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The Origin of Bulk Magnetoresistivity in Manganites

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On substitution of Ca^{2+} for La^{3+} in $LaMnO_3$, the compound $La_{1-x}Ca_xMnO_3$ becomes a ferromagnetic metal for $0.18 \leq x < 0.5$. The hopping of an electron from Mn^{3+} to O^{2-} is associated with simultaneous hop from the latter to Mn^{4+}. The probability of the hopping by this double exchange is highest when both hopping electrons have the same spin orientation, requiring Mn ions to be ordered ferromagnetically. The metallic behavior is synergistically associated with the ferromagnetic order through electron hopping. The resistivity increases considerably near the Curie temperature (T_C) and application of a magnetic field causes a dramatic decrease in resistivity due to regeneration of metallicity. The origin of this colossal magnetoresistivity is rather enigmatic and has attracted lot of attention from researchers. We have addressed this problem using emission Mössbauer spectroscopy where the local probe $^{57}Co/^{57}Fe$ substituting Mn atoms senses the microscopic behavior of the material. We find that the long-range ferromagnetic order breaks down anomalously below T_C and the material degenerates into small spin clusters which fluctuate rapidly and which exhibit superparamagnetic-like behavior. On a time scale of 10^{-8} s, the spin clusters exhibit minimal lattice distortions. These spin clusters survive well above T_C and would constitute very effective scattering centers for charge carriers due to their rapid fluctuations. On application of an external magnetic field, the small magnetic clusters coalesce to form larger ones with more ordered spins, and the material shows enhanced conductivity through percolation. We also observe superparamagnetic-like behavior below T_C in the pyrochlore, $Tl_2Mn_2(^{57}Co)O_7$, which does not exhibit double exchange electron hopping. It seems that the breakup into small rapidly fluctuating ferromagnetic spin clusters near T_C (exhibiting superparamagnetic-like behavior) is a prerequisite for observing bulk magnetoresistivity. © 2000 Academic Press

Key Words: **Magnetoresistive manganites; superparamagnetism; emission Mössbauer spectroscopy.**

INTRODUCTION

The perovskite manganite, $LaMnO_3$, is an insulating antiferromagnet. When La^{3+} is substituted by bivalent ion like Ca^{2+}, a proportionate amount of Mn^{3+} is converted to Mn^{4+}. With the introduction of holes, the compound $La_{1-x}Ca_xMnO_3$ becomes a ferromagnetic metal for $0.18 \leq x < 0.5$. The hopping of an electron from Mn^{3+} to O^{2-} is associated with a simultaneous hop from the latter to Mn^{4+}. The probability of this double exchange (DE) depends on the orientation of the neighboring intraatomic Hund's coupled t_{2g} spins. The hopping of an e_g electron is facilitated if the spins are aligned parallel to each other. Thus the ferromagnetic alignment and the rate of electron hopping which is responsible for its metallicity are synergistically tied together (1). The probability of the hopping also depends on the Mn^{3+}–O–Mn^{4+} bond angle. Among the four $3d$ electrons of the Mn^{3+}, t_{2g}^3 electrons are weakly hybridized and constitute the localized spin ($S = 3/2$). In contrast, e_g^{1-x} orbitals have lobes directed to neighboring oxygen atoms, hybridize strongly with O_{2p} orbitals and the electron is itinerant below T_C in the ferromagnetic–metallic state and is believed to be localized in the "paramagnetic"-insulating state above T_C. The resistivity increases considerably near T_C. On application of a magnetic field, there is a sharp decrease in resistivity due to regeneration of metallicity. This drop in resistivity is known as "colossal magnetoresistance (CMR)" (2). The physics underlying the metal to insulator transition and the associated CMR is attracting considerable attention. These materials exhibit very interesting behavior because of the strong coupling between spin, charge, and phonons (3–5).

