

# Isotope Studies of the CMR Compounds $\text{La}_{1-\xi}\text{Ca}_\xi\text{MnO}_{3+\delta}$

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Oxygen isotope effect studies of the ferromagnetic Curie temperature  $T_c$  of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  are presented. The isotope exponent  $\alpha_0 = -\Delta \ln T_c / \Delta \ln m_0$  changes from 0.4 to 0.14 in the range  $0.2 < x < 0.43$ . The isotope exponent decreases strongly with increasing tolerance factor, or decreasing lattice distortion. Above  $T_c$  the conductivity is characteristic of small polarons. Raman scattering shows a prominent peak at  $230 \text{ cm}^{-1}$ . The peak width could be related to site-dependent Jahn–Teller distortions above  $T_c$ , becoming significantly smaller at and below  $T_c$ . IR reflectivity data show a much larger zero frequency IR conductivity than dc conductivity. The IR peaks are independent of temperature between 150 and 295 K.

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## 1. INTRODUCTION

The perovskite compounds  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  exist for the complete range of Ca concentrations [1]. In the range  $0.2 \leq x \leq 0.5$ , the high temperature paramagnetic phase transforms at the Curie temperature  $T_c$  into a low temperature ferromagnetic metallic phase. The transition moves rapidly to larger temperatures in magnetic fields of a few tesla. Combined with the drastic change in resistivity near  $T_c$ , this leads to colossal magnetic resistance (CMR) in these compounds. Double exchange [2], magnetic disorder induced metal–insulator transition [3], conduction due to transition from localized small polarons to delocalized large polarons [4,5], and half-metallic band structure [6] have been proposed to explain this transition. Oxygen isotope measurements showed large effects, and show the strong influence of lattice vibrations on this transition [5,7–9]. In this talk, we will discuss oxygen isotope studies in the ferromagnetic metallic regime of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ . The most detailed investigations were carried out at  $x = 0.35$ , at the optimum Ca concentration. Extensive studies were also carried out for  $x = 0.20$ , where a very large isotope effect was found previously [5].

## 2. $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$

The compounds were produced in the conventional way by repeated firing and grinding of stoichiometric mixtures at temperatures up to  $1200^\circ\text{C}$ , and checked by X-ray diffraction for phase purity. Pellets fired at this temperature and Ca concentration are quite dense and require temperatures of  $1150^\circ\text{C}$  and above to obtain reasonable exchange rates of  $^{18}\text{O}$ . One pellet pair was heated at this temperature and achieved an  $^{18}\text{O}$  concentration of 82%. The following data on resistivity, IR and Raman were taken on this pair. A second exchange was carried out at  $1000^\circ\text{C}$  on pressed powder pellets of the same material, and an  $^{18}\text{O}$  concentration of about 90% was reached at this lower temperature. The isotope shift was the same for both sample pairs.

The magnetic transition at  $T_c$  was first observed magnetically in a field of 50 G. The isotope shifts given in Table I are based on this. Full back exchange was possible in both cases.

Resistivities were measured on the pellets in a four-terminal, in-line configuration, in fields of 0, 2, and 4 T, (see Fig. 1). The resistivity peak is considerably sharper in the  $^{18}\text{O}$  sample. The peak sharpness as measured by  $\Delta R/R_{350} = (R(T_c) - R_{350})/R_{350}$  is increased by 60% at all fields. One can also use the peak position in the magnetic field as an indication of the oxygen isotope effect in a field. We find that the isotope exponent  $\alpha_0$  is essentially independent of field, up to 4 T, Fig. 1.

