

## LETTER TO THE EDITOR

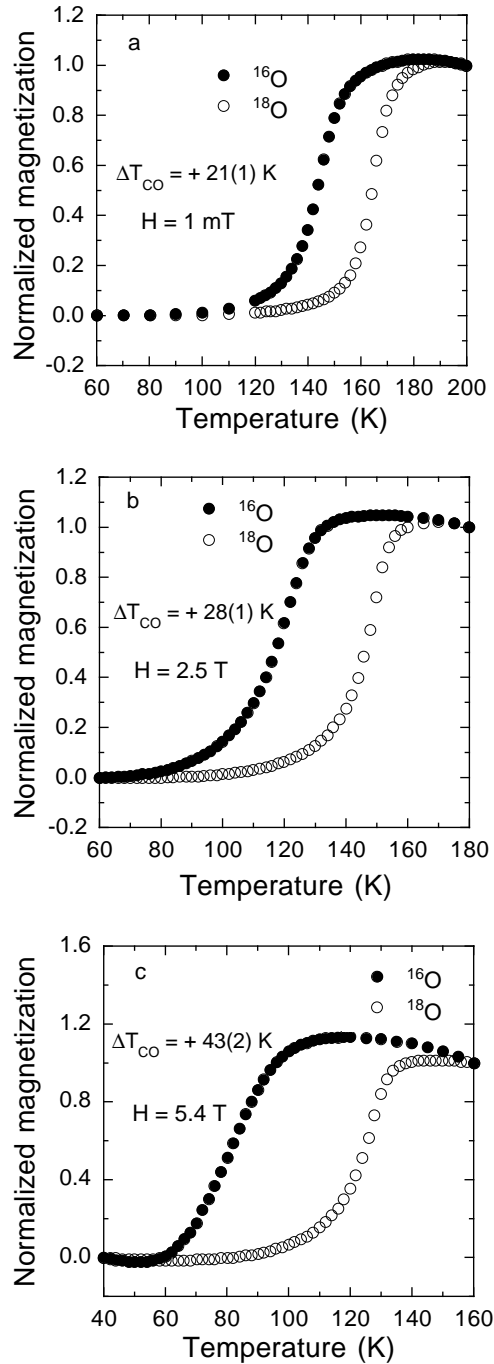
**Colossal oxygen isotope shift of the charge-ordering transition in  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$** Guo-meng Zhao<sup>†‡</sup>, K Ghosh<sup>†</sup> and R L Greene<sup>†</sup><sup>†</sup> Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20742, USA<sup>‡</sup> Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland

Received 1 October 1998

**Abstract.** A ‘colossal’ oxygen isotope shift of the charge-ordering temperature was discovered in  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . Upon replacing  $^{16}\text{O}$  with  $^{18}\text{O}$ , the charge-ordering temperature increases by 21 K under zero magnetic field. With an increase of the magnetic field, the oxygen isotope shift increases rapidly and reaches a magnitude of about 43 K under a magnetic field of 5.4 T. The very strong magnetic field dependence of the oxygen isotope effect is difficult to explain within the existing theories of the charge-ordering transition in manganites.

The real-space ordering of charge carriers in crystals is one of the most interesting phenomena in condensed matter physics. Such a charge-ordering state has been observed mostly in transition-metal-based oxides, such as  $\text{Ti}_4\text{O}_7$  [1],  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  [2],  $(\text{La,Pr,Nd})_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [3, 4],  $(\text{Pr,Nd})_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  [5, 6], etc. Since the transition-metal-based materials normally have a strong electron–electron repulsive interaction, it has been proposed that the long-range Coulomb repulsive interaction among conduction carriers might be responsible for the charge-ordering [7, 8, 9]. However, these theoretical models [7, 8, 9] might not be able to explain why the charge-ordering state in the manganites  $(\text{Pr,Nd})_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  can be destroyed by a small magnetic field ( $<10$  T) [5, 6]. Here we report a more exotic result: there exists a ‘colossal’ negative oxygen isotope shift of the charge-ordering transition temperature in  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . Upon replacing  $^{16}\text{O}$  with  $^{18}\text{O}$ , the charge-ordering temperature increases by 21 K under zero magnetic field. With an increase of the magnetic field, the oxygen isotope shift increases rapidly and has a value of about 43 K under a magnetic field of 5.4 T. The unusually strong magnetic field dependence of the oxygen isotope effect on the charge-ordering temperature is difficult to understand on the basis of the existing theories. The present results suggest that the electron–phonon interaction plays an important role in the charge-ordering, so any theoretical models for charge-ordering, if they only include electronic interactions, should be modified or ruled out.

