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Emission Mössbauer study of CMR manganite $La_{0.8}Ca_{0.2}MnO_3$. I. Anomalous ferromagnetism

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Using ^{57}Co emission Mössbauer technique we present clear evidence that in Ca-doped manganite, the magnetic and paramagnetic phases coexist below T_C , with the abundance of the latter increasing with temperature. Unlike the regular ferromagnetics, the variation of the hyperfine internal magnetic field H_{int} with temperature deviates considerably from the Brillouin relation, and exhibits an abrupt drop at T_C . These features characterize magnetic transition as the first order one. Non-Brillouin behavior of $H_{\text{int}}(T)$ and the temperature dependence of the shape of the magnetically split sextet indicate the presence of spin fluctuations in this material well below T_C .

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Recent observations of colossal negative magnetoresistance (CMR) in thin films and bulk materials of doped manganites $Ln_{1-x}M_xMnO_3$ (Ln = La et al., M = Ca et al.) have generated renewed interest in this system [1–15]. The double exchange model accounts only qualitatively for ferromagnetic ordering and transport properties [9,16–19]. $Ln_{1-x}M_xMnO_3$ has a perovskite-type crystal structure, where Mn ions are surrounded by six oxygen anions which are shared by other Mn ions in a three-dimensional network, while the Ln/M ions occupy the spaces between these octahedra. The end members, $x = 0$ and $x = 1$, are antiferromagnetic insulators, but intermediate compositions ($0.2 < x < 0.5$) with mixed Mn^{3+}/Mn^{4+} are ferromagnetic metals. The electron hopping between Mn^{3+} and Mn^{4+} is believed to occur via O^{2-} by simultaneous electron jump from Mn^{3+} to O^{2-} and from the latter to Mn^{4+}. This «double exchange» event requires that both hopping electrons have the same spin polarization: a requirement which is met when both Mn ions are ferromagnetically ordered [16–19]. Among the four $3d$ electrons of the Mn, t_{2g}^3 electrons are localized, while the e_g^{1-x} state which is strongly hybridized with O_{2p} orbitals is itinerant below T_C in the ferromagnetic–metallic state and localized in the paramagnetic–insulating state above T_C . It is believed that the main effect of the applied magnetic field is to increase T_C which leads to a large decrease in resistivity giving rise to a CMR. The basic features of this transition can be understood on the basis of the double exchange picture, however, several aspects are elusive [9]. Here we report on the unusual behavior of ferromagnetism in $La_{0.80}Ca_{0.20}Mn(^{57}Co)O_3$ as sensed by the Mössbauer effect probe involving substitution of a minuscule amount of Mn by ^{57}Co with minimal perturbation of the system.

The compound was synthesized by conventional solid state reactions and characterized by x-ray diffraction and magnetization measurements as a function of temperature. To obtain Mössbauer data, we substituted about 20 ppm of ^{57}Co for Mn in a compacted pellet of $La_{0.80}Ca_{0.20}MnO_3$, by diffusion at 950 °C for 4–5 h under O_2 flow (sample 1, $T_C = 200$ K). A few representative Mössbauer spectra of $La_{0.80}Ca_{0.20}Mn(^{57}Co)O_3$ at different temperatures are shown in Fig. 1. The observation of a single symmetrical sextet with fairly narrow line widths at 80 K indicates that the sample is homogeneous, and that the microprobe ^{57}Co occupies the unique crystallographic site of Mn. Even at 80 K, which is well below $T_C = 200$ K ($T/T_C = 0.4$), the magnetically ordered (MO) sixline component con-

