

LETTER TO THE EDITOR

Giant Oxygen Isotope Effect in Charge-Ordered Manganese Perovskites

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Spectacular oxygen isotope (¹⁸O) enhancement of charge-ordering temperatures is reported in manganese perovskites Nd_{0.5}Sr_{0.5}MnO₃ and La_{0.5}Ca_{0.5}MnO₃. The isotope shift of charge-ordering temperatures was found to increase with increasing average radius of the A-site cations, $\langle r_A \rangle$ and A-site size disorder parameter, σ^2 . While Nd_{0.5}Sr_{0.5}MnO₃ with the largest $\langle r_A \rangle$ and σ^2 in this study showed an isotope shift as high as 21 K, Pr_{0.5}Ca_{0.5}MnO₃ with the smallest $\langle r_A \rangle$ and σ^2 remained virtually unaffected by ¹⁸O exchange. © 1999 Academic Press

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The recent demonstration of the oxygen isotope effect (1) in rare earth manganates exhibiting colossal magnetoresistance underscores the significant role of electron-lattice coupling proposed earlier by Millis *et al.* (2) on the electron transport and magnetic properties of these materials. The electron-lattice coupling in manganates arises from the strong Jahn–Teller (J–T) effect of the Mn³⁺ ion which lifts the ground state degeneracy of the e_g orbitals. Electron–lattice interaction leads to the formation of polarons, units of charge carriers and associated lattice distortion. Polarons undergo remarkable changes in their dynamics at ferromagnetic Curie temperature, T_C and charge ordering temperature, T_{CO} . Zhao *et al.* (1) have found that T_C of La_{0.8}Ca_{0.2}MnO_{3+ δ} have shifted to low temperature by 21 K while subjected to ¹⁸O exchange. These authors have shown that the polaron band width, $W_{\text{eff}} \propto W \exp(-\gamma E_{JT}/\hbar\omega)$ where W is the bare conduction band width and E_{JT} is the J–T stabilization energy. ω is the optical phonon frequency which is proportional to $M^{-1/2}$ where M is the oxygen isotope mass. In the strong coupling limit, $T_C \propto W_{\text{eff}}$ and hence the observed mass induced shift to T_C .

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In this study, we have explored the oxygen isotope effect on the charge ordering temperature, T_{CO} in manganese perovskites. Charge ordering in these materials is known to occur at certain commensurate values of Mn⁴⁺/Mn³⁺ and when the interelectronic Coulombic energy is comparable with the bare conduction band width. Since T_{CO} , like T_C is also governed by Hund's energy, J_H , and J–T stabilization energy, E_{JT} , it is natural to assume significant mass dependent effects on T_{CO} . To investigate the mass dependence of T_{CO} , we have carried out oxygen isotope exchange in the wellknown charge ordered manganates, Nd_{0.5}Sr_{0.5}MnO₃, La_{0.5}Ca_{0.5}MnO₃, and Pr_{0.5}Ca_{0.5}MnO₃ (3–5). The observed oxygen isotope shift of T_{CO} is correlated with the average A-site radius, $\langle r_A \rangle$ ($\langle r_A \rangle = \sum x_i r_i$ where x_i is the fractional occupancy of the A-site ion i with radius r_i) and A-site size disorder parameter, σ^2 ($\sigma^2 = \sum x_i r_i^2 - \langle r_A \rangle^2$).

Polycrystalline samples of Nd_{0.5}Sr_{0.5}MnO₃, La_{0.5}Ca_{0.5}MnO₃, and Pr_{0.5}Ca_{0.5}MnO₃ were prepared by the standard ceramic method. La₂O₃, Nd₂O₃, PrO₂, CaCO₃, SrCO₃ and MnO₂ were used as the starting materials. The component oxides/carbonates were mixed in stoichiometric proportion, ground well, and heated in air at 1273 and 1473 K for 24 h each. The reacted powder was then pelletized and sintered at 1673 K for 24 h and at 1773 K for 12 h and cooled to room temperature in 8 h. One pellet each of the three compositions thus obtained was cut into 3 pieces. The first piece of each of the compositions was heated in normal oxygen (¹⁶O) gas at 1273 K for 48 h and cooled to room temperature in 2 h. The other two pieces of each compositions were heated in ¹⁸O gas under identical heating conditions as ¹⁶O. One of those two ¹⁸O samples of each compositions was then heated in ¹⁶O at 1273 K for 48 h to obtain the back-exchanged (¹⁸O → ¹⁶O) sample. The percentage of ¹⁸O exchange as well as back exchange was determined from the weight changes of the ¹⁶O, ¹⁸O and

