Giant Oxygen-Isotope Shift
of the Ferromagnetic Transition Temperature
in the Colossal Magnetoresistive $La_{1-x}Ca_xMnO_{3+y}$:
Evidence for Jahn-Teller Polarons*

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We report the oxygen-isotope effect on the ferromagnetic transition temperature T_C in the perovskites $La_{1-x}Ca_xMnO_{3+y}$ and $SrRuO_3$. The oxygen-isotope shift of T_C in $La_{0.8}Ca_{0.2}MnO_{3+y}$ is very large (>20 K), far larger than any isotope shift found for magnetic or electronic phase transitions in other oxides. In contrast, no sizable isotope shift was observed in the structurally-related ferromagnet $SrRuO_3$. We also show that the oxygen-isotope exponent ($\alpha_o = -$dln T_C/dlnM_o) increases rapidly with decreasing the mean ion radius at the cation site $La_{1-x}Me_x$ (Me = Ca, Sr or Ba). Since there is no oxygen-isotope effect on T_C in the ferromagnet $SrRuO_3$ with a negligible Jahn-Teller (JT) effect, the giant oxygen-isotope shift observed in the Ca-doped manganite is very likely related to the strong JT effect in this system. We suggest that a strong coupling of the charge carriers to the local JT distortions leads to the formation of JT polarons which are responsible for the observed giant oxygen-isotope effect on T_C. Our results provide a crucial test for the mechanism of the colossal magnetoresistance in manganites.

The manganese-based perovskites $La_{1-x}Me_xMnO_3$ (Me = Ca, Sr, and Ba) have recently been the subject of intensive investigations because of their unusual and potentially useful magnetic properties (e.g., the colossal magnetoresistance effect [1]). At high temperatures these materials are paramagnetic and insulating; at low temperatures they are ferromagnetic and metallic-like for $0.1 \le x \le 0.5$. The temperature at which the insulator-metal transition occurs can be increased by applying a magnetic field. As a result, the electrical resistance of the material can be decreased by a factor of 1000 or more [1, 2], if the temperature is held in the region of the transition. This phenomenon is now known as colossal magnetoresistance (CMR), and its microscopic mechanism is being actively sought.

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These materials contain a mixture of Mn^{3+} and Mn^{4+} ions at octahedral lattice sites; because the electronic ground state of Mn^{3+} is degenerate, their energy is lowered by a spontaneous distortion of its surrounding lattice (the Jahn-Teller effect). Höck *et al.* [3] studied JT ions in a conductor within a linear chain model. They showed that small JT polarons (the charge carriers accompanied by the local JT distortions) can be formed when the JT stabilization energy is comparable with the bare conduction bandwidth. In this situation, the Born-Oppenheimer adiabatic approximation (in which the electronic and lattice subsystems are decoupled) is no longer valid.

The polaronic nature of the conduction carriers can be demonstrated by the isotope effect on the effective bandwidth W_{eff} of polarons, which in turn depends on the isotope mass M [4]:

$$W_{\text{eff}} \propto W \exp\left(-\gamma E_b/\hbar\omega\right), \tag{1}$$

where W is the bare conduction bandwidth, E_b is the binding energy of polarons, and is independent of the isotope mass M, γ is a demensionless constant ($0 \leq \gamma \leq 1$) depending on E_b/W, ω is the characteristic frequency of the optical phonons ($\omega \propto 1/\sqrt{M}$). For JT polarons, the binding energy of polarons E_b can be replaced by the JT stabilization energy E_{JT} [5]. Since the JT state of Mn^{3+} has a sizable E_{JT} of about 0.5 eV [6], one will expect from Eq. (1) that the isotope effect on W_{eff} is substantial in the manganites.

