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Emission Mössbauer study of the electronic phases in $La_{0.7}Ca_{0.3}MnO_3$

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A well characterized homogeneous ceramic sample of $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ shows two ferromagnetic phases below T_c in contrast to the 20% Ca compound where only one is observed. One of the phases exhibits stronger exchange interactions with more rapid electron transfer between Mn^{3+}/Mn^{4+}. At lower temperatures, there is a tendency for a single phase to exist, with well ordered spins. In both 20% and 30% Ca materials, the long-range ferromagnetic order breaks down above $T/T_c = 0.7$ and small spin clusters with superparamagneticlike behavior are formed. Above T_c, the spin clusters persist giving predominantly a single phase (as seen by the Mössbauer probe ^{57}Fe with a Larmor period of $\sim 10^{-8}$ sec). Under the influence of an external magnetic field, the small spin clusters coalesce to give larger clusters with better alignment of spins exhibiting negative magnetoresistivity by percolation. Our work raises the question whether superparamagnetic behavior is a prerequisite for observing negative magnetoresistivity.

The mixed-valence manganites, where there is direct correlation between ferromagnetic ordering and double exchange electron transfer, exhibit very interesting behavior.[1–4] We have used a very sensitive emission Mössbauer spectroscopy, where with minuscule amount of ^{57}Co substitution for Mn and minimal perturbation of the system, one can gain an insight into the microscopic behavior of the manganites. This local microprobe is particularly suited to give information about changes in electron density, local dynamics and magnetic phases. Our earlier work[5,6] showed that the ferromagnet $La_{0.8}Ca_{0.2}MnO_3$ behaves in an anomalous fashion above $T/T_c = 0.65$; the long-range ferromagnetic ordering breaks down and small magnetic clusters exhibiting superparamagnetic-like behavior start forming below T_c. When an external magnetic field is applied, the magnetic clusters grow to form larger clusters where the spins are more ordered and they contribute to the electrical conductivity via percolation.[5–7] A direct correlation between the growth of spin clusters to form ferromagnetic metallic regions and magnetoresistivity was observed. Zhang and Yang have given a theoretical treatment using similar features.[8] Recently, Fäth *et al.*[9] with the help of scanning tunneling spectroscopy have reported coexistence of clusters of metallic and insulating regions below the Curie temperature.

The question arises whether electronic phase mixtures exist below T_c in stronger ferromagnets like $La_{0.7}Ca_{0.3}MnO_3$. We find that the compound with 30% Ca is even more inhomogeneous on the microscopic scale than the compound with 20% Ca and exhibits three electronic phases with interesting interrelationships. The electronic inhomogeneity arises from aliovalent substitution.

The material was prepared by conventional solid state reaction as followed earlier for preparation of $La_{0.8}Ca_{0.2}MnO_3$.[6,10] In addition, the compacted pellets were annealed at 1500 °C in air for 16 h. The surface material was scraped off as a precautionary measure eliminating material which could have lost traces of Ca at the rather high annealing temperature. This treatment gives a more homogeneous material as indicated by ferromagnetic resonance measurements.[11] Our electron diffraction measurements and high resolution electron microscopy with point resolution of 1.8 Å attest to the good crystallinity and homogeneity of the sample. The reconstruction of the reciprocal space confirms the cell parameters and the *Pnma* space group of the orthorhombic cell. Magnetization investigations show that the material has a Curie temperature of about 245 K as reported in the literature.

^{57}Co activity was diffused into the compacted pellet by repeated thermal treatments at 1150–1200 °C under O_2 flow till a reproducible Mössbauer spectrum was obtained. A standard $K_4[Fe(CN)_6]$ pellet containing 0.20 mg/cm^2 of ^{57}Fe was used as an absorber. A constant acceleration spectrometer with triangular reference signal was used. Mössbauer effect measurements were performed in the temperature range 78–300 K. Temperature stability was about ±0.2 K and the accuracy of the temperature determination was ±1 K at all temperatures. A standard gas flow cryostat (from APD Cryogenics) was modified as described in Ref. 10 allowing application of relatively high magnetic field from the compact LakeShore EM4-CV electromagnet incorporated into the experimental setup. The procedures adopted for fitting the Mössbauer spectra have been discussed earlier.[10]

The computer analyzed Mössbauer spectra at 78 K for the $La_{0.7}Ca_{0.3}(^{57}Co)MnO_3$ is compared with that for $La_{0.8}Ca_{0.2}(^{57}Co)MnO_3$ in Fig. 1. In the former compound, we observe 6–7 % of superparamagnetically relaxed magnetic clusters. Their abundance does not change up to about $T/T_c = 0.75$ (Fig. 2). This component can perhaps be attrib-

