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Isotope and pressure effects in manganites: Important experimental constraints on the physics of manganites

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The oxygen-isotope effect on the ferromagnetic transition temperature T_C has been studied on the manganites $La_{1-x}Ca_xMnO_{3+y}$ as a function of x. As x increases, both the oxygen-isotope exponent α_O and the pressure-effect coefficient $\beta = d \ln T_C/dP$ increase, reach a maximum at a composition near the metal-insulator phase boundary x_{MI}, and then decrease monotonically. For $x_{MI} < x < 0.33$, the isotope exponent follows: $\alpha_O = 21.9 \exp(-0.016T_C)$, which is simply proportional to β. The present results demonstrate that the observed oxygen-isotope effect is an intrinsic property of manganites, which arises from a strong electron-phonon coupling. [S0163-1829(99)05138-3]

The manganese-based perovskites $La_{1-x}A_xMnO_3$ (where A is a divalent element) have recently been the subject of intensive investigations. Although these materials have been studied for more than four decades,[1,2] the current burst of activity was stimulated by the discovery of very large (''colossal'') magnetoresistance (CMR) in thin films of these compounds.[3,4] The physics in manganites has primarily been described by the double-exchange model.[5,6] Millis, Littlewood, and Shraiman[7] have pointed out, however, that double exchange alone cannot fully explain the data of $La_{1-x}Sr_xMnO_3$. They proposed that polaronic effects due to strong electron-phonon coupling [arising from a strong Jahn-Teller (JT) effect] should be involved. Many recent experiments have provided strong evidence for the existence of polaronic charge carriers in manganites,[11–18] and thus strongly support these theoretical models.[7–10]

However, Nagaev[19] has recently raised a serious criticism of these theoretical models. One of his major arguments is that a large number of other ferromagnetic semiconductors also show a resistivity peak at T_C and CMR, but none of them exhibits a Jahn-Teller effect. The second argument is that the observed giant oxygen-isotope effects in manganites are not caused by a strong electron-phonon coupling, but rather by an oxygen-mass dependence of excess oxygen. The first argument is not sound since the microscopic mechanisms for CMR are not necessarily universal, and a material without a JT effect could have a strong electron-phonon coupling (e.g., $La_{2-x}Sr_xNiO_4$). If the second argument were relevant, one would accept that the physics of manganites were not related to a strong electron-phonon interaction. Here we show that the giant oxygen-isotope shift of T_C is an intrinsic property of manganites, and is not caused by the presence of excess oxygen. The oxygen-isotope exponent is simply proportional to the pressure-effect coefficient ($d \ln T_C/dP$), and is a unique function of T_C in the doping region of $0.20 < x < 0.35$. The present results thus demonstrate that the extreme sensitivity of the electrical and magnetical properties to the external pressure and to the oxygen-isotope mass is caused by a strong electron-phonon interaction.

Samples of $La_{1-x}Ca_xMnO_3$ were prepared by conventional solid-state reaction using dried La_2O_3, MnO_2, and $CaCO_3$. The well-ground mixture was heated in air at 1000 °C for 20 h, 1100 °C for 20 h with one intermediate grinding. The powder samples were then pressed into pellets and sintered at 1260 °C for 72 h, and 1160 °C for 72 h with one intermediate grinding. Two pieces were cut from the same pellet for oxygen-isotope diffusion. The diffusion was carried out for 50 h at 1000 °C and oxygen pressure of about 1 bar. The cooling rate was 300 °C/h. The oxygen-isotope enrichment was determined from the weight changes of both ^{16}O and ^{18}O samples. The ^{18}O samples had $\sim$90% ^{18}O and $\sim$10% ^{16}O.