In the ferromagnetic manganites such as $La_{1-x}Ca_xMnO_{3+y}$, it is easy to study the isotope effect on W_{eff}. This is due to the fact that in the strong-coupling limit, where the Hund's rule coupling J_H is very large compared to W_{eff} ($J_H \gg W_{\text{eff}}$), the Curie temperature $T_C \propto W_{\text{eff}}$ (Ref. [6, 7]). The isotope dependence of W_{eff} can also be investigated in a ferromagnet $SrRuO_3$, where T_C strongly depends on W_{eff}, as indicated by a large pressure effect [8]. In the ferromagnet $SrRuO_3$, however, the JT effect is very weak, so the isotope dependence of W_{eff} might be very weak. Therefore, studies of the oxygen-isotope effect on the Curie temperature in these ferromagnets can assess the importance of the JT effect in the formation of polarons. Here we report the oxygen-isotope effect on the ferromagnetic transition temperature T_C in the perovskites $La_{1-x}Ca_xMnO_{3+y}$ and $SrRuO_3$ (also see Ref. [9]). The oxygen-isotope shift of T_C in $La_{0.8}Ca_{0.2}MnO_{3+y}$ is very large (> 20 K), far larger than any isotope shift found for magnetic or electronic phase transition in other oxides. In contrast, no sizable isotope shift was observed in the structurally-related ferromagnet $SrRuO_3$. The results suggest that the charge carriers in manganites are strongly coupled to the JT lattice distortions so that JT polarons are formed. The formation of JT polarons in manganites may be crucial to the understanding of the colossal magnetoresistance effect.

Samples of $La_{1-x}Ca_xMnO_{3+y}$ were prepared by a conventional solid state reaction using La_2O_3, $CaCO_3$ and MnO_2. The powders were mixed, ground thoroughly, and fired in air at 1050 °C for ~20 h. The samples were then pressed into pellets, and sintered in air at 1080 °C for ~48 h. Similar con-

ditions were used for preparing samples of $SrRuO_3$. The samples are single-phase, as checked by X-ray diffraction. The ^{16}O and ^{18}O samples were pre-pared from the same batch of the starting material, and were subjected to the same thermal treatment in closed ampoules (one was filled with $^{16}O_2$ gas, and another with $^{18}O_2$). The diffusion was carried out for 48 h at 950°C and in an oxygen pressure of ~ 1.0 bar. The cooling was very slow, with a rate of 30°C/h. The oxygen-isotope enrichment was determined from the weight changes of both ^{16}O and ^{18}O samples. The ^{18}O samples of $La_{1-x}Ca_xMnO_{3+y}$ had $\sim 95\%$ ^{18}O and $\sim 5\%$ ^{16}O. The ^{18}O samples of $SrRuO_3$ had $80 \pm 15\%$ ^{18}O and $20 \pm 15\%$ ^{16}O. The field-cooled magnetization of the samples was measured with a commercial SQUID 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 20 minutes at that temperature, data were collected upon warming. The magnetic field was kept unchanged throughout each series of measurements.

In Fig. 1a and b we show the magnetization (normalized to the mag-netization well below T_c) for pairs of ^{16}O and ^{18}O samples (i.e., 2 for each isotope) of (a) $La_{0.8}Ca_{0.2}MnO_{3+y}$ and (b) $SrRuO_3$. The oxygen isotope shifts of T_C were determined from the differences between the midpoint tempera-tures on the transition curves of the ^{16}O and ^{18}O samples. For the CMR ferromagnet $La_{0.8}Ca_{0.2}MnO_{3+y}$, the ^{18}O samples have lower T_C's than the ^{16}O samples by ~ 21 K, while the two ^{16}O samples (as well as the two ^{18}O samples) have the same T_C's. On the other hand, no oxygen isotope effect on T_C could be detected in the ferromagnet $SrRuO_3$ with a negligible JT effect. If we define the oxygen isotope exponent as $\alpha_O = -d\ln T_C / d\ln M_O$ (where M_O is the oxygen isotope mass), then we obtain $\alpha_O = 0.85$ for $La_{0.8}Ca_{0.2}MnO_{3+y}$. For $La_{0.9}Ca_{0.1}MnO_{3+y}$, we found a slightly smaller ex-ponent $\alpha_O = 0.70$ (see Fig. 2). These exponents are considerably larger than those recently observed in the Sr-doped system $La_{1-x}Sr_xMnO_{3+y}$ (e.g., $\alpha_O = 0.19$ for $x = 0.10$; $\alpha_O = 0.14$ for $x = 0.15$; $\alpha_O = 0.07$ for $x = 0.3$ [10]).

