

Very strong magnetic-field dependence of the oxygen isotope shift of the charge-ordering transition in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

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Oxygen isotope effect on the charge-ordering transition was studied in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Upon replacing ^{16}O with ^{18}O , the charge-ordering temperature increases by 9 K under zero magnetic field. With an increase of the magnetic field, the oxygen isotope shift increases rapidly and reaches a magnitude of about 40 K under a magnetic field of 5.4 T. The present results cannot be explained by the existing theories of the charge-ordering transition in manganites. [S0163-1829(99)00601-3]

It is well known that the observation of the oxygen-isotope effect in conventional superconductors is important for the development of the microscopic theory of superconductivity. Recently, Zhao and co-workers¹⁻³ have initiated the studies of oxygen isotope effects in the colossal magnetoresistive manganese perovskites. The observed strong oxygen isotope effects in the manganites give clear evidence for the existence of small lattice polarons in these systems. The isotope effects along with many other experimental results⁴⁻⁷ strongly support those theoretical models^{8,9} where a strong coupling of conduction electrons to local Jahn-Teller distortions is considered to be important for the basic physics in manganites.

Recently much attention has turned to charge ordering in the manganites $\text{Ln}_{0.5}\text{A}_{0.5}\text{MnO}_3$ (where Ln is a rare earth and A is a divalent cation).¹²⁻¹⁵ This phenomenon has been observed in other transition-metal-based oxides such as Ti_4O_7 (Ref. 10), and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ (Ref. 11). In particular, the charge ordering in those manganites exhibit some remarkable features. As an example, the charge-ordering state in the manganites $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ can be destroyed by a small magnetic field (< 10 T).^{14,15} This implies that the charge ordering state in these systems is not so stable, which appears to be in contradiction with a large energy gap observed from both photoemission¹⁶ and tunneling¹⁷ experiments. Theoretically, it has been proposed that the long-range Coulomb repulsive interaction among conduction carriers might be responsible for the charge ordering in these systems.¹⁸⁻²⁰ However, these models¹⁸⁻²⁰ might not be able to explain why a small magnetic field can destroy the charge-ordering state with a large energy gap. Here we report a study of the oxygen isotope effect on the charge-ordering transition temperature in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Upon replacing ^{16}O with ^{18}O , the charge-ordering tempera-

ture increases by about 10 K under zero magnetic field. With an increase of the magnetic field, the oxygen isotope shift increases rapidly and reaches a value of about 40 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 do suggest that the electron-phonon interaction plays an important role in the charge ordering of manganites.

The samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ were prepared by standard solid-state reaction using dried high-purity La_2O_3 , CaCO_3 , and Mn_3O_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 clean 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 oxygen pressure of about 1 bar. The cooling rate was 90 °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 $\sim 95\%$ ^{18}O and $\sim 5\%$ ^{16}O .

Magnetization of the samples was measured with a Quantum Design superconducting quantum interference device magnetometer (SQUID). The data were taken after the samples had been cooled in a field from 300 K. In Fig. 1, we show the temperature dependence of the magnetizations for the ^{16}O and ^{18}O samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ under a magnetic field of 0.5 T [Fig. 1(a)], 2.5 T [Fig. 1(b)], and 5.4 T [Fig. 1(c)]. Since the weights of the two isotope samples are very similar (15.6 mg for the ^{16}O sample and 15.4 mg for the ^{18}O sample), we only show the raw data that are not divided