Field-cooled magnetization was measured with a Quantum Designed superconducting quantum interference device magnetometer in a field of 5 mT. The samples were cooled directly to 5 K, then warmed up to a temperature well below T_C. After waiting for 5 min at that temperature, data were collected upon warming to a temperature well above T_C. In Fig. 1, we show the temperature dependence of the low-field magnetization (normalized to the magnetization well below T_C) for the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with $x = 0.10$ (a), $x = 0.25$ (b), $x = 0.33$ (c), and $x = 0.40$ (d). It is evident that the ferromagnetic transition of the samples is sharp, indicating a good sample quality. The oxygen-isotope shift of T_C was determined from the differences between the midpoint temperatures on the transition curves of the ^{16}O and ^{18}O samples. In all the cases, there are substantial oxygen-isotope shifts of T_C. For $x = 0.33$, the isotope shift is about 10 K, which is in excellent agreement with our previous result.[13]

Figure 2 demonstrates how the magnetic transition of $La_{0.8}Ca_{0.2}MnO_{3+y}$ changes upon the oxygen-isotope exchange (a) and with the annealing temperature (b). It is striking that upon replacing ^{16}O with ^{18}O, the ferromagnetic transition temperature T_C decreases by 21 K, while the magnetic transition has no significant change with the annealing temperature T_A when $T_A \geq 1000$ °C. This implies that the ^{16}O sample annealed at 1000 °C should have nearly the same oxygen content as the sample annealed at 1260 °C, and that both samples should be almost stoichiometric according to Ref. 20. This is justified by the fact that both the ferromagnetic transition temperature ($\simeq$190 K) and the Curie-Weiss constant ($\simeq$200 K) in the present ^{16}O sample are the same as those in the stoichiometric sample reported in Ref. 21. For

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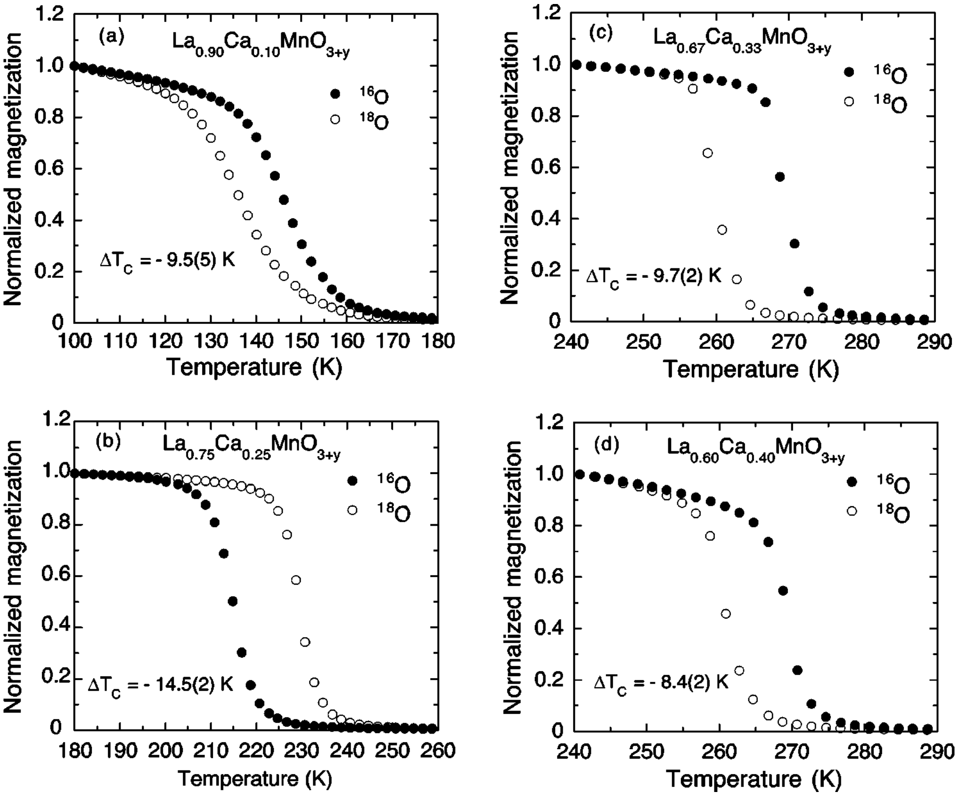