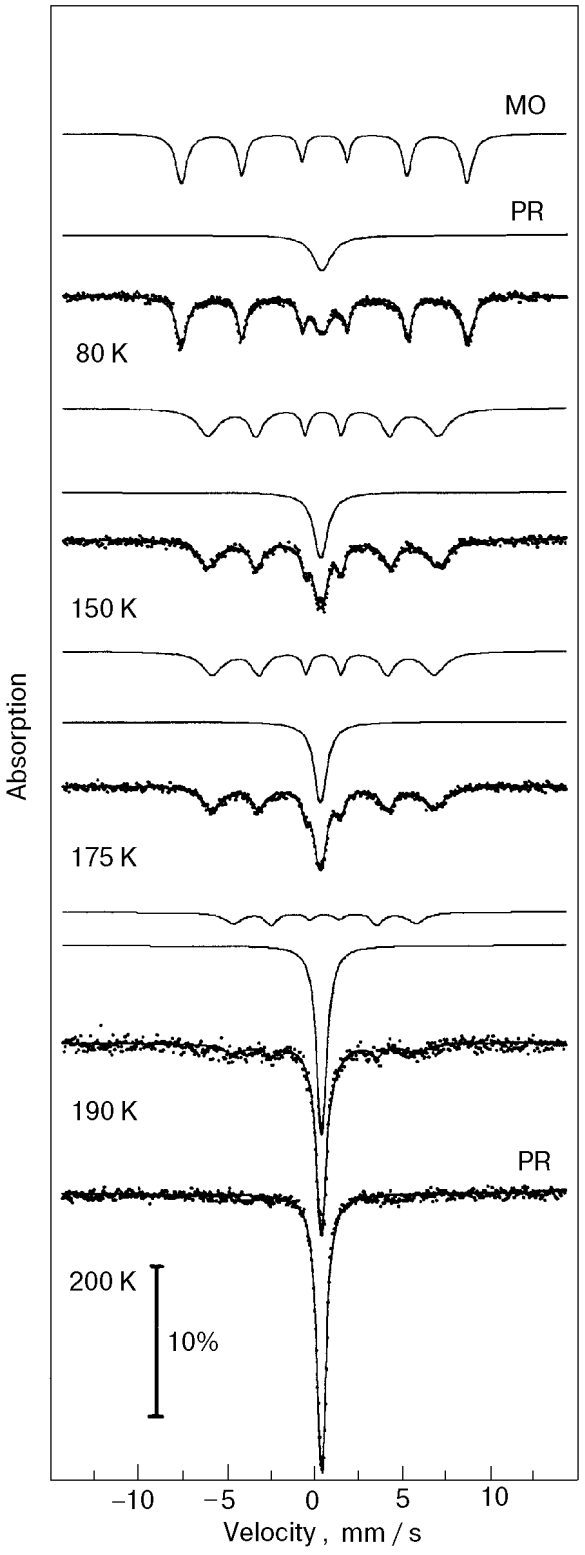

Fig. 1. Emission Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at different temperatures: magnetically ordered (MO); paramagnetically relaxed (PR).

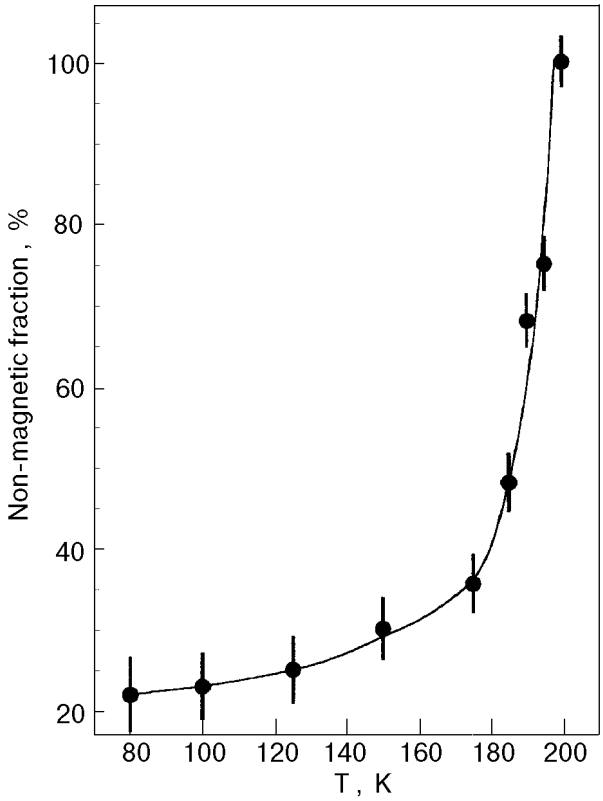

Fig. 2. The fraction of non-magnetic component versus temperature. Line connecting experimental points with error bars is a guide for the eye.