The samples of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  were prepared by standard solid state reaction using dried high-purity  $\text{Nd}_2\text{O}_3$ ,  $\text{SrCO}_3$  and  $\text{Mn}_3\text{O}_4$ . The well-ground mixture was heated in air at 1000 °C for 12 h, 1100 °C for 12 h and 1250 °C for 20 h with several intermediate grindings. The powder samples were then pressed into pellets and sintered at 1400 °C for 20 h in air. The samples are single-phase, as checked by x-ray diffraction. Two pieces were cut from the same pellet for oxygen isotope diffusion. The diffusion was carried out for 40 h at 980 °C and at an oxygen pressure of about 1 bar. The cooling rate was 90 °C h<sup>-1</sup>.

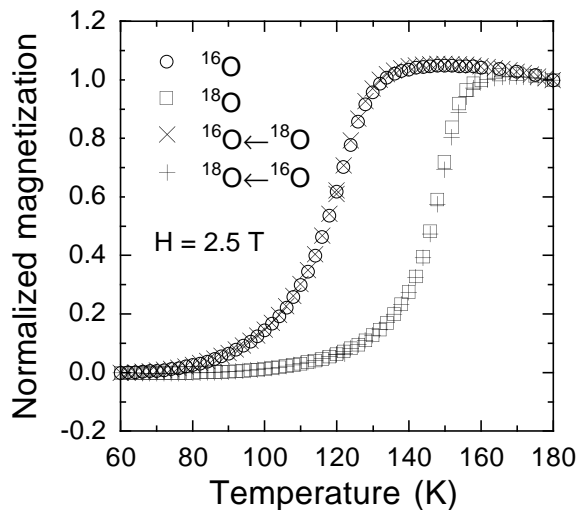


**Figure 1.** Oxygen isotope effect on the charge-ordering temperature of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . The temperature dependence of the normalized magnetization for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples under magnetic fields of (a) 1 mT, (b) 2.5 T and (c) 5.4 T are shown. We define the mid-point temperature on the transition curve as the charge-ordering temperature ( $T_{\text{CO}}$ ). The charge-ordering temperature for the  $^{18}\text{O}$  sample is higher than for the  $^{16}\text{O}$  sample by 21 K under  $H = 1 \text{ mT}$ , by 28 K under  $H = 2.5 \text{ T}$ , and by 43 K under  $H = 5.4 \text{ T}$ .

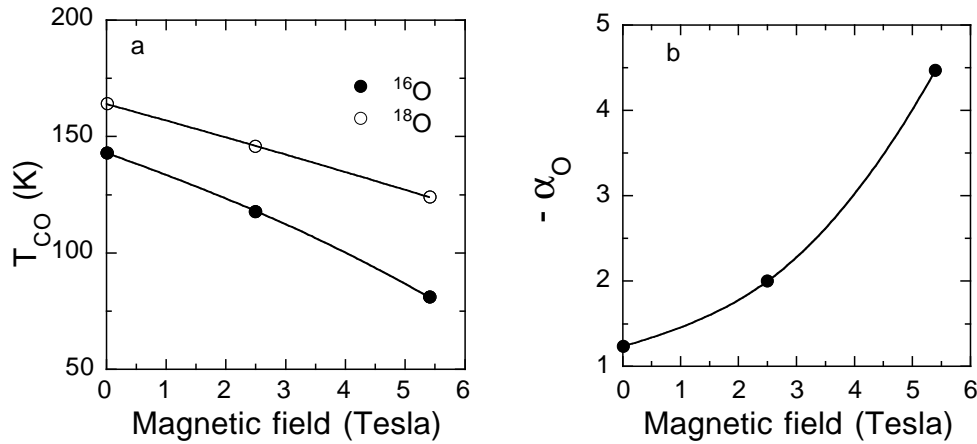
The oxygen isotope enrichment was determined from the weight changes of both  $^{16}\text{O}$  and  $^{18}\text{O}$  samples. The  $^{18}\text{O}$  samples had  $\sim 95\%$   $^{18}\text{O}$  and  $\sim 5\%$   $^{16}\text{O}$ .

