

## Strong Oxygen-Mass Dependence of the Thermal-Expansion Coefficient in the Manganites $(\text{La}_{1-x}\text{Ca}_x)_{1-y}\text{Mn}_{1-y}\text{O}_3$

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Thermal-expansion and magnetic susceptibility measurements were performed on oxygen-isotope substituted manganites  $(\text{La}_{1-x}\text{Ca}_x)_{1-y}\text{Mn}_{1-y}\text{O}_3$  with a  $\text{Mn}^{4+}$  concentration of  $\sim 33\%$ . The linear thermal-expansion coefficient  $\beta(T)$  exhibits an asymmetric peak at the Curie temperature  $T_C$ , indicative of a second-order ferromagnetic transition. Upon replacing  $^{16}\text{O}$  with  $^{18}\text{O}$ ,  $T_C$  is lowered by about 10 K, while the second-order jump in the thermal-expansion coefficient  $[\Delta\beta(T_C)]$  is raised by about 20%. Such a “colossal” oxygen-isotope effect on  $\Delta\beta(T_C)$  is very surprising, but can be explained quantitatively on the basis of double exchange and strong polaronic effects. [S0031-9007(96)02269-7]

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The manganese-based perovskites  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  ( $M = \text{Ca}, \text{Sr}, \text{and Ba}$ ) have recently been the subject of intensive investigations because of their unusual and potentially useful magnetic properties (e.g., the colossal magnetoresistance effect [1,2]). The undoped parent compound  $\text{LaMnO}_3$  (with  $\text{Mn}^{3+}$ ) is an insulating antiferromagnet [3]. When  $\text{Mn}^{4+}$  ions are introduced by substituting divalent ions for  $\text{La}^{3+}$ , the materials become ferromagnetic and metallic at low temperature for  $0.2 \leq x \leq 0.5$  [4]. The ferromagnetic and metallic ground state has also been observed in the cation-deficient  $(\text{LaMn})_{1-y}\text{O}_3$  compound, which contains  $\sim 33\% \text{Mn}^{4+}$  [5]. Moreover, it was shown that the  $\text{Mn}^{4+}$  concentration in cation-deficient materials can be adjusted by simply changing the anneal temperature [6]. This convenient feature makes it an attractive candidate for studying the effect of changing the  $\text{Mn}^{4+}$  concentration.

The physics in manganites has primarily been described by the double-exchange model [7,8]. Millis, Littlewood, and Shraiman [9] have pointed out, however, that double exchange alone cannot fully explain the data of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ . They proposed that polaronic effects due to strong electron-phonon coupling (arising from a strong Jahn-Teller effect) should be involved. The strong coupling between the electronic and lattice subsystems has been demonstrated by the recent observation of a giant oxygen-isotope shift of the ferromagnetic transition in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [10]. This scenario is also supported by thermal expansion [11,12] and small-angle neutron scattering experiments [13]. Here we report an observation of a “colossal” oxygen-isotope effect on the height of the thermal-expansion jump  $\Delta\beta(T_C)$  at a second-order ferromagnetic transition in the perovskite  $(\text{La}_{1-x}\text{Ca}_x)_{1-y}\text{Mn}_{1-y}\text{O}_3$  with a  $\text{Mn}^{4+}$  concentration of  $\sim 33\%$ . The  $T_C$  can be changed by varying either the  $\text{Mn}^{4+}$  concentration or the oxygen mass. Increasing the  $\text{Mn}^{4+}$  concentration does not change the thermal-expansion jump  $\Delta\beta(T_C)$ , while increasing the oxygen mass does increase  $\Delta\beta(T_C)$  by  $\sim 20\%$ .

We propose a model to explain these unusual isotope effects.