To show that the observed oxygen isotope shifts are intrinsic, we have performed isotope back-exchange experiments ($^{16}O \rightarrow {}^{18}O$; $^{18}O \rightarrow {}^{16}O$). In Fig. 3 we show the normalized magnetization for the ^{16}O and ^{18}O samples of $La_{0.8}Ca_{0.2}MnO_{3+y}$ before and after isotope back-exchange. It is evident that the T_C of the ^{16}O (^{18}O) sample goes back completely to that of the original ^{18}O (^{16}O) sample after the isotope back-exchange. This clearly indi-cates that the shift of T_C is caused only by changing the oxygen isotope mass.

It is also important to check whether the observed isotope shifts may arise from a difference in the oxygen contents of the ^{16}O and ^{18}O samples. We think this is very unlikely for the following reasons. First of all, the T_C of the $La_{1-x}Ca_xMnO_{3+y}$ system is hardly changed even upon some extreme thermal treatments (e.g., annealing under 200 bars of oxygen pressure at ~ 600°C and quenching from 1300°C) [11], and the present ^{16}O and ^{18}O
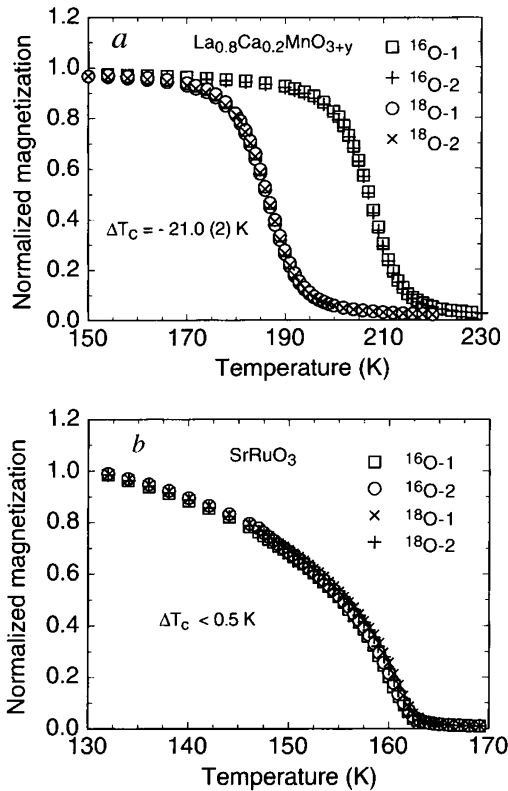
Fig. 1. Oxygen isotope effect on the Curie temperature of $La_{0.8}Ca_{0.2}MnO_{3+y}$ and $SrRuO_3$: Temperature dependence of the normalized magnetization for the ^{16}O and ^{18}O samples of (a) $La_{0.8}Ca_{0.2}MnO_{3+y}$; (b) $SrRuO_3$. There is a large oxygen isotope effect on Curie temperature ($\sim$21 K) in $La_{0.8}Ca_{0.2}MnO_{3+y}$ with a strong JT effect, but no observable effect in the ferromagnet $SrRuO_3$ with a negligible JT effect. Note that the two independent ^{16}O samples (as well as the two independent ^{18}O samples) have the same T_C, demonstrating an excellent reproducibility of the isotope experiments.

samples were treated under the same thermal condition. Secondly, the ^{16}O and ^{18}O samples of the related $LaMnO_{3.17}$ compound were shown to have the same oxygen contents [12].