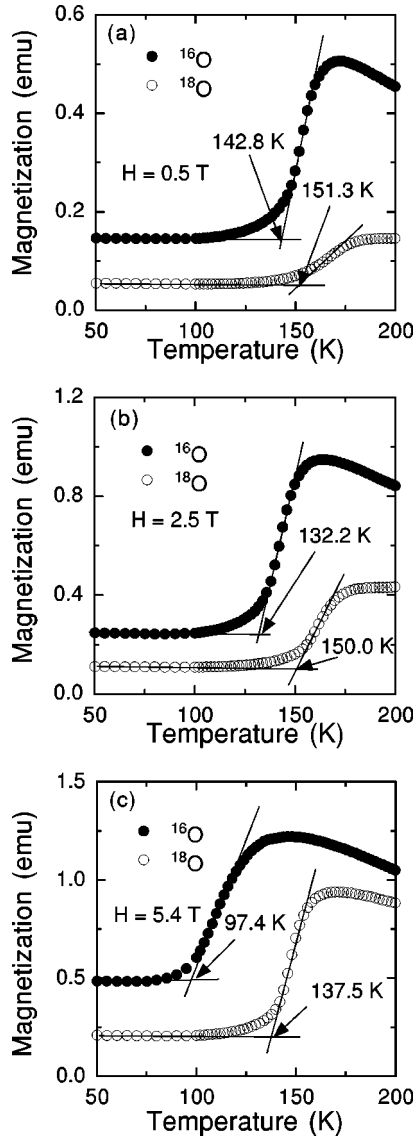


FIG. 1. Oxygen isotope effect on the charge-ordering temperature of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$: Temperature dependence of the magnetizations for the ^{16}O and ^{18}O samples under magnetic fields of 0.5 T (a); 2.5 T (b); 5.4 T (c). The charge-ordering temperature for the ^{18}O sample is higher than for the ^{16}O sample by 9(1) K under $H = 0.5$ T, by 18(1) K under $H = 2.5$ T, and by 40(2) K under $H = 5.4$ T.

by the sample weights. The transition from a high magnetization to a low magnetization state is a signature of the transition from a ferromagnetic to a charge-ordering (CO) state.^{14,15} Here we define the charge-ordering temperature (T_{CO}) as the temperature where the steepest straight line on the transition curve intersects with the low-temperature base line (marked by the arrows in the figure). With this definition, we find that the charge-ordering temperature for the ^{18}O sample is higher than for the ^{16}O sample by 9(1) K under $H = 0.5$ T, by 18(1) K under $H = 2.5$ T, and by 40(2) K under $H = 5.4$ T. The isotope shift in low magnetic field observed in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is similar to that observed in $\text{La}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$.²¹ However, the presence of the oxygen isotope shift of T_{CO} reported in Ref. 21 is not quite certain because their samples are not homogenous and only a small portion of the samples has a charge-ordering state. Our

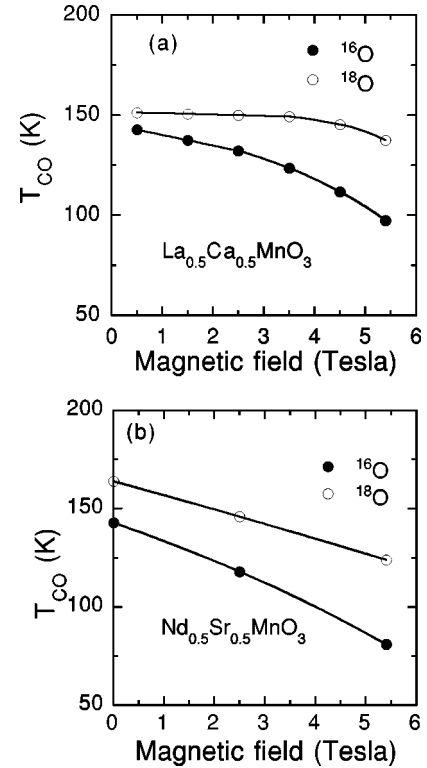


FIG. 2. Magnetic-field dependence of the charge-ordering temperatures of the ^{16}O and ^{18}O samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (a), and of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (b). The data for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ are from Ref. 22. It is clear that, with an increase of the external magnetic field, the charge-ordering temperatures of both ^{16}O and ^{18}O samples decrease, but the decreasing rate for the ^{18}O samples is much slower than for the ^{16}O samples. This leads to a dramatic increase in the oxygen isotope shift with increasing magnetic field.

