RAPID COMMUNICATIONS

PHYSICAL REVIEW B **77**, 100406(R) (2008)

Unusual temperature dependence of the oxygen-isotope effect on the exchange-energy of $La_{1-x}Ca_xMnO_3$ at high temperatures

Guo-meng Zhao* and John Mann

Department of Physics and Astronomy, California State University, Los Angeles, California 90032, USA

(Received 7 March 2008; published 28 March 2008)

We report magnetic susceptibility $\chi(T)$ measurements on oxygen-isotope exchanged $La_{1-x}Ca_xMnO_{3+y}$ up to 700 K. The $1/\chi(T)$ data show that the ferromagnetic exchange-energy J strongly depends on the oxygen-isotope mass. The isotope effect on J decreases with temperature up to 400 K and then increases again with temperature above 400 K. This unusual temperature dependence of the isotope effect cannot be explained by existing theories of the colossal magnetoresistance effect for doped manganites. The present results thus provide essential constraints on the physics of manganites.

DOI: 10.1103/PhysRevB.77.100406 PACS number(s): 75.47.Lx, 71.38.−k, 71.45.Lr

Doped manganites such as $La_{1-x}Ca_xMnO_{3+y}$ ($x>0.20$) show a colossal magnetoresistance (CMR) effect.[1] This novel physical property makes them potentially important in technological applications. The understanding of the microscopic mechanism responsible for CMR has become one of the outstanding problems in condensed matter physics because no consensus concerning the CMR mechanism has been reached[2–5] despite tremendous theoretical and experimental efforts for over 10 years. Some outstanding problems of particular interest include the observations of intrinsic inhomogeneity,[6,7] the giant oxygen-isotope effect on the Curie temperature (T_C),[8,9] and the transition from a ferromagnetic metallic ground state to an antiferromagnetic charge-ordered insulating ground state by simply replacing ^{16}O with ^{18}O isotope.[10,11] These novel isotope effects have never been predicted by any conventional theories based on the Migdal approximation. The fact that lattice vibrations can significantly modify the electrical and magnetic properties of doped manganites suggests that the electron-phonon interactions are so strong that electronic and lattice subsystems are no longer decoupled.

The physics of manganites has primarily been described by the double-exchange (DE) model.[12] However, Millis, Littlewood, and Shraiman[2] (MLS) pointed out that the carrier-spin interaction in the DE model is too weak to lead to the carrier localization in the paramagnetic state and, thus, a second mechanism such as a small polaronic effect is needed to explain the observed resistivity data in doped manganites. The central point of the model is that in the paramagnetic state, the electron-phonon coupling constant λ is large enough to form small polarons, while the growing ferromagnetic order increases the bandwidth and, thus, decreases λ sufficiently to form a large polaron metallic state. Many experiments[6,8,9,13–16] have provided a strong evidence for the existence of small polarons in the paramagnetic state and qualitatively support the MLS and related models.[2–4] On the other hand, Alexandrov and Bratkovsky[5] (AB) argued that the MLS model cannot quantitatively explain CMR and, thus, proposed an alternative CMR theory. The basic idea of their model is that the small polarons form localized bound pairs (bipolarons) in the paramagnetic state, while the competing exchange interaction of polaronic carriers with localized spins drives the ferromagnetic transition. The transition is accompanied by a giant increase in the number of small polarons, which are mobile carriers and move coherently at low temperatures. The AB model is consistent with the observed oxygen-isotope effect on the intrinsic resistivity in the ferromagnetic state[17] and the temperature dependence of the resistivity at low temperatures.[18] Moreover, the observed oxygen-isotope effects on the intrinsic resistivity and thermoelectric power in the paramagnetic state[19] appear to be well explained by the existence of localized bipolaronic charge carriers, which also supports the AB model.

Here, we report magnetic susceptibility measurements on oxygen-isotope exchanged $La_{1-x}Ca_xMnO_{3+y}$ ($x=0.25$ and 0.33) up to 700 K. The data of the inverse paramagnetic susceptibility $1/\chi(T)$ show that the ferromagnetic exchange energy J strongly depends on the oxygen-isotope mass. The isotope effect on J decreases with temperature up to about 400 K, and then increases again with temperature above 400 K. This unusual temperature dependence of the isotope effect cannot be explained by both AB and MLS models.

Samples of $La_{1-x}Ca_xMnO_3$ were prepared by a conventional solid state reaction using dried La_2O_3, MnO_2, and $CaCO_3$. The well-ground mixture was calcined in air at 1000 °C for 20 h, and at 1100 °C for 20 h with one intermediate grinding. The powder samples were then pressed into pellets and sintered at 1260 °C for 72 h, and at 1160 °C for 72 h with one intermediate grinding. Two pieces were cut from the same pellet for oxygen-isotope diffusion. The diffusion was carried out for 50 h at 1000 °C and in an oxygen partial pressure of about 1 bar. The cooling rate was 300 °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 ~90% ^{18}O and ~10% ^{16}O.