FIG. 1. The temperature dependence of the low-field magnetization (normalized to the magnetization well below T_C) for the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with $x=0.10$ (a), $x=0.25$ (b), $x=0.33$ (c), and $x=0.40$ (d).

the samples annealed below 1000 °C, it is possible that there exists excess oxygen and the amount depends on the annealing temperature. Indeed, the T_C of the present ^{16}O sample increased by about 20 K after it was annealed for 40 h at 950 °C and in 1 bar oxygen pressure.

It is clear that the T_C of the stoichiometric sample is lower, but the oxygen-isotope shift is the same as that of the nonstoichiometric sample.[12] If the unusually large isotope shift for this composition were caused by the excess oxygen, one would expect that the oxygen-isotope exponent observed in the present samples should be smaller than that observed in the samples of Ref. 12. In fact, the oxygen-isotope exponent $\alpha_O = d\ln T_C/\ln M_O$ (where M_O is the oxygen-isotope mass) obtained in the present samples is about 1.0, which is larger than that (0.85) observed in the samples having excess oxygen.[12]

The doping dependences of both oxygen-isotope exponent and T_C for the Ca-doped system are shown in Fig. 3(a). Here T_C is defined as the midpoint temperature on the transition curve, which would correspond to an average transition temperature. The doping dependence of T_C shown in Fig. 3(a) is similar to that reported in Ref. 22. Around $x_{MI} \simeq 0.18$, there is a boundary between the metallic and insulating ground states.[22] It is interesting to see that the oxygen-isotope exponent exhibits a local maximum near x_{MI}.

In Fig. 3(b), we plot the doping dependence of the pressure-effect coefficient for the $La_{1-x}Sr_xMnO_{3+y}$ system where the pressure effect has been studied for a wide doping range. The data for $x=0.12$ and 0.15 are taken from Ref. 23, and the others from Ref. 24. It is remarkable that the pressure-effect coefficient also shows a sharp maximum near x_{MI}. A similar doping dependence of the pressure-effect coefficient was also found for $La_{1-x}Ca_xMnO_{3+y}$.[26] The magnitude of $d\ln T_C/dP$ for $x=0.21$ is 0.18 GPa^{-1}, which is three times as large as that (0.06 GPa^{-1}) for $x=0.33$.[26] Similarly, the oxygen-isotope exponent α_O for $x=0.20$ is 0.85 in the nonstoichiometric samples,[12] or 1.0 in the stoichiometric samples, which is also about three times as large as that (~ 0.3) for $x=0.33$. This indicates that the oxygen-isotope exponent is proportional to the pressure-effect coefficient. The observed unusually large pressure and isotope effects near x_{MI} may be related to the enhanced electron-phonon coupling near this composition, which has been demonstrated by Moritomo, Asamitsu, and Tokura.[25]

In order to quantitaively compare the pressure-effect coefficient and the oxygen-isotope exponent, we plot, in Fig. 4, the pressure-effect coefficient (for a fixed $x=0.3$) and the oxygen-isotope exponent ($0.2<x<0.33$) as a function of T_C. The data for the pressure effect were summarized in Ref. 13, and the data for α_O were summarized in a review article.[27] It is striking that the data can be well fit by $\alpha_O = 4d\ln T_C/dP = 21.9\exp(-0.016T_C)$. Thus, the oxygen-isotope exponent is simply proportional to the pressure-effect coefficient, and is a unique function of T_C for $0.2<x<0.33$. Since the pressure effect is an intrinsic property of a material (no chemical composition is changed under a pressure), such a simple proportionality between α_O and $d\ln T_C/dP$ implies that the observed oxygen-isotope effects must be intrinsic.