Magnetization of the samples was measured with a Quantum Design SQUID magnetometer after the samples had been cooled in a field from 300 K to a temperature well above charge-ordering. The samples were kept at that temperature for 20 minutes for thermal equilibrium, and measurements were then carried out upon cooling. In figure 1, we show the temperature dependence of the normalized magnetizations for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples under a magnetic field of 1 mT (figure 1(a)), 2.5 T (figure 1(b)) and 5.4 T (figure 1(c)). The normalized magnetization is defined as  $(M(T) - M_L)/(M_H - M_L)$ , where  $M_L$  and  $M_H$  are the magnetizations at the lowest and highest temperatures shown in figure 1, respectively. With this normalization procedure, the curves for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples are parallel shifted. The transition from a high magnetization to a low magnetization state is indicative of the transition from a ferromagnetic to a charge-ordering (CO) state [5, 6]. Here we define the mid-point temperature on the transition curve as the charge-ordering temperature ( $T_{CO}$ ). With this definition, we find that the charge-ordering temperature for the  $^{18}\text{O}$  sample is higher than for the  $^{16}\text{O}$  sample by 21 K under  $H = 1$  mT, by 28 K under  $H = 2.5$  T, and by 43 K under  $H = 5.4$  T. This is the first observation of a colossal negative oxygen isotope shift of the charge-ordering temperature.

To show that the observed oxygen isotope shifts are intrinsic, we have performed isotope back-exchange experiments ( $^{16}\text{O} \rightarrow ^{18}\text{O}$ ;  $^{18}\text{O} \rightarrow ^{16}\text{O}$ ). In figure 2 we show the normalized magnetization for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples before and after isotope back-exchange. It is evident that the  $T_{CO}$  of the  $^{16}\text{O}$  ( $^{18}\text{O}$ ) sample goes back to that of the original  $^{18}\text{O}$  ( $^{16}\text{O}$ ) sample after the isotope back-exchange. This clearly indicates that the shift of  $T_{CO}$  is caused only by changing the oxygen isotope mass.



**Figure 2.** Oxygen isotope back-exchange result for  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . The temperature dependence of the normalized magnetization for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples before and after isotope back-exchange are shown. The symbol  $\times$  denotes the  $^{16}\text{O}$  sample which has been back-exchanged from the original  $^{18}\text{O}$  sample (denoted  $\square$ ). The symbol  $+$  represents the  $^{18}\text{O}$  sample which has been back-exchanged from the original  $^{16}\text{O}$  sample (denoted  $\circ$ ). It is evident that the  $T_{CO}$  of the  $^{16}\text{O}$  ( $^{18}\text{O}$ ) sample reverts to that of the original  $^{18}\text{O}$  ( $^{16}\text{O}$ ) sample after the isotope back-exchange.

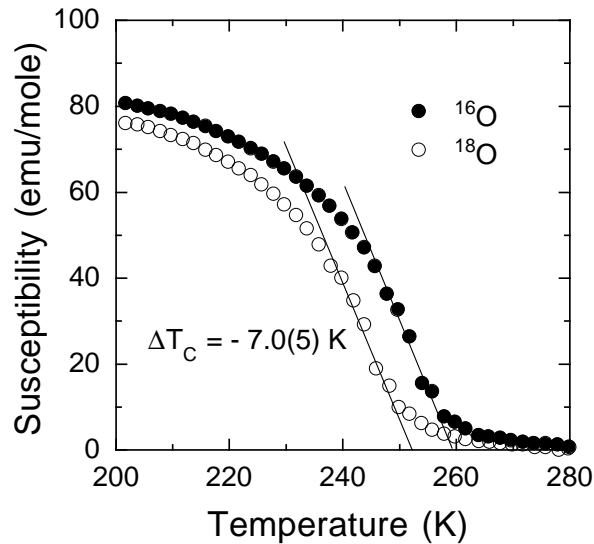


**Figure 3.** The charge-ordering temperatures of the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples as a function of the external magnetic field (a), and the magnetic field dependence of  $\alpha_O$  (b). Here the exponent of the oxygen isotope effect on  $T_{CO}$  is defined as  $\alpha_O = -d \ln T_{CO} / d \ln M_O$ . It is clear that, with an increase of the external magnetic field, the magnitude of  $\alpha_O$  increases rapidly.

