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Origin of the giant oxygen-isotope effect in the manganite $La_{0.8}Ca_{0.2}MnO_3$

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Emission Mössbauer effect measurements for the internal hyperfine magnetic field(s), superparamagnetic behavior, and Debye-Waller factors at the Mn site for the ^{16}O- and ^{18}O-substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ compounds are reported. Surprisingly, the exchange interactions between Mn^{3+}/Mn^{4+} were observed to be about the same for both compounds at 78 K even though the Curie temperatures differ by about 25 K. Also, very significantly, the population of the softer phonons in the ^{18}O compound was found to be about 12%–15% larger than that for the ^{16}O compound. The high degree of anharmonicity in Mn-^{18}O-Mn vibrations at higher temperatures further enhances the population of soft phonons, which results in a breakdown of ferromagnetic order at a lower temperature. [S0163-1829(99)14119-5]

I. INTRODUCTION

The parent compound $LaMnO_3$ is an insulating antiferromagnet. When Ca^{2+} is substituted for La^{3+}, the compound $La_{1-x}Ca_xMnO_3$ becomes a ferromagnetic metal for $0.18 \leqslant x < 0.5$. The electron hopping between the ferromagnetically ordered core spins of Mn^{3+} and Mn^{4+} is facilitated by double exchange (DE) via bridging $O^{=}$.[1] These materials exhibit a transition at T_c from a ferromagnetic metal to a ''paramagnetic'' insulator as the temperature is increased. Application of a magnetic field gives a large decrease in resistivity near T_c, an effect known as the colossal magnetoresistance (CMR).[2] The physics underlying the transition and associated CMR is currently attracting lot of attention.[3,4]

Electron-phonon coupling has been proposed to explain the large magnitude of resistivity near T_c.[5,6] There is a growing realization that a strong electron-lattice coupling is responsible for a wide variety of other interesting observations. For instance, all Mn-O bond lengths were observed to be equal below T_c while a distribution was seen above T_c,[7–11] there is an anomalous volume change near T_c,[10,12,13] the full width at half maximum of the ion-channeling angular scan exhibits a dramatic decrease near T_c,[14] there is an anomalously large increase in amplitude of vibration of Mn atoms near T_c,[10,11,15] local distortions were observed below T_c,[16] phase transitions on application of a magnetic or electric field,[17–19] growth of small spin clusters to larger clusters with better ordering of spins,[20] and the strong pressure dependence of physical properties.[21–24] Recently, Zhao *et al.*[25] reported a giant oxygen-isotope shift of the transition temperature of $La_{0.80}Ca_{0.20}MnO_3$. By replacing ^{16}O with ^{18}O, a decrease in T_c of >20 K was observed, dramatic evidence of strong electron-lattice coupling. Franck *et al.*[26] report that the magnitude of the decrease in T_c may depend on the oxygen content of the manganite. Babushkina *et al.*[27] observed that substitution of ^{18}O for ^{16}O induces a metal-to-insulator transition in $La_{0.175}Pr_{0.525}Ca_{0.30}MnO_3$; ^{18}O favors the insulating charge-ordered state. Similar transitions were observed by Zhao *et al.*[28] and Isaac and Franck[29] in $(La_{0.5}Nd_{0.5})_{0.67}Ca_{0.33}MnO_3$ and $La_{0.57}Ca_{0.43}MnO_3$ compounds, respectively.

Here we report emission Mössbauer studies and observe that the exchange interactions between Mn^{3+}/Mn^{4+} are about the same for the ^{18}O and ^{16}O compounds at 78 K. On the other hand, at the same temperature, the mean-square amplitudes at the Mn sites in the ^{18}O compound are about 6% larger than that in the ^{16}O compound. The greater population of softer phonons in the ^{18}O compound at higher temperatures is responsible for the lower T_c.

