-ordering transition does not take place until the temperature is lowered to about 175 K, and for this case, the magnetization is about 0.65 emu, 25% higher than the value for the warming procedure. The two curves merge again at 90 K and yield a single curve down to 5 K. This hysteretic behavior implies that the charge ordering, antiferromagnetic transition is first order. We also noticed that the value of the equilibrium magnetization at 5 K when the sample is measured while being slowly cooled down, is less than its value when the temperature is brought down to 5 K, and then measured while being warmed up.

In Fig. 3(b), we present similar results for the sample containing the lighter oxygen isotope, ^{16}O. There is only a small hysteretic behavior on cooling and warming. The charge-ordering transition is absent when the sample is measured on warming. A weak evidence of that transition exists at a temperature of 140 K on cooling. The value of the magnetization at 5 K did not change much in this case between fast and slow cooling, and remained close to 0.7 emu.

Studies of similar compounds, e.g., La_2CuO_4[5,6] showed that the anomalies in the temperature dependence $\chi(T)$ mea-
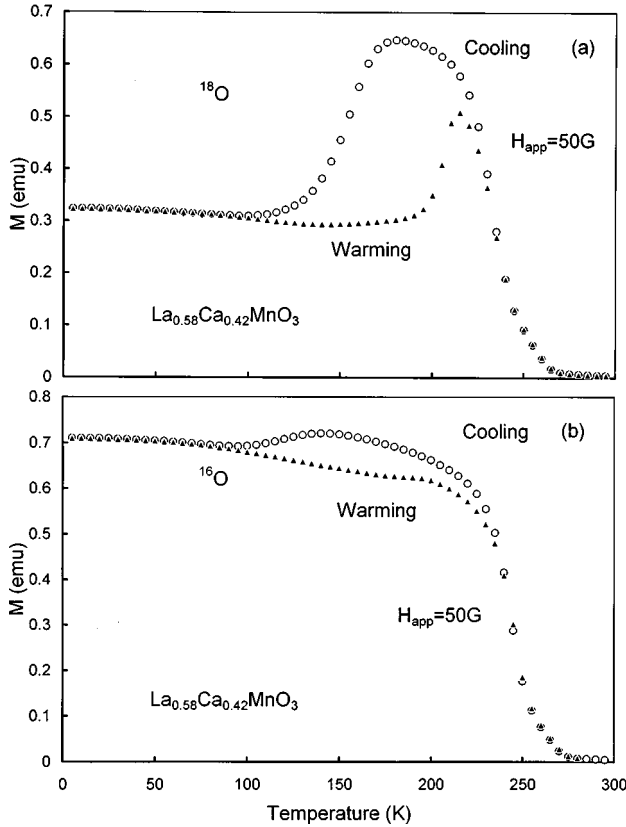
FIG. 3. Magnetic moment for $x=0.42$ on cooling and warming for samples containing different oxygen isotopes; (a) ^{18}O, (b) ^{16}O. Hysteretic behavior is observed at the charge-ordering transition, but is more prominent in the ^{18}O sample.

sured in low magnetic field (<100 G) is determined not only by the amount of nonstoichiometric oxygen but also by the distribution of nonstoichiometric oxygen in the orthorhombic crystal lattice. This means that oxygen inhomogeneities result in a phase separation into an oxygen-depleted AFM phase and an oxygen-enriched metallic phase. This might explain the two-stage transition in La$_{1-x}$Ca$_x$MnO$_3$, $0.41<x<0.5$. At the boundaries of this region the compound single phase is either FM for $x=0.41$ or insulating AFM for $x=0.5$. When x increases from 0.41, the compound phase separates into a minor AFM phase that coexists with the dominant FM phase. The AFM phase is characterized by Néel transition temperature T_N, while the FM phase is characterized by Curie transition temperature T_C. In this case T_N is slightly less than T_C. The result is a superposition of two temperature dependencies of magnetization for which the signatures of the two transitions are evident [Figs. 1(b) and 1(c)].