Samples of  $(\text{LaMn})_{1-y}\text{O}_3$  were prepared by conventional solid state reaction using  $\text{La}_2\text{O}_3$  and  $\text{MnO}_2$ . The  $\text{La}_2\text{O}_3$  was dried for 6 h at  $900^\circ\text{C}$  prior to weighing. The powders were mixed, ground thoroughly, and pressed into pellets. These pellets were then fired in air at  $1040^\circ\text{C}$  for  $\sim 48$  h with one intermediate grinding. To obtain samples with small grains and enough porosity, we re-ground the samples thoroughly, pressed them into pellets, and annealed them in air at  $1010^\circ\text{C}$  for 12 h.

Each pellet was broken in half, and the halves were then subjected to  $^{16}\text{O}$  and  $^{18}\text{O}$  isotope diffusion. The diffusion was carried out for 48/40 h at  $950/930^\circ\text{C}$  and oxygen pressure of about 1 bar. The cooling rate was  $30^\circ\text{C}/\text{h}$ . The oxygen isotope enrichment was determined from the weight changes of the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples. The  $^{18}\text{O}$  samples had  $\sim 95\% \text{ }^{18}\text{O}$  and  $\sim 5\% \text{ }^{16}\text{O}$ . The samples are single phase as checked by x-ray diffraction. The structure at room temperature is rhombohedral, and the x-ray pattern was refined in the space group  $R3c$ , hexagonal description. In this description, lattice parameters for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples (annealed at  $930^\circ\text{C}$ ) were the same:  $a_h = 5.5196(2)$ ,  $c_h = 13.348(1)$ , and unit volume =  $58.69(2) \text{ \AA}^3$ . From the relation between  $y$  and the unit volume [6], we estimated  $y = 0.055(6)$ , corresponding to a  $\text{Mn}^{4+}$  concentration of  $35(5)\%$  in agreement with the thermogravimetric analysis [14]. The samples of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  were prepared in a high temperature ( $1250^\circ\text{C}$ ). The detailed procedures for sample preparation and isotope exchange will be published elsewhere [14].

The thermal expansion was measured using a capacitance dilatometer with a length resolution of  $\sim 0.1 \text{ \AA}$ . Data were collected during warming and subsequent cooling at the same constant rate of  $3 \text{ mK/s}$ . Field-cooled magnetization was measured with a commercial SQUID magnetometer in a field of 4 mT. The samples were cooled directly to 5 K, then warmed up to a temperature well

below  $T_C$ . After waiting for 20 min at that temperature, data were collected upon warming to a temperature well above  $T_C$ .

In Fig. 1(a) we show the temperature dependence of the low-field magnetization (normalized to the magnetization well below  $T_C$ ) for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $(\text{LaMn})_{0.945}\text{O}_3$ , which were annealed at  $930^\circ\text{C}$ . It is evident that the ferromagnetic transition of the samples is very sharp and that the transition widths of the two isotope samples are the same (i.e., the two curves are the same but for a parallel shift). The oxygen-isotope shift of  $T_C$  was determined from the differences between the midpoint temperatures on the transition curves of the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples. The  $^{18}\text{O}$  sample has lower  $T_C$  than the  $^{16}\text{O}$  sample by  $\sim 12\text{ K}$  [i.e.,  $\delta T_C/T_C = -4.6(2)\%$ ]. In Fig. 1(b) we show the field dependence of the magnetization at  $5\text{ K}$  for the two isotope samples. The magnetization starts to saturate above a magnetic field of  $1\text{ T}$ , which indicates a normal ferromagnetism and that the two isotope samples have the same saturation moment [ $3.99(1)\mu_B$ ]. The saturation moment is just that expected for an effective spin of  $1.85$  in samples with  $30\%$   $\text{Mn}^{4+}$