II. EXPERIMENT

$La_{0.80}Ca_{0.20}MnO_3$ was prepared by the following procedure. La_2O_3 was predried in air at 1000 °C for 12 h, and MnO_2 was pretreated at 1000 °C for 20 h to give Mn_3O_4. Stoichiometric amounts of La_2O_3, Mn_3O_4, and $CaCO_3$ were mixed, ground, and heated at 900 °C for 12 h, following by a grinding and thermal treatment at 1100 °C for 12 h. The same sequence was repeated at 1100 °C when x-ray diffraction showed a single phase.[20] The material was heated further at 1250 °C for 10 h and then compacted into a pellet. The pellet was sintered at 1350 °C for 12 h. A few parts per 10^6 of ^{57}Co were substituted for Mn by a procedure discussed elsewhere[11,20] in the two similar samples cut from the pellet. These two samples were treated with O_2, one in $^{16}O_2$ and the other in $^{18}O_2$ (1 atm) under similar conditions in a parallel-processing system described elsewhere.[26] The samples were gas exchanged at 950 °C for 10 h. This resulted in a $^{18}O_2$ bulk concentration of about 80% by weight and almost complete substitution within about 50–100 μm from the sample surface where ^{57}Co resides. Magnetization and resistivity measurements were carried out on this pair along with Mössbauer studies. To perform precise comparative Mössbauer effect study of ^{16}O- and ^{18}O-containing samples over a range of temperatures and magnetic fields, a special experimental setup was designed to permit simultaneous measurement for both samples.

The observed Mössbauer spectra at 10 K and in the temperature range of 78–300 K are complex, and their computer analyses were accomplished in several stages depending on the nature of desired information, including fitting of additional runs in expanded scales and different external magnetic fields. The shape of the magnetically split component and its evolution with temperature have been discussed earlier.[20] The distribution in hyperfine internal fields is quite symmetrical, which allows us to approximate the magnetic component by individual sextet(s) with broadened lines and obtain meaningful information.[20]

In a preliminary fit, the intensities of the different lines of the magnetically split spectra as well as their linewidths were estimated with good accuracy by an approximation of the experimental spectra as a superposition of three doublets instead of a sextet and a singlet (or doublet with small quadrupole splitting ΔQ) representing the ''paramagnetic component.'' This helps in feeding information to the final fitting program which yields the hyperfine parameters, i.e., internal magnetic field H_{int}, ΔQ (if any), the associated angle Θ between the major axis of the electric field gradient (EFG), and the direction of the magnetization and center (isomer) shift, at different temperatures.[20]

III. OBSERVATIONS AND DISCUSSIONS

Since ^{57}Co(^{57}Fe) prefers an octahedral configuration in oxides, the Mn-O skeleton is preserved and the minuscule amount of the substituent faithfully probes the subtle changes in electron density, local dynamics, and magnetic behavior of the dominant host material in a system with delocalized electrons.[30,31]

In Fig. 1, we depict the Mössbauer spectra of the ^{18}O compound $La_{0.8}Ca_{0.2}Mn(^{57}Co)^{18}O_3$ at various temperatures. One can see that a central peak grows at the expense of the magnetically split sextet(s) with increasing temperature; the bulk ferromagnetic order beaks down, and small spin clusters are formed even below T_c. The spin clusters interact with each other rather strongly. This behavior is not related to particle size as the grain size is larger than a micron. If at any specific temperature the available thermal energy kT is sufficient to overcome the anisotropic barrier, then the magnetic vector of the cluster can oscillate between the two easy directions at a frequency higher than the Larmor frequency of the excited ^{57}Fe($\sim 10^8$ sec^{-1}) and the net magnetic field experienced by the nucleus could be zero. If there is some distribution in cluster size and/or the bulk ferromagnet continues to form fresh clusters as temperature increases, the central peak representing the superparamagnetically relaxed component will grow at the expense of the bulk. This behavior is similar to one observed for the regular ^{16}O compound.[20] T_c was determined by observing the temperature at which the sextet vanishes completely; T_c for ^{16}O and ^{18}O compounds is 195 and 170 K, respectively.

On application of an external magnetic field $H_{\mathrm{ext}} = 1.8$ T, the central peak arising from superparamagnetic relaxation of the small spin clusters vanishes completely for both ^{16}O and ^{18}O compounds (Fig. 2). The spin clusters coalesce to give regular bulk ferromagnetism (component $M1$) and intermediate size clusters with somewhat poorer ordering of spins (component $M2$) and thereby exhibiting a smaller H_{int}. The abundance of the collapsed component (SR) is about 55% for the ^{18}O compound at 150 K. On application of $H_{\mathrm{ext}} = 1.8$ T, about 37% units convert into the bulk ferromagnetic component ($M1$) and the remaining 18% units convert into the intermediate-size cluster component ($M2$).