stitutes only 80%, the rest is paramagnetically relaxed (PR) species. The paramagnetic fraction grows at the expense of the magnetically ordered phase with increasing temperature till the MO component vanishes completely at T_C (Figs. 1 and 2). It is worthy of note that the temperature dependence of the amount of paramagnetic fraction in Fig. 2 perfectly mimics the resistivity behavior below T_C . These observations support the inferences drawn by Lynn et al. from their neutron scattering studies of $La_{0.67}Ca_{0.33}MnO_3$ [20]. They observe a quasielastic component which increases with temperature at the expense of the main spin-wave excitations. They conjecture that this component can be attributed to a paramagnetic phase where the electrons diffuse on a short length scale (~ 12 Å). However this component was not observed for manganites with lower concentrations of Ca, e.g. 0.175.

The magnetic transition, as evidenced by the temperature dependence of the hyperfine internal magnetic field on the daughter ^{57}Fe nuclei, is quite sharp: the hyperfine splitting drops abruptly from about 50% of the maximum expected saturation value ($\leq$ 550 kOe) to zero at T_C = 200 K (Fig. 3). This feature and the coexistence of the paramagnetic and ferromagnetic species near T_C characterize

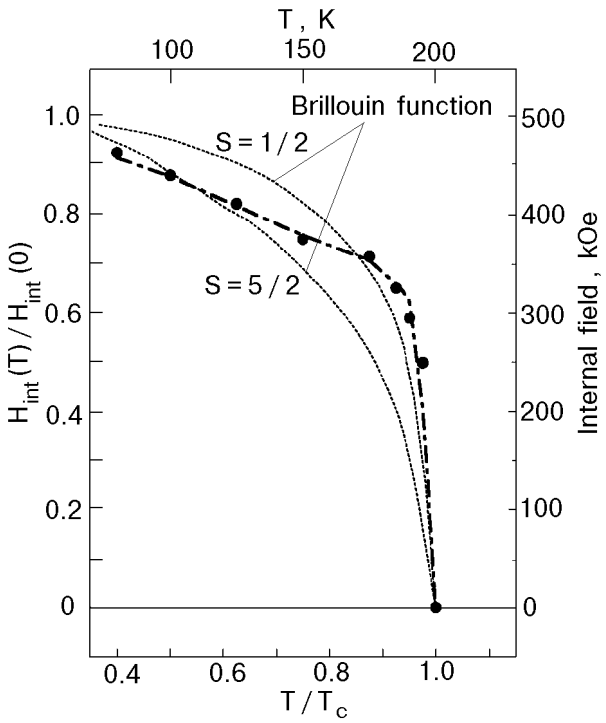

Fig. 3. The normalized internal magnetic field versus normalized temperature. Solid line connecting experimental points is a guide for the eye; dotted lines are the Brillouin functions for the spin 1/2 and 5/2. The error bars are smaller than the dimension of the circles.

this transition as the first order one [21]. The order of the transition is also supported by earlier reports of a significant change in volume at T_C [22–25]. It may be mentioned that a sharp transition is also expected in an ideal superparamagnetic material with no spread in the sizes of magnetic clusters when it approaches its blocking temperature. However, we did not find any reliable evidence for superparamagnetism from our observations. Moreover, the value of T_C obtained from the magnetization and Mössbauer effect measurements agrees well.