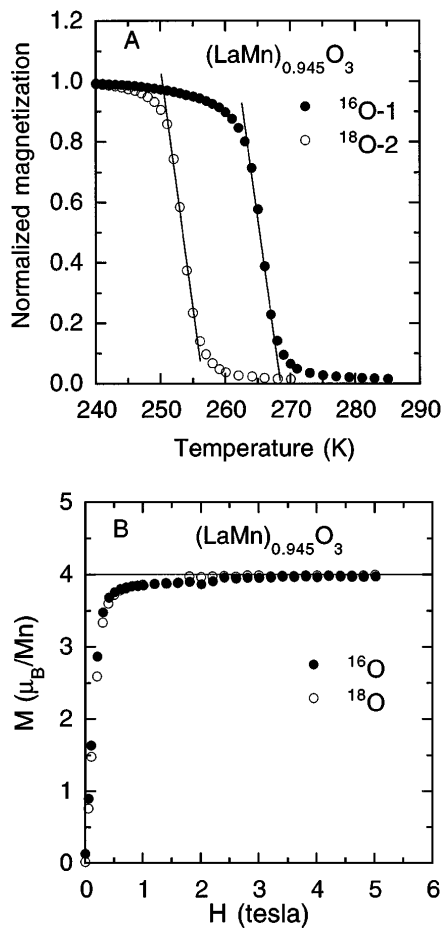


FIG. 1. The temperature dependence of the low-field magnetization (normalized to the magnetization well below  $T_C$ ) for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $(\text{LaMn})_{0.945}\text{O}_3$  [Fig. 1(a)]; the field dependence of magnetization at  $5\text{ K}$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $(\text{LaMn})_{0.945}\text{O}_3$  [Fig. 1(b)].

(the saturation moment for a spin of  $2$  is about  $4.3\mu_B$  in this system [15]). This implies that the  $\text{Mn}^{4+}$  concentration in our samples is about  $30\%$  in agreement with the value determined above. The normal ferromagnetic behaviors observed in our cation-deficient samples are also consistent with our resistivity measurements, which show a metallic ground state, similar to the Ca-doped compound  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ .

In Fig. 2 we show the linear thermal-expansion coefficient  $\beta(T)$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $(\text{LaMn})_{0.945}\text{O}_3$  [Fig. 2(a)] and of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  [Fig. 2(b)]. The thermal-expansion coefficient has a sharp asymmetric peak at  $T_C$ , corresponding to a large thermal-expansion jump  $\Delta\beta(T_C)$ . The peak in  $\beta(T)$  occurs at a temperature where the magnetization is close to its maximum value. There is no hysteresis in  $\beta(T)$  within the accuracy of our measurements ( $\sim 0.1\text{ K}$ ). From the temperature dependence of the sample length, we find that the volume change due to the ferromagnetic transition