Our present results thus strongly argue against a speculation that the giant oxygen-isotope shift observed in $La_{0.8}Ca_{0.2}MnO_{3+y}$ is due to the presence of the excess oxygen.[28,19] As a matter of fact, the compound $(LaMn)_{0.945}O_3$ has the largest access oxygen content, but its isotope effect is very similar to the compound $La_{0.67}Ca_{0.33}MnO_3$ having no excess oxygen and a similar T_C.[13] Furthermore, the largest oxygen-isotope exponent (~ 5) has been found for the compound $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ where there is no excess oxygen

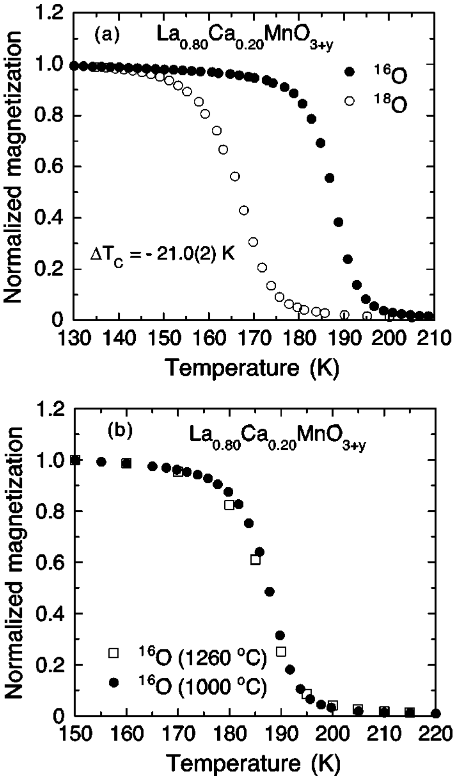

FIG. 2. (a) The temperature dependence of the low-field magnetization for ^{16}O and ^{18}O samples of $La_{0.80}Ca_{0.20}MnO_3$; (b) the temperature dependence of the low-field magnetization for a ^{16}O sample of $La_{0.80}Ca_{0.20}MnO_3$ which was annealed at 1000 and 1260 °C.

content.[29] Such a large α_O is due to the fact that this material has a very low T_C, and a very large pressure effect.

Now we try to understand why both oxygen-isotope exponent and the pressure-effect coefficient decrease with increasing doping in the composition range of the metallic ground state ($0.2<x<0.4$). In this doping region, double exchange plays a dominant role in the ferromagnetic exchange, so that the kinetic energy of charge carriers mainly determine the ferromagnetic transition temperature. Because of the strong polaronic nature of the charge carriers, the change in the lattice vibration frequency either by the external pressure or by the oxygen-isotope mass will strongly change the effective mass of the carriers and thus the double-exchange interaction. When doping increases, the electron-phonon coupling decreases due to an increased screening effect of charge carriers. As a result, both α_O and $d\ln T_C/dP$ should decrease. This could qualitatively explain the observed results. Nevertheless, a more sophisticated theory is needed to quantitatively explain the simple empirical relation: $\alpha_O = 21.9\exp(-0.016T_C)$.

On the other hand, it is quite puzzling why both α_O and β decrease with a decrease of doping for $x<x_{MI}$. One possible explanation is that at low doping, the double exchange interaction is much weaker than the ferromagnetic superexchange, so that T_C is mainly determined by the ferromagnetic superexchange which should be independent of the oxygen-isotope mass. The lower the Mn^{4+} concentration, the less the ferromagnetic exchange contributed from the double exchange, and the smaller the oxygen-isotope shift of T_C.