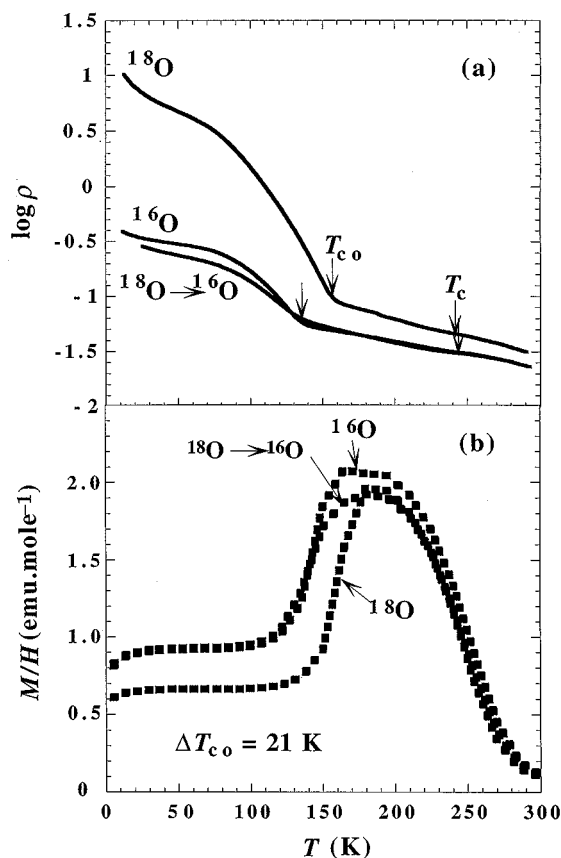


FIG. 1. Temperature dependence of (a) logarithm of resistivity and (b) magnetic susceptibility of ^{16}O , ^{18}O and back-exchanged ($^{18}\text{O} \rightarrow ^{16}\text{O}$) samples of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

back-exchanged samples. The ^{18}O enrichment in all the compositions was found to be $85 \pm 5\%$.

The phase analyses of the ^{16}O , ^{18}O as well as back-exchanged samples were carried out by X-ray powder diffraction using a Mac Science MXP18 rotating anode X-ray diffractometer. The room temperature X-ray patterns of all the samples showed single phase orthorhombic structure with $Pnma$ symmetry. The resistivities of the samples were measured by the dc four-probe method in the temperature range 10–300 K. Magnetic measurements were performed from 5 to 300 K at an applied field of 0.5 T using a commercial SQUID magnetometer (Quantum Design MPMS).

In Fig. 1 we show the temperature variation of resistivities and magnetic susceptibilities of ^{16}O , ^{18}O and back-exchanged samples of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. The ^{18}O samples showed higher resistivity at all temperatures compared to ^{16}O sample due to the mass enhanced lattice hardening. We find a dramatic increase in the charge ordering temperature, T_{CO} (~ 21 K) of ^{18}O sample determined from both magnetic as well as resistivity data compared to ^{16}O sample. The reversibility of the resistivity and magnetic behavior on back exchange confirmed that the observed increase in T_{CO} is due to the incorporation of ^{18}O . We notice that the

decrease in the ferromagnetic Curie temperature is very small (~ 2 K) and could be attributed to the relatively large A-site radius, $\langle r_A \rangle$ (1.236 Å) of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. This is in accordance with Zhao *et al.* who found that the oxygen isotope shift to T_{C} decreases with increasing $\langle r_A \rangle$ because of the increase in the bare conduction band width in non-charge-ordered manganates.