The temperature dependence of the H_{int} on ^{57}Fe nuclei shows no saturation well below T_C and differs considerably from the Brillouin function typical for magnetic materials (Fig. 3). In addition, the experimental spectra shown in Fig. 1 reveal a temperature-dependent broadening of the line widths of the magnetic component. These two different observations presumably have the same origin. In a regular magnetically ordered material, the shape of the sextet is temperature-independent because the frequency of collective excitations is much higher than the Larmor frequency of the daughter ^{57}Fe (~ 10^8 s^{-1}). Therefore the Zeeman splitting (H_{int}) of the sextet is proportional to the time averaged z-component of the magnetic moment of an ion, $\langle S_z \rangle$, and mimics the temperature dependence of the spontaneous magnetization, i.e., the Brillouin function. In contrast, in the Ca-doped manganites, the heterogeneous distribution and the ionic radius mismatch of the substituent unavoidably introduce some disorder in the spin system. At any temperature below T_C , a certain fraction of the spin system is weakly ordered (and predestined to convert to paramagnetic component at a slightly higher temperature) and is likely to be surrounded by some paramagnetic ions in the vicinity. In these regions, due to dipole-dipole interactions, the weakly ferromagnetic spins fluctuate about the average value. Consequently, z-component of the spins becomes time dependent, $S_z(t) = \langle S_z \rangle + \Delta S_z(t)$, where $\Delta S_z(t)$ is the instantaneous spin deviation from the mean value $\langle S_z \rangle$. This in turn induces a time-dependent hyperfine internal magnetic field $H_{\text{int}}(t) = \langle H_{\text{int}} \rangle (S_z(t)/S)$. The theory [26 and references therein] predicts two effects, inhomogeneous line broadening:

$$\Delta\gamma = (\nu_{eg} H_{\text{int}} / S)^2 \langle \Delta S_z \rangle^2 \tau \ ; \qquad (1)$$

and line shifts relative to their positions in the absence of electronic spin fluctuations:

$$\Delta\delta = (\nu_{eg} H_{\text{int}} / S)^3 \langle \Delta S_z \rangle^3 \tau^2 \ , \qquad (2)$$

where ν_{eg} is the magnetic hyperfine parameter; τ is the relaxation time, which is not exactly the same in (1) and (2), but assumed to be equal for the sake of simplicity. If the time of spin relaxation overlaps with the Mössbauer effect time scale (~ 10^{-7}–10^{-11} s), one will observe the temperature-dependent line shape. The temperature dependence of H_{int} does not reflect the true macroscopic magnetization as it arises mainly from the temperature-dependent value of $\langle \Delta S_z \rangle$.

Moreover, as the conversion of the ferromagnetic to paramagnetic species progresses with temperature, it is accompanied by a change in the Mn^{4+}/Mn^{3+} ratio (see discussion in Part II) and thereby the internal magnetic field.

In sharp contrast to the paramagnetic spectra consisting of two unresolved doublets (Fig. 4,*a*), the magnetically ordered component consists of only a single sextet (Figs. 1, 4,*b*) with an isomer shift (IS) intermediate between the values obtained for this temperature by extrapolating the IS vs. T plots for PR_1 and PR_2 species. It means that the transition into the magnetically ordered state is accompanied by a complete delocalization of holes in the band, which makes all the magnetically