Our results show a strong mass dependence of the charge-ordering transition. The heavier mass favors charge ordering. It appears, therefore, that thermal motion is unfavorable, as might be expected. It is, however, quite unexpected that the rather small mass change from 16 to 18 for the oxygen site can induce this transition in a sample where it did not previously exist. Moreover, the robustness of the charge-ordered state is affected by the commensurability of the charge-carrier concentration with the periodicity of the crystal lattice. In the lanthanum manganites, a fully commensurate

TABLE I. Oxygen isotope dependence on calcium doping in La$_{1-x}$Ca$_x$MnO$_3$.

x	$T_C(^{16}$O$)$	$T_C(^{18}$O$)$	ΔT_C	α_O	r_A	t
0.35	270.7	261.7	9	0.29	1.353	0.9710
0.41	273.6	267.5	6.1	0.191	1.352	0.9740
0.42	257.3	251.6	5.7	0.189	1.352	0.9747
0.43	260.3	255.9	4.4	0.144	1.351	0.9749

state occurs at $x=0.5$. In this case, the Mn^{3+}/Mn^{4+} relative concentration is 1:1 and the charge-ordered phase is robust. As x deviates from 0.5, the carrier concentration departs from commensurability and becomes more incommensurable with decreasing x. Robustness reaches its minimum at $x=0.42$ where the isotopic substitution (^{16}O to ^{18}O) is capable of quenching the charge-ordered phase. Such quenching of the phase, from charge ordering to metallic ferromagnetism, has been previously carried out using external magnetic field up to 12 T,[7,8] in similar perovskites.

A second interesting result is the small positive oxygen isotope effect of the ferromagnetic Curie temperature. More extensive results over the whole ferromagnetic conducting range by the authors[9] have shown that the isotope exponent α_O decreases over this range, and is essentially a function of the tolerance factor

$$t = \frac{1}{\sqrt{2}} \frac{r_A + r_O}{r_B + r_O}. \tag{1}$$

Here, r_A is the average radius of the A site (La or Ca), r_B is that of the B site (Mn^{3+} or Mn^{4+}), and r_O is that of oxygen. α_O becomes small as the tolerance factor approaches 1, i.e., as the distortion from the ideal perovskite structure becomes small. Materials that exhibit relatively low t show strong colossal magnetoresistance. They are ferromagnetic metals, dominated by the double exchange mechanism (DE). No charge ordering may occur in this range since charge ordering inhibits the electron transfer process associated with DE and therefore cannot coexist with ferromagnetism in manganites. The compound La$_{0.65}$Ca$_{0.35}$MnO$_3$ exemplifies such materials. At larger t, materials in this region do not exhibit ferromagnetism. For example, the compound Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ becomes charge ordered at 200 K and antiferromagnetic upon further cooling to 140 K.[7] For an intermediate range of t, a ferromagnetic metallic state similar to that seen in strong colossal-magnetoresistance materials transforms to an antiferromagnetic, charge-ordered insulating state. Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ is an example.[8]

We calculated the tolerance factor for the compound La$_{1-x}$Ca$_x$MnO$_3$ in the range $0.41 \leq x \leq 0.43$. The results are presented in Table I along with average r_A and r_B. Values obtained for $x=0.35$ are shown for comparison. The ionic radii that have been used are those of Shanon[10] in the 12-fold coordination for the A atom, and 6-fold coordination for the B atom. These values are $r(\text{La}^{3+})=1.36$, $r(\text{Ca}^{2+})=1.34$, $r(\text{Mn}^{3+})=0.645$, and $r(\text{Mn}^{4+})=0.53$. For $r(\text{O}^{2-})$ we used 1.40. Charge conservation implies that the Mn^{4+} concentration is equal to x for oxygen contents O$_{3.0}$. Our measurements showed that the isotope exponent decreases monotoni-

cally with increasing t. The effect of calcium doping is more prominent on the tolerance factor than on the average A-site atomic radius.

In conclusion, we measured the isotope effect on the magnetic transition of the perovskite $La_{1-x}Ca_xMnO_3$ for calcium concentration $x = 0.41$, 0.42, and 0.43. A gradual transition from the ferromagnetic phase to the charge-ordered phase was observed at low temperatures. At a concentration of $x = 0.42$, isotopic substitution ^{16}O to ^{18}O was able to induce a charge-ordered phase. This indicates the sensitivity of the transition to lattice phonons. In the three cases that have been studied, the isotope exponent α_O is positive for the paramagnetic transition and negative for the charge-ordering one. We also found that the isotope exponent decreases with increasing the tolerance factor. This shows that the relative magnitudes of the Mn—O—Mn bonds and bond angles play an important role in the transition dynamics.

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