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**Table I.** Oxygen Isotope Dependence of the Paramagnetic to Ferromagnetic Conducting Transition of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ 

$x$ (%)	$T_c$ ( $^{16}\text{O}$ ) (K)	$T_c$ ( $^{18}\text{O}$ ) (K)	$\Delta T_c$ (K)	$\alpha_0$	$\langle r_A \rangle$	$t$
20	222.7	202.0	20.7	0.83	1.356	0.9638
20 <sup>a</sup>	200.8	192.8	8.0	0.34	1.356	0.9638
20 <sup>b</sup>	187.2	178.3	8.9	0.41	1.356	0.9638
22	259.5	248.6	10.9	0.36	1.356	0.9647
25	266.8	257.0	9.8	0.32	1.355	0.9662
30	272.0	262.4	9.6	0.30	1.354	0.9686
35	270.7	261.7	9.0	0.29	1.353	0.9710
40	271.3	265.0	6.3	0.20	1.352	0.9735
41	274.0	266.0	8.0	0.25	1.352	0.9740
42	257.3	251.6	5.7	0.19	1.352	0.9744
43	260.3	255.9	4.4	0.14	1.351	0.9749

<sup>a</sup>After 24 h in argon at 950°C.<sup>b</sup>48 h in  $\text{O}_2$  (1 atm) at 1225°C, quenched to room temperature.

Above  $T_c$ , we attempted to fit the resistivity to both the variable range hopping expressions

$$\rho = \text{const.} \exp(T/T_0)^n \quad (1)$$

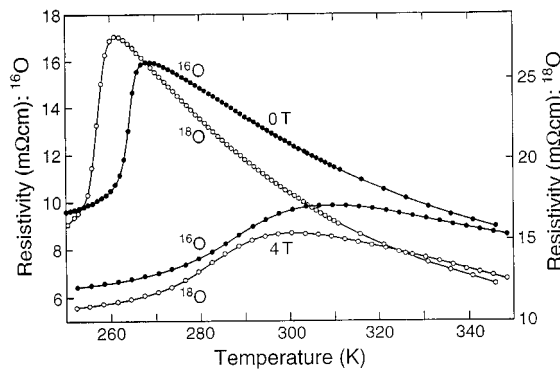
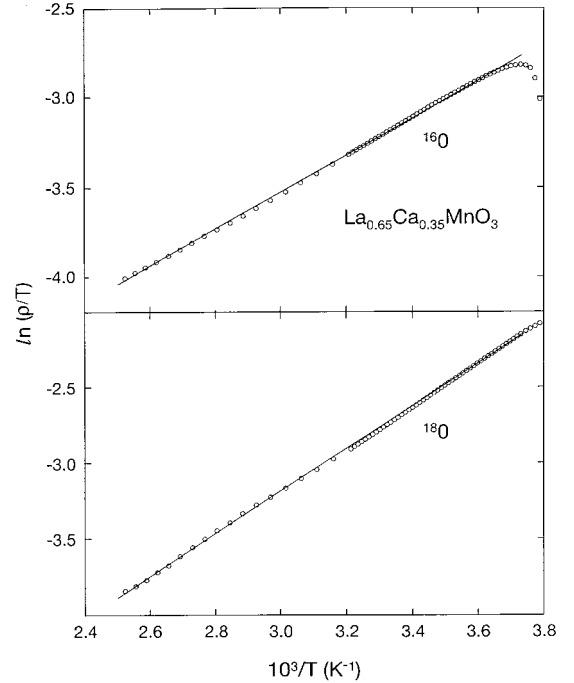
$n = 0.25$  or  $0.50$  [10], and to the small polaron conduction expression of Emin and Holstein [11]:

$$\rho = \rho_0 T^n \exp(E_a/k_B T) \quad (2)$$

$n = 1$  (adiabatic) or  $n = 1.5$  (nonadiabatic). As shown in Fig. 2, excellent agreement is found for the small polaron case, with numerical values for  $\rho_0$  and  $E_a$  in good agreement with data obtained elsewhere [12].

The behavior of the resistive, as well as the magnetic properties is quite reversible with  $^{16}\text{O}$  back-exchange. The original broader resistivity peak for the  $^{16}\text{O}$  sample is restored for back-exchange from  $^{18}\text{O}$  to  $^{16}\text{O}$ .