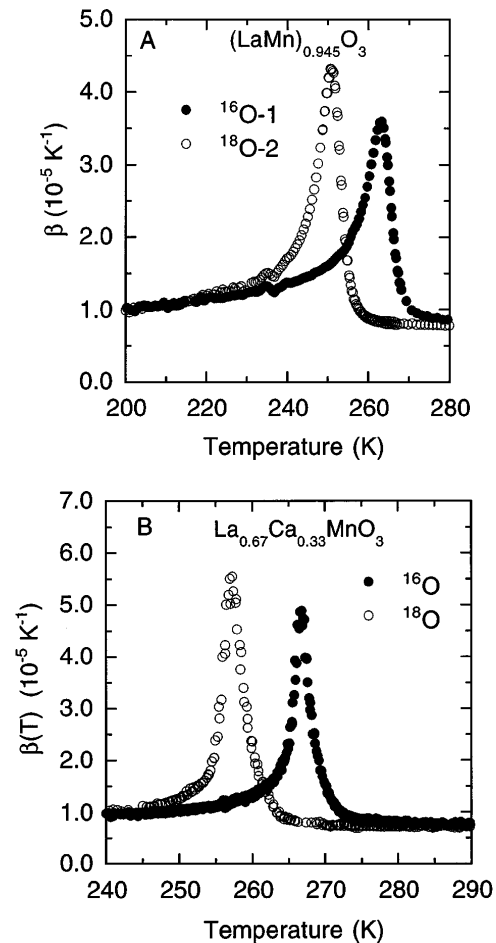


FIG. 2. The linear thermal-expansion coefficient  $\beta(T)$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $(\text{LaMn})_{0.945}\text{O}_3$  [Fig. 2(a)] and of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  [Fig. 2(b)]. The thermal-expansion jumps  $\Delta\beta(T_C)$  for the  $^{18}\text{O}$  samples of  $(\text{LaMn})_{0.945}\text{O}_3$  and  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  are raised by  $+24(3)\%$  and  $16(3)\%$  relative to the  $^{16}\text{O}$  samples, respectively. The oxygen-isotope shift of  $T_C$  is  $9.7(3)\text{ K}$  for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ .

(accompanied by an insulator-metal transition) is about 0.15%, which is very close to that ( $\sim 0.13\%$ ) observed in  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  [12].

It is surprising that the jump  $\Delta\beta(T_C)$  depends strongly on the oxygen mass. Although the magnitude of the jump depends on the sharpness of the transition, the relative change in the jump is independent of the transition width provided that two samples have the same transition width. This is the case for the two isotope samples, as seen from the magnetization curves above [see Fig. 1(a)]. If we define the jump  $\Delta\beta(T_C)$  as the difference between the peak and base-line values of  $\beta(T)$ , where the baseline is the high-temperature part of  $\beta(T)$  above  $T_C$ , then  $\Delta\beta(T_C)$  for the  $^{18}\text{O}$  sample is larger than that for the  $^{16}\text{O}$  sample by 24(3)% for  $(\text{LaMn})_{0.945}\text{O}_3$ , and by 16(3)% for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . This is the first observation of a colossal oxygen-isotope effect on the thermal-expansion jump at the ferromagnetic transition.

It is important to show that the observed oxygen-isotope effects are intrinsic. To do that, we first took one piece of the  $^{16}\text{O}$  sample of  $(\text{LaMn})_{1-y}\text{O}_3$  (which had been annealed at  $950^\circ\text{C}$  in 1 bar  $^{16}\text{O}_2$  gas for 48 h) then annealed it at  $930^\circ\text{C}$  in 1 bar  $^{16}\text{O}_2$  gas for 40 h. The  $T_C$  of the sample is raised by  $\sim 10$  K due to the increase in the  $\text{Mn}^{4+}$  concentration, but the jump  $\Delta\beta(T_C)$  is nearly unchanged, as seen from Fig. 3(a). This implies that the jump  $\Delta\beta(T_C)$  does not depend on the  $\text{Mn}^{4+}$  concentration within the range studied. Subsequently, we took the same piece of  $^{16}\text{O}$  sample and annealed it at  $930^\circ\text{C}$  in 1 bar  $^{18}\text{O}_2$  gas for 40 h. The  $T_C$  of the  $^{18}\text{O}$  sample (which has been exchanged from the  $^{16}\text{O}$  sample) decreases by  $\sim 12$  K, while  $\Delta\beta(T_C)$  is enhanced by  $\sim 24\%$  [see Fig. 3(b)]. These results clearly show that the change effected in  $\Delta\beta(T_C)$  arises only from the change in oxygen mass and that the observed large oxygen-isotope effects on both  $T_C$  and the thermal-expansion jump are intrinsic.