Field-cooled magnetization below 300 K was measured with a Quantum Design superconducting quantum interference device magnetometer in a field of 50 Oe. The samples were cooled directly to 5 K, then warmed up to a temperature well below T_C. After waiting for 5 min at that temperature, data were collected upon warming to a temperature well above T_C. Magnetization between 300 and 700 K was measured with a Quantum Design vibrating sample magnetometer in a field of 10 kOe. The data were taken upon cooling from 700 K, at which the samples were kept for about 5 min.

In Fig. 1, we show temperature dependencies of the nor-

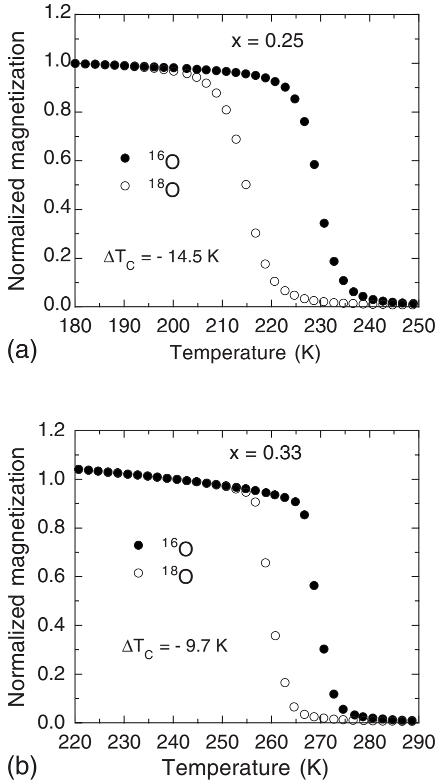

FIG. 1. Temperature dependencies of the normalized magnetizations (normalized to the magnetization well below T_C) for the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with (a) x=0.25 and (b) x=0.33.

malized magnetizations (normalized to the magnetization well below T_C) for the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with x=0.25 and 0.33. The oxygen-isotope shift of T_C was determined from the differences between the midpoint temperatures on the transition curves of the ^{16}O and ^{18}O samples. There are substantial oxygen-isotope shifts of T_C for both compositions, as indicated in the figures.

Figure 2 shows temperature dependencies of the inverse susceptibilities of the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with (a) x=0.25 and (b) x=0.33 in the high-temperature region (320–700 K). It is apparent that the inverse susceptibility depends on the oxygen-isotope mass in the whole temperature range studied. At higher temperatures, the oxygen-isotope effect even becomes larger. In the paramagnetic state of the ferromagnetic manganites, the susceptibility $\chi(T)$ should follow the Curie–Weiss law: $\chi(T)=C/(T-\theta)$, where θ is proportional to the ferromagnetic exchange energy J within the mean-field theory. Plotting the inverse susceptibility $1/\chi(T)$ against T will show a straight line if θ is independent of temperature.

In Fig. 3, we show the inverse susceptibilities of the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with x=0.25 in the temperature regions of (a) 320–400 K and (b) 550–670 K. The intercept of the linear line to the temperature axis determines the θ value. In the temperature region of 320–360 K, the θ value is lowered from 247.4 to 235.7 K upon replacing ^{16}O with ^{18}O. The oxygen-isotope shift in the θ value is 11.7 K, which is slightly smaller than the oxygen-isotope shift of the

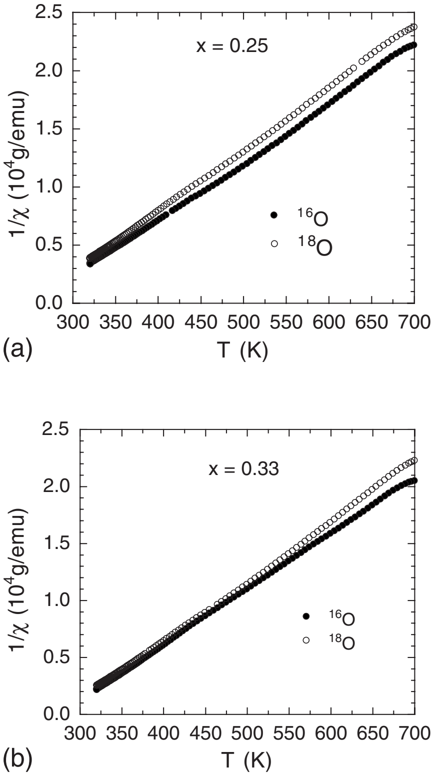

FIG. 2. Temperature dependencies of the inverse susceptibilities of the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with (a) x=0.25 and (b) x=0.33 in the high-temperature region (320–700 K).