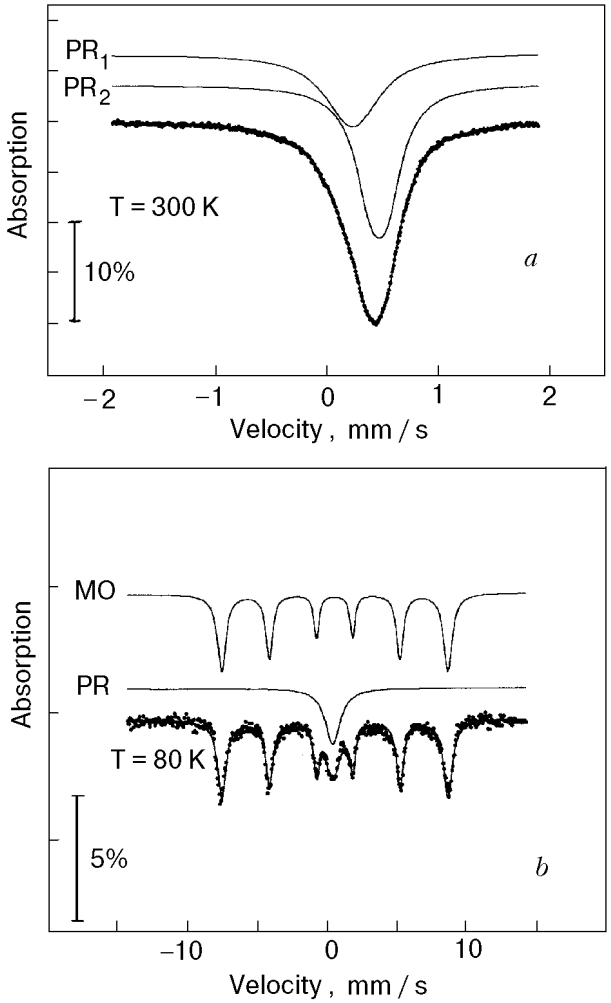

Fig. 4. Computer fit of the Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at $T = 300$ K (*a*); and 80 K (*b*). PR_1 and PR_2 are the two paramagnetic doublets; $PR = PR_1 + PR_2$ (paramagnetic fraction in all the spectra collected in the wide velocity range was approximated by a single line without loss of the accuracy); MO is magnetically ordered component.

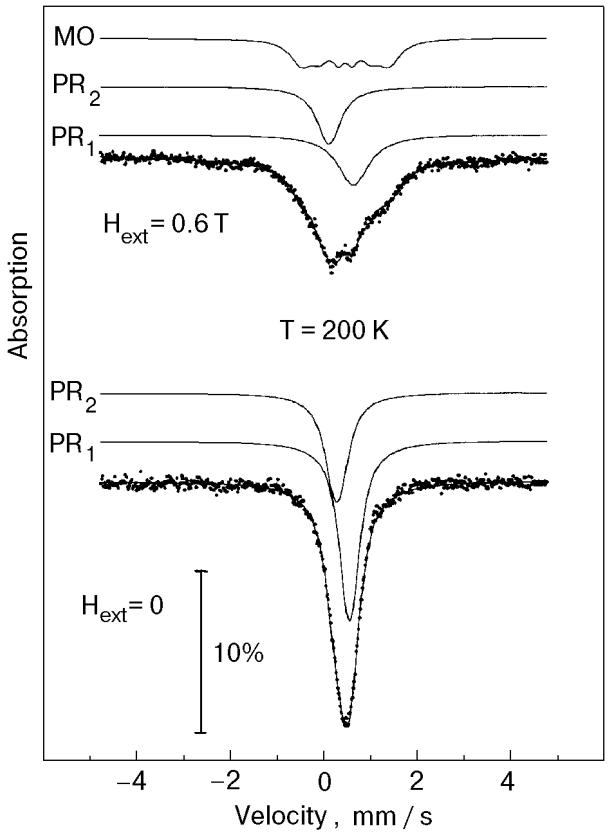

Fig. 5. Decomposition of Mössbauer spectrum of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at $T \approx T_C$ with and without external magnetic field. Abundance of magnetically ordered component (MO) is 40%. PR_1 and PR_2 are the two paramagnetic doublets.

ordered iron atoms indistinguishable in the Mössbauer spectrum regardless of their initial valence state in the lattice above T_C .

Preliminary results show that an external magnetic field of only 0.6 T applied at $T_C = 200$ K generates about 40% of magnetically ordered phase with an internal magnetic field of 64 kOe (Fig. 5). This ferromagnetic phase is metallic as indicated by the isomer shift as well as by a decrease of about 25% in resistivity of the sample.

The small magnitudes of quadrupole splittings even above T_C represent a relatively small degree of Jahn–Teller distortion of the oxygen octahedron in $La_{0.8}Ca_{0.2}MnO_3$. However, it is possible that we might be observing the mean value of the dynamic Jahn-Teller distortions.

In summary, we find that unlike normal ferromagnets, $La_{0.8}Ca_{0.2}MnO_3$ consists of a mixture of paramagnetic and ferromagnetic regions within the same matrix below T_C , and the fraction of paramagnetic component increases with temperature. Also, the temperature dependence of the internal hyperfine field does not follow the Brillouin function. This, together with temperature-dependent line widths of the magnetic component, is an evidence of the presence of spin relaxation processes well below T_C . These two aspects directly bear on the magnetic and transport behavior and the CMR of doped manganites, and should be taken into account in any theoretical model attempting to explain these effects. An abrupt fall of the hyperfine magnetic field at T_C and the coexistence of the paramagnetic and ferromagnetic regions characterize this transition as the first order one. We also present a microscopic evidence of the hole delocalization induced by ferromagnetic ordering.

Acknowledgments

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