Now the question arises: Why are the oxygen isotope exponents α_O in Ca-doped $La_{1-x}Ca_xMnO_{3+y}$ much larger than those in Sr-doped $La_{1-x}Sr_xMnO_{3+y}$? This is possibly due to the difference in the ionic radii of Ca^{2+} and Sr^{2+}. In Fig. 4 we show the dependence of α_O on the mean ionic radius $\langle r_A \rangle$ at the cation site $La_{1-x}Me_x$. The ionic radii of $La_{1-x}Me_x$ were calculated from tabulated values (La^{3+}: 1.172 Å; Ca^{2+}: 1.140 Å; Sr^{2+}: 1.320 Å (Ref. [13]). It is evident that α_O increases rapidly with decreasing

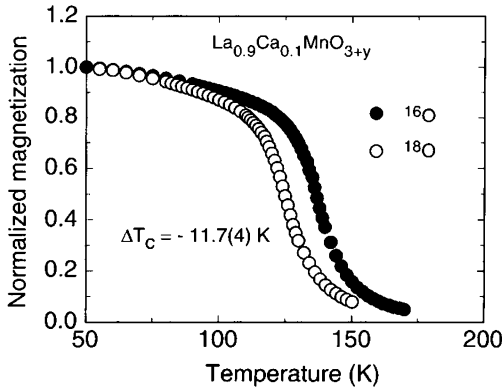**Fig. 2.** Oxygen isotope effect on the Curie temperature of $La_{0.9}Ca_{0.1}MnO_{3+y}$: Temperature dependence of the normalized magnetization for the ^{16}O and ^{18}O samples of $La_{0.9}Ca_{0.1}MnO_{3+y}$.
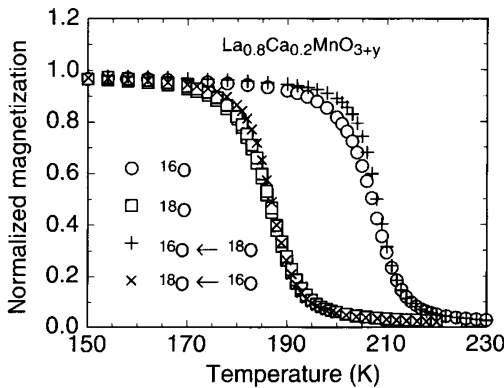

Fig. 3. Isotope back-exchange result for sample pair 1 of $La_{0.8}Ca_{0.2}MnO_{3+y}$: Temperature dependence of the normalized magnetization for the ^{16}O and ^{18}O samples of $La_{0.8}Ca_{0.2}MnO_{3+y}$ before and after isotope back-exchange. The symbol (+) denotes the ^{16}O sample which has been back-exchanged from the original ^{18}O sample (denoted by open square). The symbol (×) represents the ^{18}O sample which has been back-exchanged from the original ^{16}O sample (denoted by open circle). It is evident that the T_C of the ^{16}O (^{18}O) sample goes back completely to that of the original ^{18}O (^{16}O) sample after the isotope back-exchange.

$\langle r_A \rangle$. Although α_O may also depend on the Mn^{4+} concentrations, it is clear from Fig. 4 that $\langle r_A \rangle$ is a dominant parameter in connection with α_O. A similar correlation between the magnitude of the magnetoresistance (MR)
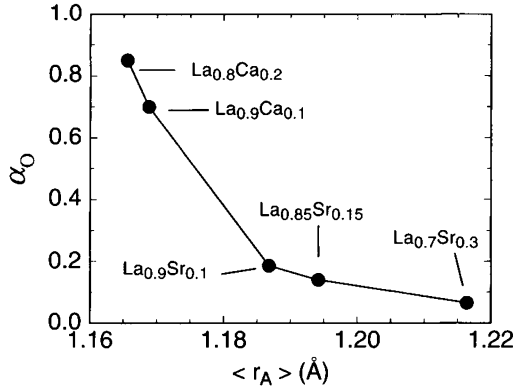
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Fig. 4. The dependence of the oxygen isotope exponent α_o on the mean ionic radius $\langle r_A \rangle$ at the cation site of $La_{1-x}Me_x$. The results for the Sr-doped compounds are taken from Ref. [10]. The solid line is to guide the eye. The isotope exponent α_o increases rapidly with decreasing $\langle r_A \rangle$.