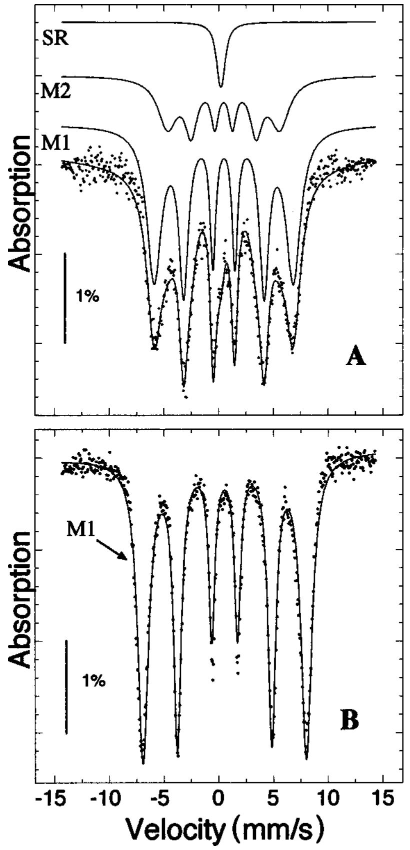

FIG. 1. Computer analyzed Mössbauer spectra of $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ with $T_c = 245$ K (A) and $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ with $T_c = 195$ K (B) at 78 K.

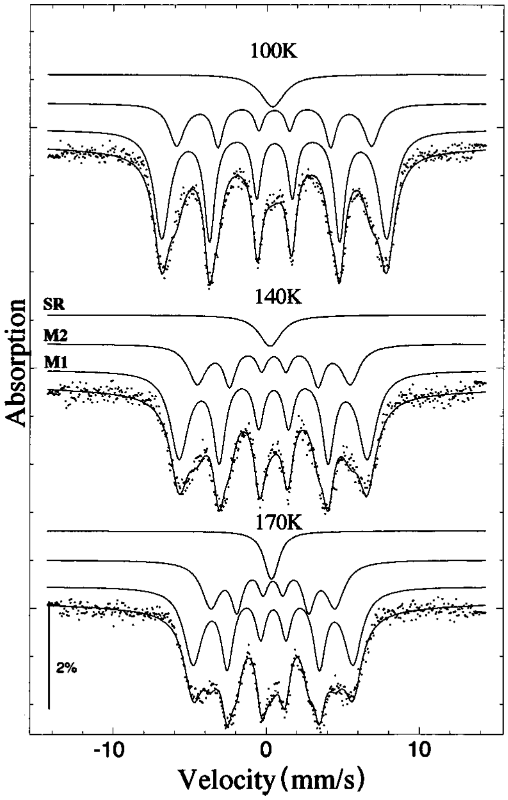

FIG. 2. Computer analyzed Mössbauer spectra of $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ at some intermediate temperatures showing two distinct electronic phases designated as $M1$ and $M2$.

uted to ^{57}Co resident at the surface of grains where exchange interactions are weaker. A similar observation has been reported for another batch of 20% Ca compound.[12] More importantly, the spectra for the 30% Ca compound can be fit consistently with two magnetically split sextets $M1$ and $M2$ (Figs. 1 and 2) in contrast to a single one for 20% Ca system.[6,12] Three species fit in Figs. 1(A) and 2 was adopted after analyzing these spectra without any fitting model, i.e., by a set of doublets. From the line intensities ratio which was around 1:(3.4–3.6):3 as well as from the distorted line shapes seen by the naked eye, it follows that we have to introduce a second sextet with much smaller splitting to correct the above problem (similar considerations led to two sextets fits in Ref. 6, Fig. 3). This information is fed to the final fitting program which yelds the hyperfine parameters.[10] The presence of two sextets indicates that for a certain fraction of Mn^{3+}/Mn^{4+} the rate of double exchange electron transfer is slower than for others, and therefore the exchange interactions are weaker. Interestingly, the relative abundances of $M1$ and $M2$ vary as a function of temperature [Fig. 3(A)]. $M2$ converts into $M1$ with well-aligned spins at lower temperatures and the manganite behaves like a regular ferromagnet at low temperatures. The electronic inhomogeneity presumably arises from the potentials created by aliovalent substitution, namely Ca^{2+} for La^{3+}.

The long-range ferromagnetic order in 30% Ca compound starts breaking down above $T/T_c = 0.8$ in contrast to $T/T_c = 0.7$ for 20% Ca compound [Figs. 3(A) and 3(B)]. The formation of magnetic clusters with superparamagneticlike behavior is indicative of short-range magnetic order. We attribute this break-down at higher temperatures to stretching of Mn-O bonds and large torsional oscillations of Mn-O octahedra with respect to each other. Both of them arise due to the considerable anharmonicity of Mn-O-Mn vibrations.[6,10] It may be underscored that the breakdown of the long-range ferromagnetic order is an intrinsic property of magnetoresistive manganites. This type of behavior has been observed using Mössbauer spectroscopy for some other compounds including $LiFeO_2$ (Ref. 13) and $YFeO_3$.[14] In the former compound, long range ferromagnetic order is observed on the time scale of neutron scattering, while Mössbauer effect measurements indicate superparamagneticlike behavior (10^{-8} sec time scale).