The conventional theory of ferromagnetism, in which the electron-phonon interaction is not taken into account, cannot explain the oxygen-isotope effects observed here. In order to find an explanation, we may relate  $\Delta\beta(T_C)$  to the pressure effect ( $d \ln T_C/dP$ ). If the ferromagnetic transition is of second order, as is the case in the optimally doped manganites (with a  $\text{Mn}^{4+}$  concentration of 33%) [16], then

$$d \ln T_C/dP = 3\Delta\beta(T_C)/\Delta C_P(T_C), \quad (1)$$

where  $C_P$  is the specific heat. For  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\Delta\beta(T_C) = 4.2 \times 10^{-5} \text{ K}^{-1}$  [see Fig. 2(b)],  $\Delta C_P = 50 \text{ J/mole K}$  [17], and unit volume =  $60 \text{ \AA}^3$ . Substituting the above values into Eq. (1), we obtain  $d \ln T_C/dP = 0.07 \text{ GPa}^{-1}$ , in excellent agreement with the measured value ( $\sim 0.06 \text{ GPa}^{-1}$  [21]). Thus the ferromagnetic transition in the optimally doped samples is indeed of second order.

We now turn to the isotope dependence of  $\Delta\beta(T_C)$ . From Eq. (1) we see that there must be a corresponding dependence of  $d \ln T_C/dP$  on the oxygen mass  $M$ , provided

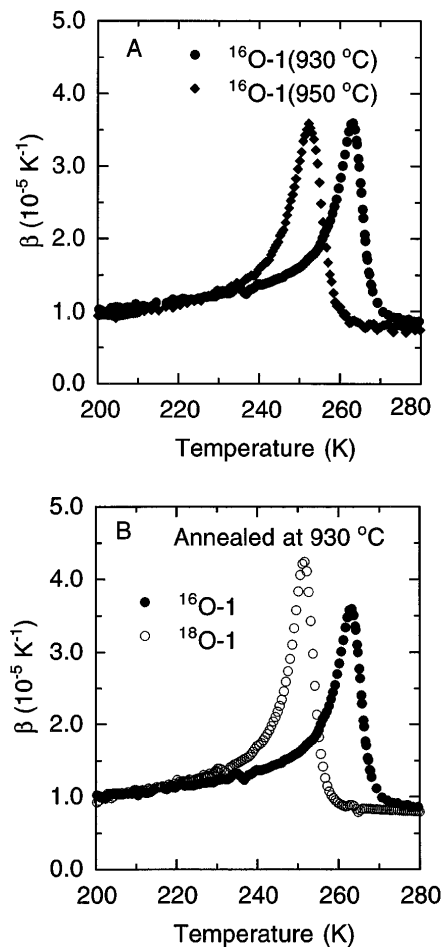


FIG. 3. The dependence of the linear thermal-expansion coefficient  $\beta(T)$  on the  $\text{Mn}^{4+}$  concentration [Fig. 3(a)], and on the oxygen mass [Fig. 3(b)]. A piece of the  $^{16}\text{O}$  sample of  $(\text{LaMn})_{1-y}\text{O}_3$  was first annealed at  $950^\circ\text{C}$ , and then at  $930^\circ\text{C}$  in  $^{16}\text{O}_2$  gas. The same piece of the sample was finally annealed at  $930^\circ\text{C}$  in  $^{18}\text{O}_2$  gas. It is clear that  $T_C$  of the samples depends both on the  $\text{Mn}^{4+}$  concentration and on the oxygen mass, while the jump  $\Delta\beta(T_C)$  changes only with the oxygen mass.

that  $\Delta C_P(T_C)$  is independent of  $M$ . This should be the case, since  $\Delta C_P(T_C)$  arises from entropy changes due to a combination of ferromagnetic ordering of the Mn spins and delocalization of charge carriers [17,19], neither of which contributions should be influenced by  $M$ . We can understand the  $M$  dependence of  $d \ln T_C/dP$  in terms of double exchange [7–9] and polaronic effects [20]. In the strong coupling limit of double exchange,  $T_C \propto W^*$  [9], where  $W^*$  is the effective bandwidth. Thus  $d \ln T_C/dP$  should, in general, depend on  $W^*$ . Zhao *et al.* have recently shown [10] that polaronic effects must play a central role in the manganites, since the oxygen mass is shown strongly to influence  $T_C$  and thus  $W^*$ . This means that  $d \ln T_C/dP$  should depend on the oxygen mass.