In figure 3(a), we show the charge-ordering temperatures of the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples as a function of the external magnetic field. It is clear that, with an increase of the external magnetic field, the charge-ordering temperatures of both  $^{16}\text{O}$  and  $^{18}\text{O}$  samples decrease, but the rate of decrease for the  $^{18}\text{O}$  sample is slower than for the  $^{16}\text{O}$  sample. This leads to a dramatic increase in the oxygen isotope shift with increasing magnetic field. The exponent of the oxygen isotope effect on  $T_{CO}$  is defined as  $\alpha_O = -d \ln T_{CO} / d \ln M_O$  (where  $M_O$  is the oxygen mass). The magnetic field dependence of  $\alpha_O$  is shown in figure 3(b). It can be seen that the magnitude of  $\alpha_O$  increases rapidly with increasing magnetic field, and may go to an infinite value at a critical magnetic field where the charge-ordering state of the  $^{16}\text{O}$  sample disappears completely.

The observed negative oxygen isotope effect on the charge-ordering temperature (i.e. that  $T_{CO}$  is higher for heavier oxygen mass) is in contrast with the positive oxygen isotope effect on the ferromagnetic transition temperature  $T_C$  reported in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [10]. For the present samples of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ , a positive oxygen isotope effect on  $T_C$  is also observed as shown in figure 4. The  $T_C$  for the  $^{16}\text{O}$  sample is higher than that for the  $^{18}\text{O}$  sample by about 7.0 K. The isotope shift of  $T_C$  in this system is quite small ( $\Delta T_C / T_C = -2.7\%$ ), but the isotope shift of  $T_{CO}$  is colossal ( $\Delta T_{CO} / T_{CO} = +53\%$  at  $H = 5.4$  T). It should be noted that  $\Delta T_C / T_C$  is nearly independent of applied magnetic field.

The very large oxygen isotope shift of the charge-ordering temperature and its strong dependence on applied magnetic field are difficult to understand on the basis of the existing theories. In contrast, it is quite easy to explain the observed oxygen isotope effect on the ferromagnetic transition temperature  $T_C$ . This is because  $T_C \propto W_{eff}$  according to the double-exchange mechanism [11, 12], and the effective conduction bandwidth  $W_{eff}$  depends on the oxygen mass if the electron-phonon interaction is strong enough to form polaronic charge carriers [10]. So the observation of the oxygen isotope effect on the ferromagnetic transition in manganites provides strong evidence for the existence of polaronic charge carriers, and thus supports the theoretical models [13, 14]. On the other hand, the charge-ordering phenomenon is much more complicated. In most theoretical models, the charge-ordering arises from a long-range Coulomb interaction between carriers [7, 8, 9]. So these



**Figure 4.** Oxygen isotope effect on the Curie temperature  $T_C$ . The temperature dependence of the susceptibility for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . The  $T_C$  of the  $^{16}\text{O}$  sample is 259.3(2) K, and 252.3(2) K for  $^{18}\text{O}$ .

models predict no isotope effect, and cannot explain our present results.

Now we consider a theory of bipolaronic charge ordering [15, 16]. On the basis of this theory, the bipolaron charge ordering temperature is a function of both the repulsive interaction  $v$  among bipolarons and the bipolaron hopping integral  $t$ . Since both  $v$  and  $t$  could strongly depend on the isotope mass [16], one might expect a large oxygen isotope effect on the charge-ordering temperature. Thus, this model could explain the observed isotope effect under zero magnetic field. However, it might not explain the strong magnetic field dependence of the isotope effect since it does not include any magnetic interactions. In addition, other experiments that support the bipolaron picture in manganites are rather rare.

In summary, we have observed a very large oxygen isotope shift of the charge-ordering temperature and its strong dependence on applied magnetic field in  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . The unusual results cannot be explained by the existing theories. We believe that the present isotope-effect experiment will be crucial to the development of a correct microscopic theory for the charge-ordering in manganites.

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