The temperature variation of resistivities and magnetic susceptibilities of ^{16}O as well as ^{18}O samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ are given in Figs. 2 and 3 respectively. The resistivity data of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ samples is plotted as $d \log \rho / dT^{-1}$ to clearly bring out the isotope shift of T_{CO} . As can be seen from the figures, while $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ showed an enhanced oxygen isotope shift of T_{CO} of 16 K, $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ showed a negligibly small shift of 3 K. Unlike in the case of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ where ferromagnetic ground state exists above T_{CO} , $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ exhibits paramagnetic ground state. The absence of ferromagnetism and dynamic Jahn–Teller effect in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ could be partly responsible for the absence of significant isotope effect. However, the

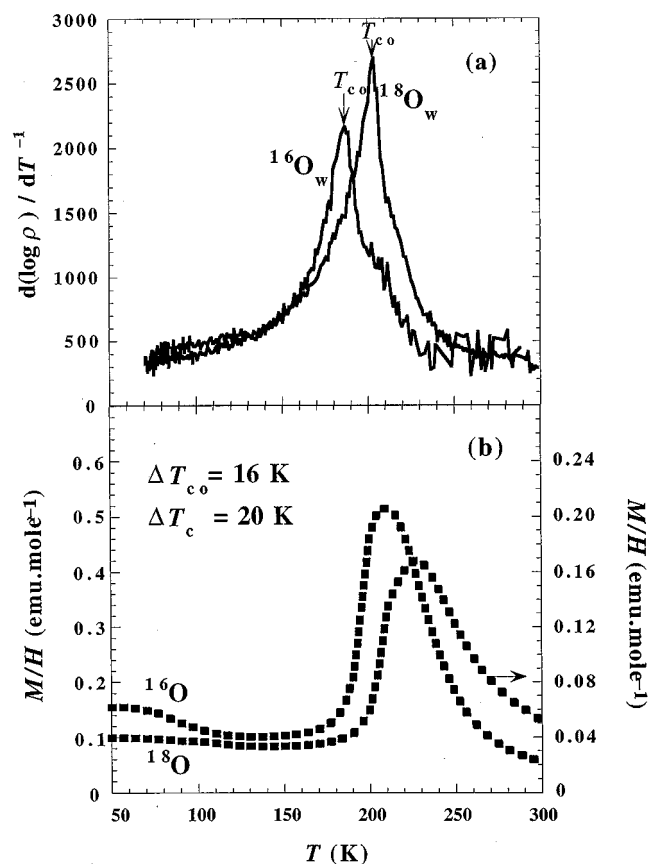


FIG. 2. Temperature dependence of (a) resistivity as $d \log \rho / dT^{-1}$ and (b) magnetic susceptibility of ^{16}O and ^{18}O samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The subscript “w” denotes the data collected on warming. $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ shows huge thermal hystereses in resistivity and magnetization.

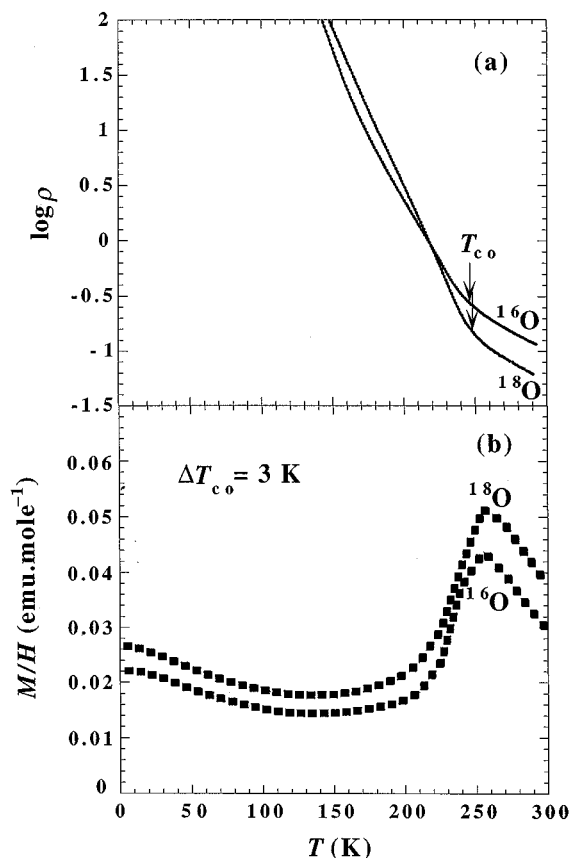


FIG. 3. Temperature dependence of (a) logarithm of resistivity and (b) magnetic susceptibility of ^{16}O and ^{18}O samples of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

real origin of the isotope shift of T_{CO} in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is yet to be understood.