More specifically, Eq. (1) implies that there should be the same relative change in  $d \ln T_C/dP$  as in  $\Delta\beta(T_C)$  in response to a small change in  $W^*$ , no matter how this arises. Such a change in  $W^*$  can be measured by

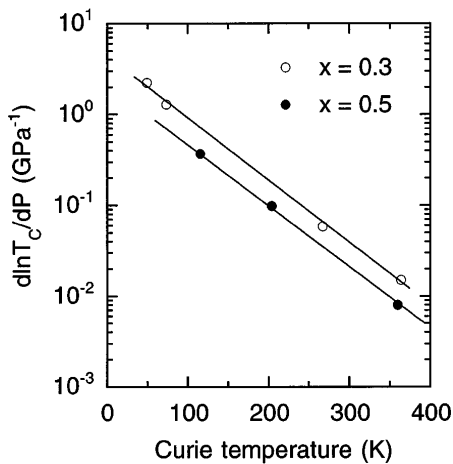


FIG. 4. The relation between  $d \ln T_C/dP$  and  $T_C$  for  $Mn^{4+}$  concentrations of 30% and 50%. The experimental data are as follows:  $d \ln T_C/dP = 2.23 \text{ GPa}^{-1}$  at  $T_C = 49 \text{ K}$ ,  $d \ln T_C/dP = 1.29 \text{ GPa}^{-1}$  at  $T_C = 73 \text{ K}$  for  $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$  [22];  $d \ln T_C/dP = 0.06 \text{ GPa}^{-1}$  at  $T_C = 267 \text{ K}$  for  $La_{0.67}Ca_{0.33}MnO_3$  [18];  $d \ln T_C/dP = 0.015 \text{ GPa}^{-1}$  at  $T_C = 364 \text{ K}$  for  $La_{0.7}Sr_{0.3}MnO_3$ ,  $d \ln T_C/dP = 0.008 \text{ GPa}^{-1}$  at  $T_C = 360 \text{ K}$  for  $La_{0.5}Sr_{0.5}MnO_3$  [21];  $d \ln T_C/dP = 0.37 \text{ GPa}^{-1}$  at  $T_C = 115 \text{ K}$  for  $(Sm_{0.875}Nd_{0.125})_{0.5}Sr_{0.5}MnO_3$  [23];  $d \ln T_C/dP = 0.098 \text{ GPa}^{-1}$  at  $T_C = 204 \text{ K}$  for  $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_3$  [24]. It is clear that  $d \ln T_C/dP$  depends exponentially on  $T_C$  for fixed  $Mn^{4+}$  concentrations of  $\sim 30\%$  and  $50\%$ .

a change in  $T_C$ , providing the  $Mn^{4+}$  concentration  $x$  remains constant. Thus a small change in any relevant parameter on which  $T_C$  (or  $W^*$ ) depends, should cause the same relative change in  $d \ln T_C/dP$  as in  $\Delta\beta(T_C)$ , for the same change in  $T_C$ . Now,  $T_C$ , and thus  $W^*$  varies with the oxygen mass and the mean ionic radius  $\langle r_A \rangle$  at the cation site  $La_{1-x}Me_x$  for fixed  $x$ . From inspection of direct studies of the pressure dependence of  $T_C$  [18,21–24], we find, moreover, that for fixed  $x \sim 0.3$  and  $0.5$ , varying  $\langle r_A \rangle$  causes  $d \ln T_C/dP$  to change exponentially with  $T_C$  (or  $W^*$ ) over a wide range of  $T_C$  that encompasses our own data:

$$d \ln T_C/dP \propto \exp(-0.016T_C), \quad (2)$$

as shown in Fig. 4. Thus the relative change in  $d \ln T_C/dP$  due to a small change in  $W^*$  is equal to  $-0.016\delta T_C$ . For  $\delta T_C = -12$  or  $10 \text{ K}$  (as is caused in our samples by the change in the oxygen mass), one should observe a rise in  $d \ln T_C/dP$  of 20 or 16%, which is in fair agreement with our measured value of 24(3)% or 16(3)% for the relative change in  $\Delta\beta(T_C)$ . This provides quantitative support for the proposal that the observed colossal oxygen-isotope effect on  $\Delta\beta(T_C)$  arises from the oxygen-mass dependence of the effective bandwidth  $W^*$  due to polaronic effects.