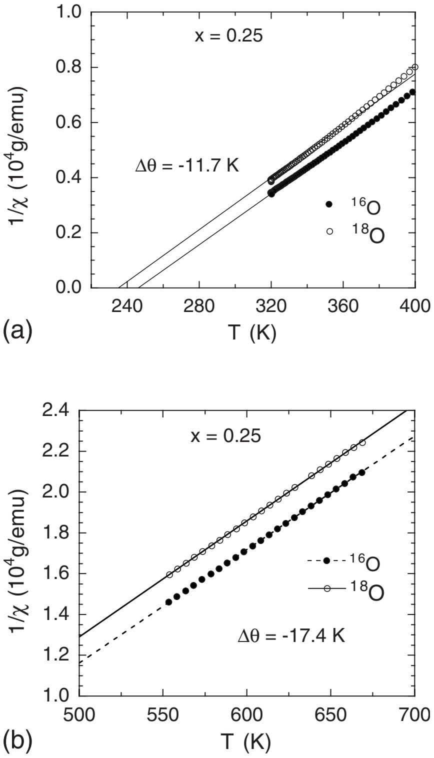

FIG. 3. Temperature dependencies of the inverse susceptibilities of the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with x=0.25 in the temperature regions of (a) 320–400 K and (b) 550–670 K.

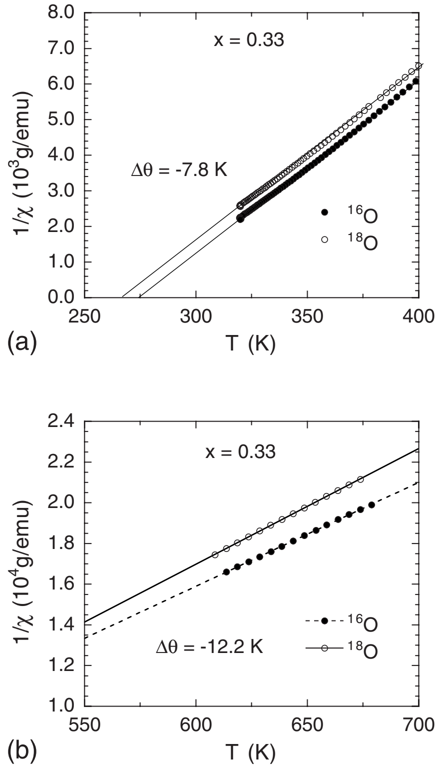

FIG. 4. Temperature dependencies of the inverse susceptibilities of the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with $x=0.33$ in the temperature regions of (a) 320–400 K and (b) 600–680 K.

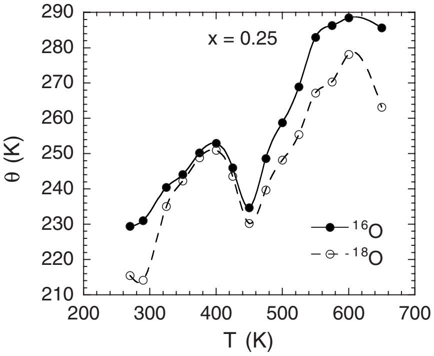

FIG. 5. Temperature dependencies of the θ values for the ^{16}O and ^{18}O samples of $La_{0.75}Ca_{0.25}MnO_3$. The θ value at each temperature is obtained from fitting the inverse susceptibility data within an ~30 K temperature interval by the Curie–Weiss law.

Curie temperature (14.5 K). On the other hand, in the temperature region of 550–670 K, the θ value is lowered from 290.8 to 273 K upon replacing ^{16}O with ^{18}O. The oxygen-isotope shift in the θ value is 17.4 K, which is slightly larger than the oxygen-isotope shift of the Curie temperature.

Figure 4 shows the inverse susceptibilities of the ^{16}O and ^{18}O samples of $La_{1-x}Ca_xMnO_3$ with $x=0.33$ in the temperature regions of (a) 320–400 K and (b) 600–680 K. In the temperature region of 320–360 K, the θ value is lowered from 274.8 to 267.0 K upon replacing ^{16}O with ^{18}O. The oxygen-isotope shift in the θ value is 7.8 K, which is slightly smaller than the oxygen-isotope shift of the Curie temperature (9.7 K). In the temperature region of 600–680 K, the θ value is lowered from 301.4 to 289.2 K upon replacing ^{16}O with ^{18}O. The oxygen-isotope shift in the θ value is 12.2 K, which is slightly larger than the oxygen-isotope shift of the Curie temperature.