Raman scattering experiments identified five peaks. A prominent peak at  $230 \text{ cm}^{-1}$  arises from  $0(1)$

**Fig. 1.** The resistive transitions for  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ , in 0 and 4 T.**Fig. 2.** The resistivity in the paramagnetic range,  $T > T_c$ , for  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ . The straight lines are fits to the small polaron resistivity, Eq. (2). The fitting parameters are:  $E_a = 89.4 \text{ meV}$  ( $^{16}\text{O}$ ),  $102.6 \text{ meV}$  ( $^{18}\text{O}$ );  $\rho_0 = 1.30 \times 10^{-6} \Omega \text{ cm}$  ( $^{16}\text{O}$ ),  $1.13 \times 10^{-6} \Omega \text{ cm}$  ( $^{18}\text{O}$ ).

vibrations. This peak hardens considerably at  $T_c$ , and continues to harden with falling temperatures below  $T_c$ . The line width sharpens also considerably. We relate this to site dependent Jahn–Teller distortions above  $T_c$ . These distortions decrease significantly at, and, below  $T_c$ , in agreement with neutron data [13]. The line-width of the  $^{18}\text{O}$  is smaller than the  $^{16}\text{O}$  sample.

IR data were obtained in the range 150–295 K and for frequencies from 30 to  $5000 \text{ cm}^{-1}$ . Five phonon frequencies were observed. The zero frequency conductivity was obtained by Kramers–Kronig analysis (Fig. 3). The zero frequency IR conductivities are much larger than the directly measured DC conductivities. Similar observations were published by Kim *et al.* [14]. It appears that the dc conductivity is dominated by grain boundary effects, and that the IR conductivity is more representative of the bulk behavior. For  $T \ll T_c$  the  $^{18}\text{O}$  sample has the larger conductivity. In contrast to the Raman peaks we observe no temperature dependence of the IR lines, from room temperature to 150 K (Fig. 4). This is in contrast to earlier data of Kim *et al.* [15].

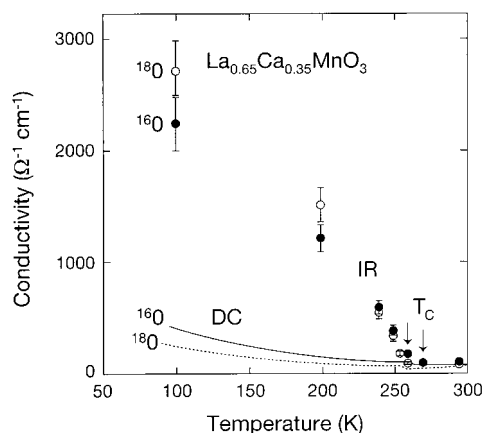


Fig. 3. Zero frequency conductivities obtained from Kramers-Kronig analysis of IR reflection data in the range 30 to 5000  $\text{cm}^{-1}$ , compared with the dc conductivity.

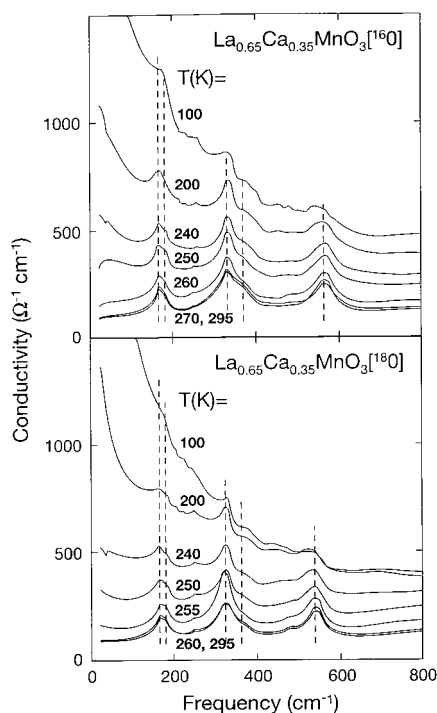


Fig. 4. IR conductivity as function of temperature.