Our isotope results thus provide a crucial test for the nature of charged carriers in manganites. The charged

carriers must be of polaronic type, so that the effective bandwidth strongly depends on the oxygen mass. Any correct theory for the colossal magnetoresistance effect has to take the polaronic effect into account. It appears that the theoretical models proposed by Millis *et al.* [9,25] and by Röder *et al.* [26] are consistent with our isotope-effect results.

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- [1] S. Jin *et al.*, *Science* **264**, 413 (1994).
- [2] R. von Helmolt *et al.*, *Phys. Rev. Lett.* **71**, 2331 (1993).
- [3] E.O. Wollan and W.C. Koeler, *Phys. Rev.* **100**, 545 (1955).
- [4] G.H. Jonker and J.H. van Santen, *Physica (Utrecht)* **16**, 337 (1950).
- [5] R. Mahendiran *et al.*, *Phys. Rev. B* **53**, 3348 (1996).
- [6] J.A. Alonso, M.J. Martinez-lope, and M.T. Casais, *Eur. J. Solid State Inorg. Chems.* **33**, 331 (1996).
- [7] P.W. Anderson and H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).
- [8] C. Zener, *Phys. Rev.* **82**, 403 (1951).
- [9] A.J. Millis, P.B. Littlewood, and B.I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995).
- [10] Guo-meng Zhao, K. Conder, H. Keller, and K.A. Müller, *Nature (London)* **381**, 676 (1996).
- [11] M.R. Ibarra *et al.*, *Phys. Rev. Lett.* **75**, 3541 (1995).
- [12] P.G. Radaelli *et al.*, *Phys. Rev. Lett.* **75**, 4488 (1995).
- [13] J.M. De Teresa *et al.*, *Phys. Rev. B* **54**, 1187 (1995).
- [14] M.B. Hunt, Guo-meng Zhao, and H. Keller (to be published).
- [15] H.Y. Hwang *et al.*, *Phys. Rev. Lett.* **75**, 914 (1995).
- [16] R.H. Heffner *et al.*, *Phys. Rev. Lett.* **77**, 1869 (1996).
- [17] A.P. Ramirez *et al.*, *Phys. Rev. Lett.* **76**, 3188 (1996).
- [18] J.J. Neumeier *et al.*, *Phys. Rev. B* **52**, R7006 (1995).
- [19] J.M.D. Coey *et al.*, *Phys. Rev. Lett.* **75**, 3910 (1995).
- [20] A.S. Alexandrov and N.F. Mott, *Int. J. Mod. Phys.* **8**, 2075 (1994).
- [21] Y. Moritomo, A. Asamitsu, and Y. Tokura, *Phys. Rev. B* **51**, 16491 (1995).
- [22] J.-S. Zhou, W. Archibald, and J.B. Goodenough, *Nature (London)* **381**, 770 (1996).
- [23] Y. Tokura *et al.*, *Phys. Rev. Lett.* **76**, 3184 (1996).
- [24] K. Khazeni *et al.*, *Phys. Rev. Lett.* **76**, 295 (1996).
- [25] A.J. Millis, B.I. Shraiman, and R. Mueller, *Phys. Rev. Lett.* **77**, 175 (1996).
- [26] H. Röder, Jun. Zang, and A.R. Bishop, *Phys. Rev. Lett.* **76**, 1356 (1996).