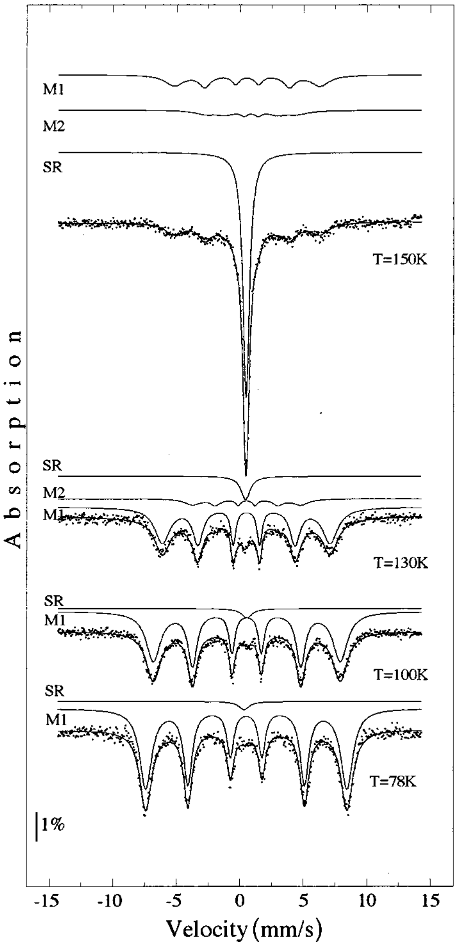

FIG. 1. Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)^{18}O_3$ at different temperatures. $M1=$ bulk ferromagnetic component, $M2=$intermediate size clusters component, and SR $=$superparamagnetically relaxed component.

The Mössbauer spectra at 78 K for ^{16}O- and ^{18}O-substituted samples of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ are shown in Fig. 3. From the computer fit of these spectra, the observed hyperfine internal magnetic field H_{int} for ^{18}O and ^{16}O compounds is 49.2 ± 0.6 T and 50.5 ± 0.6 T, respectively. The H_{int} for both compounds is also about the same at 10 K. This shows clearly that the exchange interactions between Mn^{3+}/Mn^{4+} for the ^{16}O and ^{18}O compounds are about the same at 78 K. This is surprising in view of the fact that their T_c's differ by about 25 K. Another significant observation regards the total normalized area under the Mössbauer spectra which is proportional to the recoil-free fraction. In emission Mössbauer experiments using a ''thin'' standard absorber, the spectral area can be directly associated to the

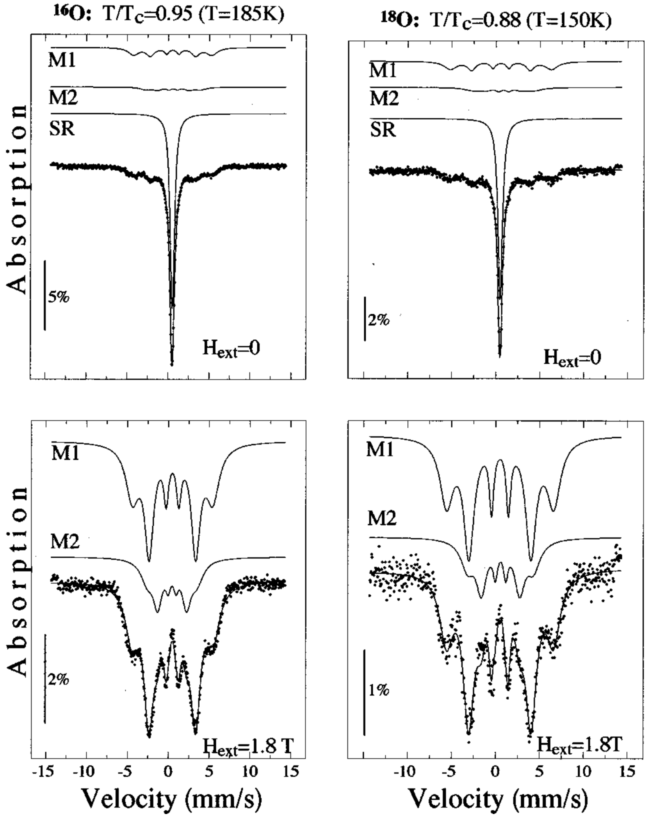

FIG. 2. Computer analyzed Mössbauer spectra of ^{16}O- and ^{18}O-subsittuted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ with and without $H_{\rm ext}=1.8$ T close to T_c. $M1=$bulk ferromagnetic component, $M2=$intermediate size clusters component, and SR $=$superparamagnetically relaxed component.