### 3. ISOTOPE EXPONENT IN $\text{La}_{1-\xi}\text{Ca}_\xi\text{MnO}_3$ , $0.22 \leq \xi \leq 0.43$

The isotopic comparison pairs in this Ca concentration range were only investigated magnetically in a field of 50 G. We find that with increasing Ca concentration the isotopic temperature shift  $\Delta T_c$ , and

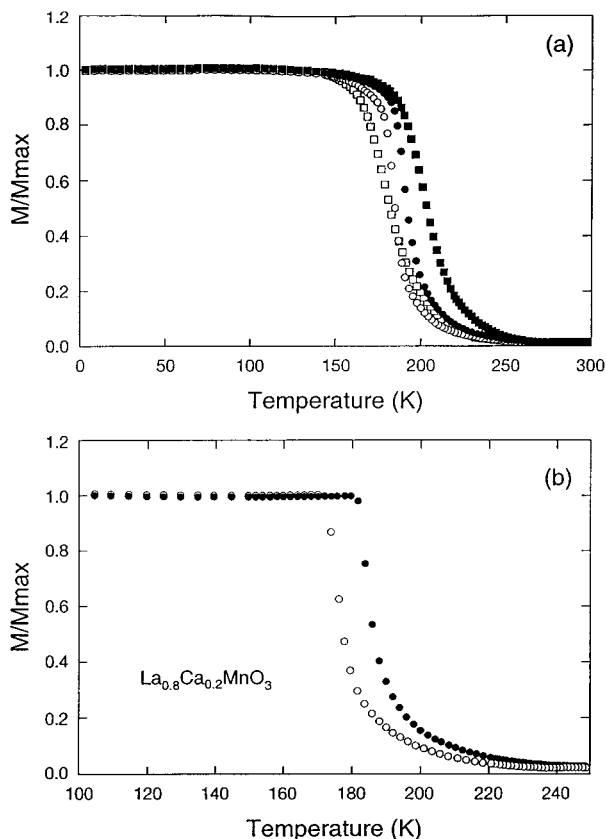


Fig. 5. The magnetic transition of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ . (a) Squares, sintered at  $950^\circ\text{C}$  for 48 hr, cooled at  $1^\circ\text{C}/\text{min}$ , circles, sintered in argon at  $950^\circ\text{C}$ , and cooled at  $1^\circ\text{C}/\text{min}$ . (b) Sintered at  $1200^\circ\text{C}$  in 1 atm of  $^{16}\text{O}_2$  or  $^{18}\text{O}_2$ , quenched to room temperature. Filled symbols are  $^{16}\text{O}$ ; open symbols  $^{18}\text{O}$  samples.

isotope exponent  $\alpha_0$  become smaller. For  $x = 0.43$ ,  $\alpha_0$  is as low as 0.14. For  $x = 0.42$  and 0.43, we were also able to observe the large, and negative isotope effect of the paramagnetic to charge ordered transition [7]. The data for this range are given in Table I and Fig. 5.

### 4. THE ISOTOPE EXPONENT IN $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3-\delta}$

For this Ca concentration, Zhao *et al.* [5] published an extremely large isotope shift,  $\Delta T_c = 21$  K,  $\alpha_0 = 0.85$ . One can see from Table I, that this large isotope shift is much larger than expected by extrapolation from larger Ca concentrations. In order to study a possible dependence on oxygen excess  $\delta$ , we studied the effect under various making conditions designed to alter  $\delta$  (see Fig. 5). When we perform the

isotope exchange at 950°C (48 hr), followed by slow cooling, we reproduce the large result, with  $\alpha_0$  found in the range 0.83–0.95 for different sample pairs. Sintering at this temperature is known to lead to oxygen excess in samples with Ca concentrations of about 0.2, or less [16,18]. We reduced the oxygen excess in two ways. First, we treated the sample pair in an argon atmosphere for 24 hr at 950°C. This leads to sharper transitions, slightly reduced transition temperatures, and a much smaller isotope exponent,  $\alpha_0 = 0.34$ . Secondly, we performed the gas-exchange between 1195 and 1225°C. These sintering conditions are known to lead to near oxygen stoichiometry,  $\delta = 0$ , in an oxygen pressure of 1 bar [16]. This also leads to an isotope exponent near 0.4. We believe, therefore, that the very large isotope exponents near 0.9 for this Ca concentration are connected to oxygen excess above 3.0, and cannot be used in systematic comparisons with results at other Ca concentrations.