present results clearly demonstrate that there is a large oxygen isotope shift of T_{CO} in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The shift is completely reversible upon oxygen isotope back-exchange, which shows that the observed isotope effect is intrinsic.²²

In Fig. 2(a), we show the charge-ordering temperatures of the ^{16}O and ^{18}O samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 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}O and ^{18}O samples decrease, but the decreasing rate for the ^{18}O sample is much slower than for the ^{16}O sample. This leads to a dramatic increase in the oxygen isotope shift with increasing magnetic field. A similar result was also observed²² in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, which is reproduced in Fig. 2(b) for comparison. The magnitudes of the isotope shift are quite different for the two compounds although the charge-ordering temperatures of both ^{16}O samples are nearly the same in zero magnetic field.

The exponent of the oxygen isotope effect on T_{CO} can be defined as $\alpha_O = -d \ln T_{CO} / d \ln M_O$ (where M_O is the oxygen mass). The magnetic-field dependence of α_O in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is shown in Fig. 3(a). It can be seen that the magnitude of α_O increases rapidly with increasing magnetic field. For comparison, the magnetic-field dependence of α_O in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (Ref. 22) is replotted in Fig. 3(b). It is clear that the magnitude of α_O in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is much larger than that in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ especially when the external magnetic field is low.

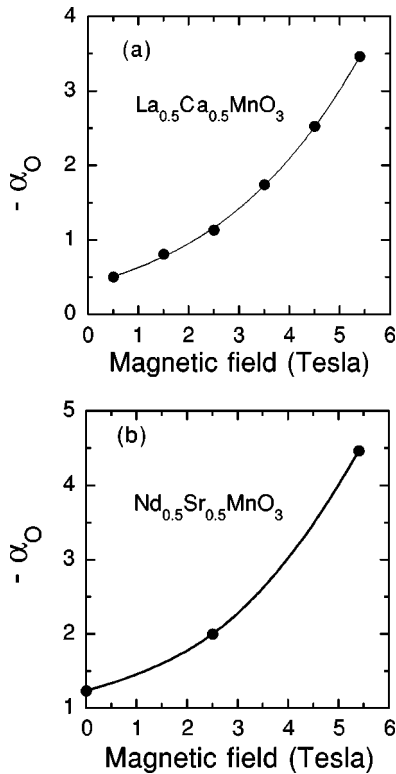


FIG. 3. Magnetic-field dependence of α_O for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (a), and for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (b). The data for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ are from Ref. 22. Here the exponent of the oxygen isotope effect on T_{CO} is defined as $\alpha_O = -d \ln T_{CO} / d \ln M_O$. It is clear that, with an increase of the external magnetic field, the magnitude of α_O increases rapidly.

The observed negative oxygen isotope effect on the charge-ordering temperature (i.e., 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 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.¹ For the present samples of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, a positive oxygen isotope effect on T_C is also observed, but the shift is small (< 7 K). The relative isotope shift of T_C ($\Delta T_C / T_C$) appears to be independent of the external magnetic field, in contrast to the relative isotope shift of T_{CO} ($\Delta T_{CO} / T_{CO}$), which strongly depends on the magnetic field.

The observed 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 most theoretical models, charge ordering is assumed to arise from a long-range Coulomb repulsive

interaction between carriers.^{18–20} So these models predict no isotope effect, and cannot explain our present results.

If the charge-ordering in the manganites is related to small polaron ordering, one may be able to explain the oxygen isotope shift of the charge-ordering temperature in zero magnetic field. This is because the effective mass of polaronic carriers is larger in samples with a heavier isotope mass, and the larger the carrier mass, the more stable the charge-ordering state. As a result, one would expect a higher T_{CO} in samples with a heavier isotope mass. Thus this model can qualitatively explain the observed isotope effect in zero magnetic field. However, it cannot explain why a small magnetic field (< 10 T corresponding to an energy of about 10 K) can destroy the charge-ordering state in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ where a large energy gap (> 1000 K) was observed.^{16,17} The observed large energy gap implies that the charge-ordering state, if it is an ordering state of polarons, must be stable and cannot be destroyed by a small magnetic field, in contradiction with the experiments.^{14,15}