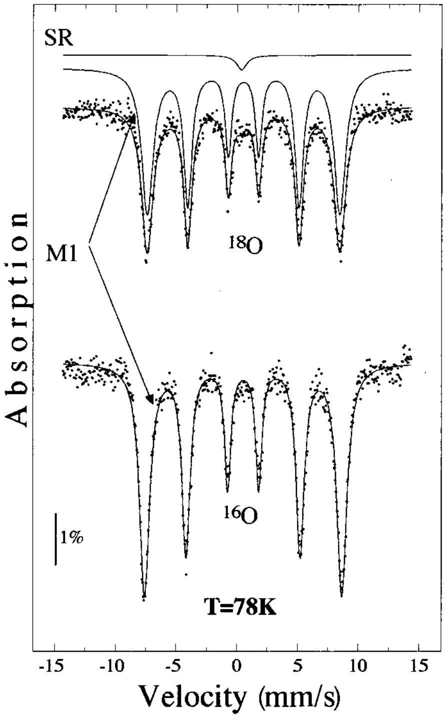

FIG. 3. Mössbauer spectra of ^{16}O- and ^{18}O-substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at 78 K. M1=bulk ferromagentic component, and SR=superparamagnetically relaxed component.

probability of recoil-free events, *f*, unlike the absorption mode where approximate corrections for ^{57}Fe content are required. The recoil-free fraction *f* is given by $f=\exp[(-4\pi^2\langle x^2\rangle)/\lambda^2]$, where λ is the wavelength of the 14.4 keV Mössbauer photon and $\langle x^2\rangle$ is the mean-square displacement of the Mössbauer site. The observed area of the Mössbauer spectra for the ^{18}O compound in the temperature range of 78–110 K is uniformly 12–15% lower than that for the ^{16}O compound under identical conditions (Fig. 4), which translates into a 6%-7% larger mean-square amplitude of vibration for the Mn site in the ^{18}O compound. This represents a weighted average over the density of states. The density of states is proportional to $(m/\kappa)^{1/2}$ where m is an effective mass at the Mn site and κ is the force constants for Mn-O bonds. The appreciable softening of phonons observed (Fig. 4) is very significant. The soft phonon density increases further, in the ^{18}O compound relative to ^{16}O one, at higher temperatures due to the high degree of anharmonicity associated with vibrations of the Mn-O-Mn moiety. The anharmonicity in conjunction with the mass effect would lead to closer spacings of vibrational levels. The anharmonicity is evidenced by the abnormal thermal expansion of maganites,[10,12,13] the presence of nonlinear temperature dependence in the oxygen root-mean-square displacements, and the anomalous increase in the Mn-O-Mn bond lengths and angles with temperature.[10,32,33] Therefore, at higher temperatures, one can expect a larger population of the more anharmonic oscillations in the Mn-^{18}O-Mn moiety. An inordinate stretching of Mn-O bond lengths would lead to decrease in hybridization and exchange interactions, which in turn would affect the degree of spin ordering and the rate of DE hopping. An increase in the amplitude of torsional oscillations between Mn-O octahedra would also tend to slow down the rate of electron hopping in the ^{18}O compound as the neighboring spins will have to wait until thermal fluctuations permit an appropriate configuration for a DE hop.[34,35] This leads to the breakup of the bulk ferromagnetism in the ^{18}O compound at a lower temperature than that for the ^{16}O compound. It seems that all the above-discussed features can also serve as rationale for the strong dependence of ''polaron'' mobility on oxygen mass.[25,36]

In summary, we compare directly with the help of the

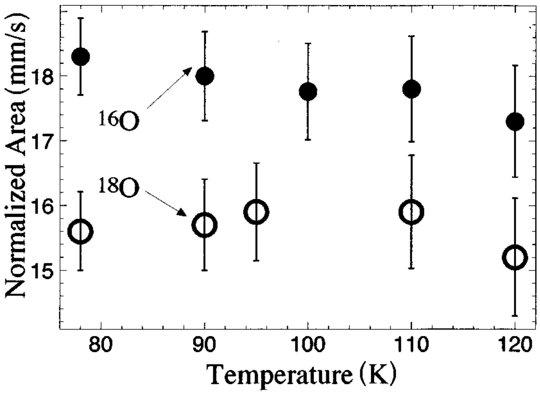

FIG. 4. Normalized areas for ^{16}O- and ^{18}O-substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ as a function of temperature.