The internal magnetic fields as a function of temperature are plotted in Fig. 4. The behavior is similar to that observed for 20% Ca samples,[12] neither of them follow the Brillouin function. Above T_c, both compounds exhibit superparamagnetic behavior, and the small clusters coalesce to form larger ones with better aligned spins under the influence of an external magnetic field.

Above T_c, both materials exhibit a predominantly homogeneous single phase on the Mössbauer time scale represented by a slightly broadened singlet with an isomer shift value close to that of Fe^{3+}/Fe^{4+} in octahedral oxygen configuration and 2–3 % of segregated Fe^{4+} (attributable to the presence of a fraction of species where the electron transfer is slower than the Mössbauer time scale). Electrons are delocalized within each spin cluster. Under the influence of an external magnetic field, the spin clusters grow in size with simultaneous enhancement of the degree of spin order. The

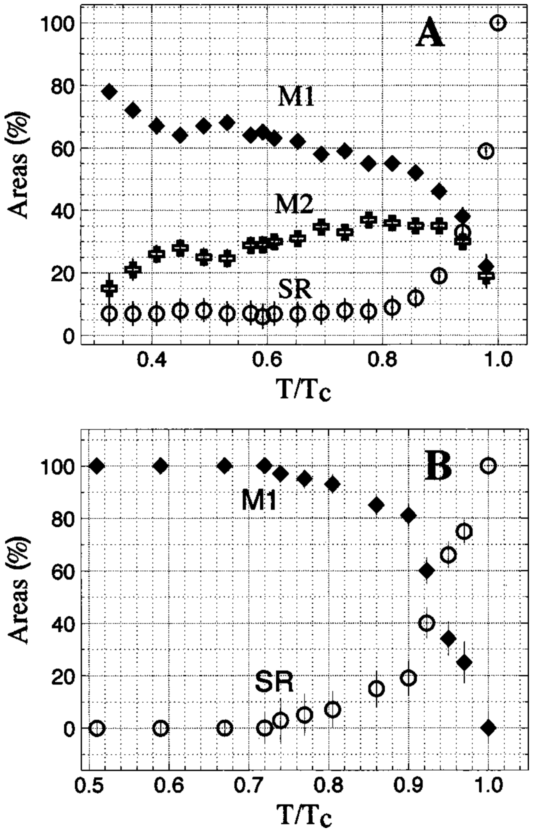

FIG. 3. The abundances (areas) of small spin clusters SR (with superparamagnetically relaxed peaks), and ferromagnetic phases ($M1$) and ($M2$) as a function of T/T_c for $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ (A) and $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ (B).

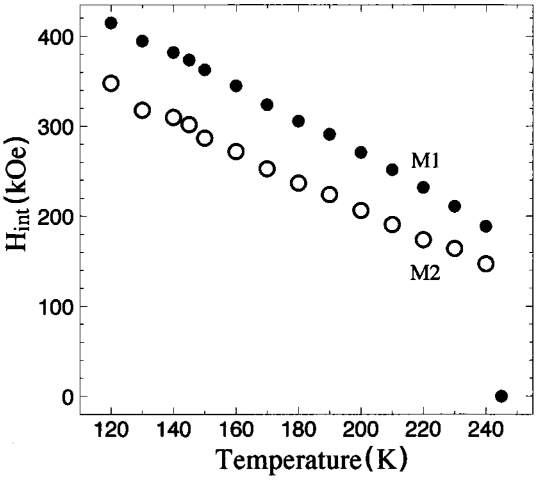

FIG. 4. The plot of internal hyperfine fields H_{int} at ^{57}Fe nuclei for the two ferromagnetic phases $M1$ and $M2$ in $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ as a function of temperature.

growth of the spin clusters is directly related to the decrease in resistivity by virtue of percolation.[5,6,15] Our observations do not support De Teresa *et al.*'s contention[16] that these magnetic clusters are present in a paramagnetic matrix. We observe a single superparamagnetic phase above T_c which converts in a very moderate external magnetic field into a magnetically ordered (at least within our time scale) phase(s) presented by one or two sextets (with some size distribution) depending on the temperature and the magnitude of the magnetic field.[6,10] Viret *et al.*[17] also show that their SANS measurements are not compatible with the presence of spin clusters in a paramagnetic matrix. In short, our observations indicate that the major difference between the ferromagnetic and superparamagnetic (above T_c) phases is that in the latter we have short range magnetic correlations. This is borne out by ESR studies by Lofland *et al.*[18] where they find that all Mn spins contribute collectively above T_c. Similarly, a single ^{55}Mn NMR peak was observed both below and above T_c by Kapusta *et al.*[19] providing evidence of magnetic correlations.

In summary, we find that a well characterized sample of $La_{0.7}Ca_{0.3}MnO_3$ exhibits two distinct electronic phases below T_c, one corresponding to weaker exchange interactions between Mn^{3+} and Mn^{4+} due to the slower rate of double exchange electron transfer. On the other hand, for $La_{0.8}Ca_{0.2}MnO_3$ only a single phase is observed in the absence of an external magnetic field. We also find that the breakdown of long-range order below T_c is an intrinsic property of magnetoresistive manganites.

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