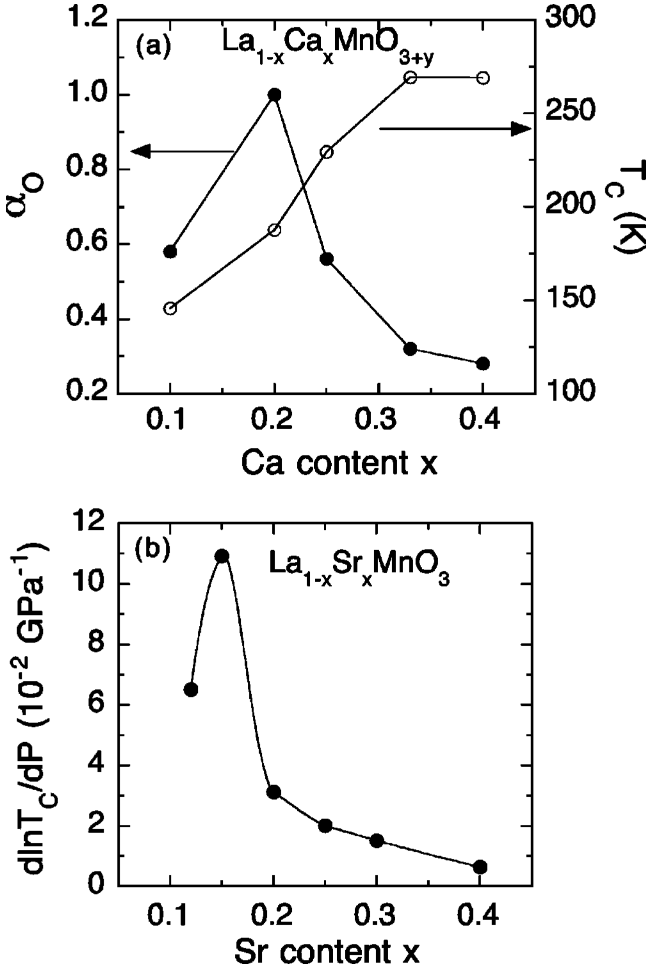

FIG. 3. (a) The doping dependence of the oxygen-isotope exponent α_O and T_C in $La_{1-x}Ca_xMnO_3$; (b) the doping dependence of the pressure-effect coefficient β in $La_{1-x}Sr_xMnO_{3+y}$. The data for $x=0.12$ and 0.15 are taken from Ref. 23, and the others from Ref. 24.

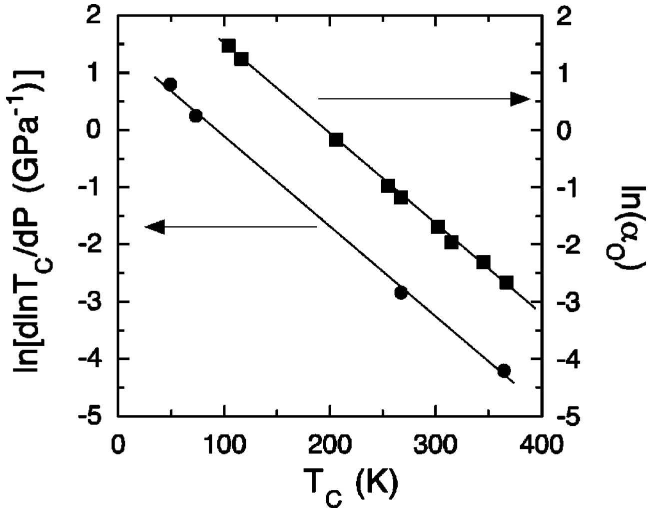

FIG. 4. The pressure-effect coefficient β (for a fixed $x=0.3$) and the oxygen-isotope exponent α_O ($0.2<x<0.33$) as a function of T_C. The data for the pressure effect were summarized in Ref. 13, and the data for α_O were summarized in a review article (Ref. 27).

In summary, our present results thus provide convincing evidence that the observed oxygen-isotope effects in manganites are intrinsic, which are caused by a strong electron-phonon interaction. The extreme sensitivity of the electrical and magnetic properties of the low-T_C manganites to both the external pressure[30] and the isotope mass[29,31] manifests a very strong polaronic effect. We believe that the strong electron-phonon coupling dominates the basic physics of manganites. The microscopic mechanism of CMR in this material should be also related to this interaction, as proposed.[7,9]

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