and $\langle r_A \rangle$ has recently been reported by Hwang *et al.* [14]. They showed that the MR decreases rapidly with increasing $\langle r_A \rangle$. Thus, the oxygen-isotope exponent α_O is correlated with the magnitude of MR.

Since there is no oxygen-isotope effect on T_C in the ferromagnet $SrRuO_3$ with a negligible JT effect, the giant isotope effect observed in the Ca-doped ferromagnets is very likely related to the strong JT effect in this system. For a compound with a strong JT effect, the electron-phonon interaction is usually large, leading to the formation of JT polarons [3]. Taking into account that the binding energy of polarons E_b in the JT compound is equal to the JT stabilization energy E_{JT} (Ref. [5], and $T_C \propto W_{eff}$ for $J_H \gg W_{eff}$ (Ref. [6, 7]), one obtains from Eq. (1)

$$W_{eff} \propto W \exp(-\gamma E_{JT}/\hbar\omega) .$$ (2)

The total isotope exponent is then given by

$$\alpha_t = -d \ln T_c/d \ln M = 0.5\, \gamma E_{JT}/\hbar\omega .$$ (3)

Because γ increases with increasing E_{JT}/W [4], the above relation indicates that the isotope exponent increases with increasing E_{JT}, but decreases with increasing W. For the manganites, an increase of $\langle r_A \rangle$ usually enhances the covalency of the $Mn-O$ bonding [15], and hence increases the bare conduction bandwidth W, leading to a decrease of α_t. This mechanism naturally explains why the oxygen-isotope exponent α_O increases with decreasing $\langle r_A \rangle$, as shown in Fig. 4.

Our results thus strongly suggest that in the CMR manganites there is a strong JT effect and thus a large electron-phonon interaction which leads to the formation of JT polarons [3]. This is also consistent with a very recent

theoretical study of the JT lattice coupling effects in the CMR manganites [16]. For the ferromagnet $SrRuO_3$ with a negligible JT effect, the electron-phonon interaction may be very small, so that no polarons are formed. That is why a negligible oxygen isotope effect on the Curie temperature is observed in the ferromagnet $SrRuO_3$.

Using the measured oxygen isotope exponent we may estimate the reduction factor of T_c due to the polaronic effect. From Eqs. (2) and (3), it is easy to see that the reduction factor f_p is $\exp(-\gamma E_{JT}/\hbar\omega) = \exp(-2\,\alpha_t)$. If we assume that the contribution to the total isotope exponent from the Mn atoms is similar to that from the oxygen atoms, then $\alpha_t \approx 2\,\alpha_O$. For $La_{0.8}Ca_{0.2}MnO_{3+y}$, $\alpha_O = 0.85$, then $f_p \approx 1/30$. So the ferromagnetic transition temperature in this compound is reduced by a factor of $\sim$30 due to the polaronic effect.

In summary, we have observed a giant oxygen isotope shift of the Curie temperature in the CMR perovskite $La_{1-x}Ca_xMnO_{3+y}$. Our results give clear evidence for the presence of polarons in the CMR manganites due to a strong JT effect. A close correlation between CMR and α_O implies that the CMR mainly arises from strong polaronic effects in these JT perovskites. Present results also lead us to suggest that there should exist JT polarons in the high-temperature superconductors (HTSC) since the Cu^{2+} in HTSC exhibits a strong JT effect.

Acknowledgements

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