Mössbauer microprobe ^{57}Co(^{57}Fe) the magnitude of exchange interactions between Mn^{3+}/Mn^{4+} and the mean-square displacements at the Mn sites for the ^{16}O- and ^{18}O-substituted compounds. We infer that the larger population of softer phonons at higher temperatures is responsible for the marked decrease in T_c upon ^{18}O substitution.

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[1] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955); J. B. Goodenough, *ibid.* **100**, 564 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).

[2] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and J. H. Chen, Science **264**, 413 (1994).

[3] A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).

[4] A. J. Millis, Nature (London) **392**, 147 (1998).

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

[6] A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).

[7] V. Caignaert, E. Suard, A. Maignan, C. Simon, and B. Raveau, C. R. Acad. Sci., Ser. IIb: Mec., Phys., Chim., Astron. **321**, 515 (1995).

[8] T. A. Tyson, J. Mustre de Leon, S. D. Conradson, A. R. Bishop, J. J. Neumeier, H. Röder, and J. Zang, Phys. Rev. B **53**, 13 985 (1996).

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

[10] P. Dai, J. Zhang, H. A. Mook, S.-H. Liou, P. A. Dowben, and E. W. Plummer, Phys. Rev. B **54**, R3694 (1996).

[11] V. Chechersky, K. Nomura, A. Nath, H. Ju, and R. L. Greene, Fiz. Nizk. Temp. **23**, 732 (1997) [Low Temp. Phys. **23**, 549 (1997)].

[12] P.G. Radaelli D. E. Cox, M. Marezio, S.-W. Cheong, P. E. Schiffer, and A. P. Ramirez, Phys. Rev. Lett. **75**, 4488 (1995).

[13] M. R. Ibarra, P. A. Algarabel, C. Marquina, J. Blasco, and J. Garcia, Phys. Rev. Lett. **75**, 3541 (1995).

[14] R. P. Sharma, G. C. Xiong, C. Kwon, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. B **54**, 10 014 (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] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science **270**, 961 (1995).

[18] S. B. Ogale, V. Talyansky, C. H. Chen, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **77**, 1159 (1996).

[19] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature (London) **388**, 50 (1997).

[20] V. Chechersky, A. Nath, I. Isaak, J. P. Franck, K. Ghosh, H.-L. Ju, and R. L. Greene, Phys. Rev. B **59**, 497 (1999).

[21] H. Y. Hwang, T. T. M. Palstra, S.-W. Cheong, and B. Batlogg, Phys. Rev. B **52**, 15 046 (1995).

[22] J.-S. Zhou, W. Archibald, and J.B. Goodenough, Nature (London) **381**, 770 (1996).

[23] K. Khazeni, Y. X. Jia, L. Lu, V. H. Crespi M. L. Cohen, and A. Zettl, Phys. Rev. Lett. **76**, 295 (1996).

[24] K. Kamenev, G. Balakrishnan, M. R. Lees, D. McK. Paul, Z. Arnold, and O. Mikulina, Phys. Rev. B **56**, 2285 (1997).

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

[26] J. P. Franck, I. Isaac, W. Chen, J. Chrzanowski, and J. C. Irwin, Phys. Rev. B **58**, 5189 (1998).

[27] N. A. Babushkina, L. M. Belova, O. Yu. Gorbenko, A. R. Kaul, A. A. Bosak, V. I. Ozhogin, and K. I. Kugel, Nature (London) **391**, 159 (1998).

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

[29] I. Isaac and J. P. Franck, Phys. Rev. B **57**, R5602 (1998).

[30] M. B. Misrock, C. J. Schramm, and A. Nath, J. Chem. Phys. **65**, 1982 (1976).

[31] A. Nath, Ch. Sauer, and A. Halpern, J. Chem. Phys. **78**, 5125 (1983).

[32] P. G. Radaelli, G. Iannone, M. Marezio, H. Y. Hwang, S.-W. Cheong, J. D. Jorgensen, and D. N. Argyriou, Phys. Rev. B **56**, 8265 (1997).

[33] Q. Huang, A. Santoro, J. W. Lynn, R. W. Erwin, J. A. Borchers, J. L. Peng, K. Ghosh, and R. L. Greene, Phys. Rev. B **58**, 2684 (1998).

[34] K. V. Mikkelsen and M. A. Ratner, Chem. Rev. **87**, 113 (1987).

[35] V. Z. Kresin and S. A. Wolf, Philos. Mag. B **76**, 241 (1997).

[36] J.-S. Zhou and J. B. Goodenough, Phys. Rev. Lett. **80**, 2665 (1998).