The charge ordering temperatures of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ are 160, 180, and

230 K, respectively. On the other hand, the oxygen isotope shift of T_{CO} varies in the order $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 > \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 > \text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Higher T_{CO} is generally found in manganates with smaller $\langle r_A \rangle$ which in turn show lower values of isotope shift. We have plotted the variation of oxygen isotope shift of T_{CO} with $\langle r_A \rangle$ as well as A-site size disorder parameter, σ^2 in Fig. 4. Oxygen isotope shift of T_{CO} increases with $\langle r_A \rangle$ and σ^2 . However, among manganates under present study both $\langle r_A \rangle$ and σ^2 are inseparable variables and the observed isotope shift arises from their combined effect.

An unusual enhancement of T_C (~ 20 K) have been detected in the ^{18}O samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (Fig. 2b). T_C was found to shift from 220 K for ^{16}O samples to 240 K for ^{18}O samples. While T_C always decreased (1, 6, 7) with ^{18}O exchange in manganates reported so far, the present observation is curious. The enhancement of T_C cannot be attributed to the variations in the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio. As the samples were heated in oxygen, a decrease of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio which could result in the enhancement of T_C is highly unlikely. Also samples with higher $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio do not show T_C (4). The effective magnetic moment of the ^{18}O sample, however, was lower than the ^{16}O samples in the entire temperature range. The temperature variation of magnetic as well as crystal structure analysis may throw light on the observed shifts of T_{CO} as well as T_C in charge ordered manganates.

In conclusion, large enhancement of charge ordering temperatures have been observed in ^{18}O exchanged manganese perovskites. The oxygen isotope shift of charge ordering temperatures show systematic variations with average A-site radius and A-site size disorder. An investigation of the origin of the oxygen isotope effect in charge ordered manganates will open new vistas in the understanding of the nature of lattice effects in these oxides.

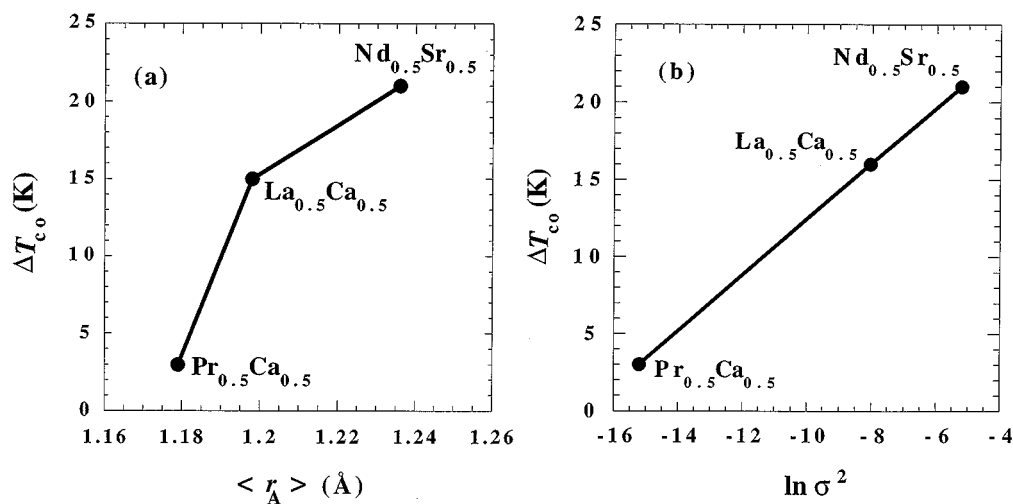


FIG. 4. Variation of oxygen isotope shift of T_{CO} (ΔT_{CO}) with (a) $\langle r_A \rangle$ and (b) logarithm of σ^2 .

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