Now we consider a theory of bipolaronic charge ordering.^{23,24} On the basis of this theory,^{23,24} the bipolaron charge ordering temperature is a function of both the repulsive interaction v between bipolarons and the bipolaron hopping integral t . Since both v and t could strongly depend on the isotope mass,²⁴ one might expect a large oxygen isotope effect on the charge-ordering temperature. Furthermore, because the energy difference between the bipolaron ordered and disordered state could be very small (depending on the magnitudes of v and t),²³ a small magnetic field could melt the bipolaron ordered state. Meanwhile there is no difficulty in explaining the observed large energy gap that could be the binding energy of the bipolarons. Although this explanation sounds plausible, other independent experimental results that support the bipolaron picture in manganites are rather rare.

In summary, we have observed a large oxygen isotope shift of the charge-ordering temperature and its strong dependence on applied magnetic field in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The results cannot be explained by the existing theories of the charge-ordering transition in manganites. 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 and perhaps in other materials, just as the isotope effect in conventional superconductors provides important insight into the pairing mechanism of superconductivity.

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¹G. M. Zhao *et al.*, Nature (London) **381**, 676 (1996).

²G. M. Zhao, M. B. Hunt, and H. Keller, Phys. Rev. Lett. **78**, 955 (1997).

³G. M. Zhao *et al.*, Solid State Commun. **104**, 57 (1997).

⁴M. Jaime *et al.*, Phys. Rev. B **54**, 11 914 (1996).

⁵S. J. L. Billinge *et al.*, Phys. Rev. Lett. **77**, 715 (1996).

⁶T. T. M. Palstra *et al.*, Phys. Rev. B **56**, 5104 (1997).

⁷C. H. Booth *et al.*, Phys. Rev. Lett. **80**, 853 (1998).

⁸A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

⁹H. Röder, J. Zang, and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996).

¹⁰M. Marezio, D. B. Mcwhan, P. D. Dernier, and J. P. Remeika, Phys. Rev. Lett. **28**, 1390 (1972).

¹¹C. H. Chen, S.-W. Cheong, and A. S. Cooper, Phys. Rev. Lett. **71**, 2461 (1993).

¹²C. H. Chen and S.-W. Cheong, Phys. Rev. Lett. **76**, 4042 (1996).

¹³M. Tokunaga, N. Miura, Y. Tomioka, and Y. Tokura, Phys. Rev. B **57**, 5259 (1998).

¹⁴H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y.

- Tokura, *Science* **270**, 961 (1995).
- ¹⁵Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, *Phys. Rev. Lett.* **74**, 5108 (1995).
- ¹⁶A. Chainani *et al.*, *Phys. Rev. B* **56**, R15 513 (1997).
- ¹⁷A. Biswas *et al.*, *J. Phys.: Condens. Matter* **9**, L355 (1997).
- ¹⁸V. I. Anisimov, I. S. Elfimov, M. A. Korotin, and K. Terakura, *Phys. Rev. B* **55**, 15 494 (1997).
- ¹⁹S. K. Mishra, R. Pandit, and S. Satpathy, *Phys. Rev. B* **56**, 2316 (1997).
- ²⁰L. Sheng and C. S. Ting, *Phys. Rev. B* **57**, 5265 (1997).
- ²¹I. Isaac and J. P. Franck, *Phys. Rev. B* **57**, R5602 (1998).
- ²²G. M. Zhao, K. Ghosh, and R. L. Greene, *J. Phys. Condens. Matter* **10**, L737 (1998).
- ²³A. S. Alexandrov and J. Ranninger, *Phys. Rev. B* **23**, 1796 (1981).
- ²⁴A. S. Alexandrov and S. N. Mott, *Polarons and Bipolarons* (World Scientific, Singapore, 1995).