#### 4. DISCUSSION

The dependence of the isotope exponent  $\alpha_0$  on Ca concentration is quite strong, it changes from about  $\alpha_0 = 0.4$  for 20% Ca to near 0.14 for 43% Ca. Over this range, the distortion of the perovskite structure decreases due to an increase in the average Mn ion size. The distortion can be measured by the tolerance factor:

$$t = \frac{1}{\sqrt{2}} \frac{r_A + r_0}{r_B + r_0} \quad (3)$$

where  $r_A$  = average  $A$  site (La, Ca) ion size,  $r_B$  = average  $B$  site ( $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ ) size,  $r_0$  = oxygen radius. The dependence of  $\alpha_0$  on Ca concentration and tolerance factor  $t$  is shown in Fig. 6. The data seem to extrapolate toward  $\alpha_0 = 0$  for  $t = 1$  (cubic perovskite). This supports the importance of double exchange for the transition  $T_c$ . Data on the isotope effect in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  [5] are also in agreement with this trend. A similar dependence on tolerance factor was also observed in the  $230\text{ cm}^{-1}$  Raman line, it hardens with increasing tolerance factor. The change in  $r_A$  is quite small over this range of Ca concentration,  $\alpha_0$  increases with larger  $r_A$ . This trend is opposite to that found in [5], although the smaller  $\Delta T_c = 9.7\text{ K}$  found in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  by Zhao *et al.* [19] tends to support our result. For Ca concentrations of about 20.9% and below, the isotope shift becomes extremely dependent on making conditions. Procedures that lead to the ideal oxygen stoichiometry of 3.0 give  $\alpha_0 \approx 0.4$ , in agreement with the trend observed for larger Ca concentrations. Sintering conditions that

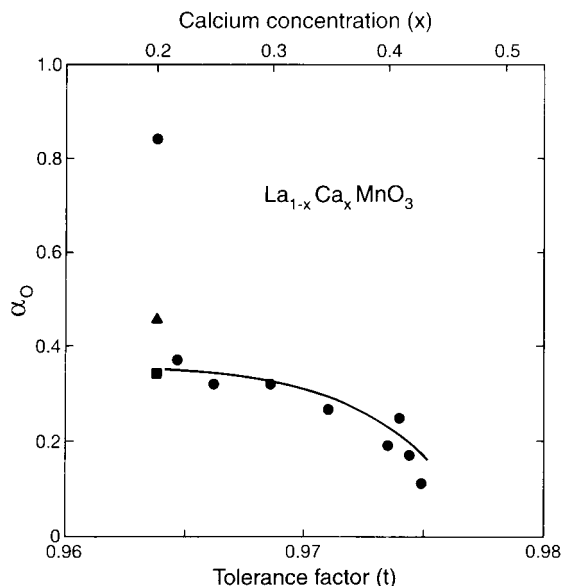


Fig. 6. The oxygen isotope exponent  $\alpha_0$  of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  in the range  $0.20 < x < 0.43$ , as a function of Ca concentration, and tolerance factor. At  $x = 0.2$  data are shown for sintering at 950°C (circle), followed by treatment in argon at 950°C (square), and sintering at 1200°C, followed by quench to room temperature.

lead to excess oxygen give  $\Delta T_c$  up to 23 K and  $\alpha_0 = 0.95$ . Oxygen excess is associated with the formation of La(Ca) and Mn vacancies, and disproportionation of  $\text{Mn}^{3+}$  into  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  [17]. It appears that a certain degree of distortion is necessary for these processes to occur.

The resistivity above  $T_c$  at 35% Ca concentration shows clear evidence for small polaron conduction, this was also seen by Worledge *et al.* [20].  $^{18}\text{O}$  substitution leads to a sharpening of the transition. Similar sharpening is also seen in the isotope studies on the thermal expansion coefficient [19]. It is interesting to observe that this sharpening is also present in transport properties, as well as in the Raman peak at  $230\text{ cm}^{-1}$ , measuring directly the lattice distortion.

The resistivity data below  $T_c$  appear to depend strongly on grain boundary effects, as pointed out already by Kim *et al.* [14]. The much larger IR conductivities, compared to the dc data, are more representative for bulk data. The complete temperature independence of the IR peaks below  $T_c$  speaks against large polaron formation below  $T_c$ . Our results are in disagreement with the data of Kim *et al.* [15], who see a pronounced temperature dependence. This is probably due to a slightly less ideal sample.

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