In Fig. 5, we plot the θ value as a function of temperature for the ^{16}O and ^{18}O samples of $La_{0.75}Ca_{0.25}MnO_3$. The θ values are obtained from fitting the inverse susceptibility data within the 25–30 K temperature interval by the Curie–Weiss law. It is apparent that the temperature dependence of the θ value is not monotonic; there is a local minimum at about 450 K, which may be related to the formation of ferromagnetic clusters.[6] Moreover, the oxygen-isotope shift of the θ value decreases with temperature up to about 400 K and then increases again with temperature above about 400 K. The much smaller isotope effect on J at around 400 K appears to be related to the much smaller isotope efect on the thermoelectric power around 400 K.[19] The temperature dependencies of these isotope effects below 400 K are consistent with the AB model. However, the increase in the isotope effect above 400 K is not expected from the AB model, which predicts a negligible isotope effect on J at high temperatures when bipolaronic carriers are diminishing. Therefore, the original AB model, which is based on the pure *p-d* exchange and the formation of oxygen-hole bipolarons, is inconsistent with the high-temperature isotope effect.

Since the observed oxygen-isotope effects on the intrinsic electrical transport properties are consistent with the formation of bipolarons,[19] we should not discard the AB model based on the formation of localized bipolarons in the paramagnetic state. Photoemission spectroscopy[20] indicates that about 23% of doped holes reside on Mn 3*d* orbitals, while 77% of doped holes sit on oxygen orbitals in the low doping range. In the heavily doped range, doped holes should have more 3*d* character so that neither the pure *p-d* exchange nor the pure double exchange is responsible for the ferromagnetism. In order to agree with the present isotope-effect results, one should assume that the ferromagnetic exchange energy in these samples also significantly depends on the effective mass of the polarons. This is possible when the ferromagnetism is also caused by the double exchange of doped holes in the Mn 3*d* orbitals (about 30%) although the pure double exchange cannot explain the ferromagnetism.[21]

In summary, we have measured high-temperature magnetic susceptibilities of the oxygen-isotope exchanged $La_{1-x}Ca_xMnO_{3+y}$. The data show that the ferromagnetic exchange energy J strongly depends on the oxygen-isotope mass. The temperature dependence of the isotope effect is very unusual, which cannot be explained by existing theories of the colossal magnetoresistance effect for doped manganites. The present results thus provide essential constraints on the physics of manganites.

This research is supported by a Cottrell Science Grant from Research Corporation. We thank the Palmdale Institute of Technology for the use of the VSM, and Lockheed Martin Aeronautics for the cryogens.

*gzhao2@calstatela.edu

[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).

[2] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); A. J. Millis, B. I. Shraiman, and R. Mueller, *ibid.* **77**, 175 (1996).

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

[4] A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1994).

[5] A. S. Alexandrov and A. M. Bratkovsky, Phys. Rev. Lett. **82**, 141 (1999).

[6] J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).

[7] M. Uehara, S. Mori, C. H. Chen, and S.-W. Cheong, Nature (London) **399**, 560 (1999).

[8] G. M. Zhao, K. Conder, H. Keller, and K. A. Müller, Nature (London) **381**, 676 (1996).

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

[10] G. M. Zhao, H. Keller, J. Hofer, A. Shengelaya, and K. A. Müller, Solid State Commun. **104**, 57 (1997).

[11] M. R. Ibarra, G. M. Zhao, J. M. De Teresa, B. Garcia-Landa, Z. Arnold, C. Marquina, P. A. Algarabel, H. Keller, and C. Ritter, Phys. Rev. B **57**, 7446 (1998).

[12] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[13] M. Jaime, M. B. Salamon, M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, Phys. Rev. B **54**, 11914 (1996).

[14] S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier, and J. D. Thompson, Phys. Rev. Lett. **77**, 715 (1996).

[15] C. H. Booth, F. Bridges, G. H. Kwei, J. M. Lawrence, A. L. Cornelius, and J. J. Neumeier, Phys. Rev. Lett. **80**, 853 (1998).

[16] D. Louca, T. Egami, E. L. Brosha, H. Röder, and A. R. Bishop, Phys. Rev. B **56**, R8475 (1997).

[17] G. M. Zhao, D. J. Kang, W. Prellier, M. Rajeswari, H. Keller, T. Venkatesan, and R. L. Greene, Phys. Rev. B **63**, 060402(R) (2000).

[18] G. M. Zhao, V. Smolyaninova, W. Prellier, and H. Keller, Phys. Rev. Lett. **84**, 6086 (2000).

[19] G. M. Zhao, Y. S. Wang, D. J. Kang, W. Prellier, M. Rajeswari, H. Keller, T. Venkatesan, C. W. Chu, and R. L. Greene, Phys. Rev. B **62**, R11949 (2000).

[20] T. Saitoh, A. E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **51**, 13942 (1995).

[21] G. M. Zhao, Phys. Rev. B **62**, 11639 (2000).