It was realized that DE alone cannot account for the very large resistivity of the $T > T_C$ phase or for the sharp drop in resistivity just below T_C, and therefore strong

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electron–phonon coupling, associated with Jahn–Teller distortions was invoked (6–8). However, Varma (9) argued that electronic localization occurs due to magnetic disorder. Electron correlation effects and the breathing mode polaronic distortions which are different around Mn^{3+} and Mn^{4+} because of large difference in ionic size increase the effective disorder parameter. An external magnetic field alters this disorder. On the other hand, Kusters and coworkers (10, 11) have been leading advocates of formation of magnetic polarons. On the basis of their magnetization measurements, spin-polarized neutron scattering observations, and the resistivity measurements available in the literature, they proposed that around and above T_C the conductivity is dominated by hopping of localized magnetic polarons and that the presence of an external magnetic field increases the ferromagnetic order and magnetic polaron formation is inhibited.

To gain an insight into the mechanism of the ferromagnetic metal to "paramagnetic" insulator transition and the origin of the CMR, we use a local probe, viz. ^{57}Co. Emission Mössbauer spectroscopy constitutes a valuable tool for exploring the microscopic behavior of materials. It is a couple of orders of magnitude more sensitive than the regular absorption mode, requiring only a few tens of parts-per-million of Mn substitution by ^{57}Co with minimal perturbation of the system, whereas one has to use 1–2% ^{57}Fe substitution for the regular absorption mode. The ferromagnetic ordering in manganites can be affected by this substitution; however, some useful information can still be obtained. 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, distortions, and magnetic behavior of the dominant host material. Our earlier work shows that the Auger aftereffects following electron-capture decay of ^{57}Co are of no consequence in systems having delocalized electrons, as is the case for manganites. We had proposed that several tens of electron volts of excitation energy deposited on a molecule during charge neutralization goes for collective excitation of plasmons. The plasmons decay in less than 10^{-14} s with each one transferring practically all its energy to an outgoing electron (12, 13). The strong coupling between plasmons formed from delocalized electrons and single electron continuum states provides a neat mode of energy dispersal leaving the ^{57}Fe site virtually unperturbed. The 14.4-keV Mössbauer gamma radiation bringing with it information about the environment is emitted with $\sim 10^{-7}$ s delay after the electron-capture decay and therefore is oblivious of the Auger event. The formation of a plasmon by excitation of delocalized electrons and its decay by ejection of an electron has been recently verified by photoemission studies of C_{60} and C_{70} (14, 15).

It may be mentioned that the ^{57}Co(^{57}Fe) probe faithfully senses subtle changes in electron density, local dynamics, magnetic behavior, and electronic phase separations in high-temperature superconducting systems Y–Ba–Cu–O (16), Nd–Ce–Cu–O (16–18), and $HoNi_2B_2C$ (16).

Using a microscopic Mössbauer probe ^{57}Co along with macroscopic measurements of magnetization, resistivity, etc., we report here our studies regarding the origin of colossal magnetoresistance in manganites as well as other systems where double exchange is absent.

EXPERIMENTAL

All the manganites were prepared by conventional solid state reaction, as described in our earlier publications (19, 20). The compounds were characterized by X-ray, (magneto)resistivity, and magnetization measurements. To obtain the Mössbauer data, a few parts per million ^{57}Co were substituted for Mn. ^{57}Co activity was diffused into the compacted pellets by repeated thermal treatments at 950–1200°C under O_2 flow till reproducible Mössbauer spectra were obtained. For the pyrochlore, $Tl_2Mn_2O_7$ ^{57}Co substitution was carried out by a thermal treatment of the material sealed in a gold foil at 400°C for 60 min to avoid degradation of the compound. A description of the experimental setup for the emission Mössbauer experiments can be found elsewhere (20). All isomer shifts presented in this paper are given with respect to α-Fe at 20°C.

All observed spectra below T_C are complex and their computer analyses were accomplished in several stages depending on the nature of desired information. Since the distribution in hyperfine internal fields is quite symmetrical (20), this allows us to approximate the magnetic component by individual sextet(s) with broadened lines rather than use a distribution fit, since several factors contribute to the line shape (discussed in a later section). 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 approximating the experimental spectra as a superposition of three doublets instead of a sextet and the central "paramagnetic" component with a singlet (or doublet with small quadrupole splitting, QS). This helps in feeding information to the final program fitting with sextet(s), which yields the major hyperfine parameters.

The experimental spectra below the Curie temperature can also be fitted with sufficient accuracy using a relaxation model, but we did not use it because several factors contribute to the line shapes below T_C, which cannot be properly taken into account during the fit: microscopic spatial inhomogeneities, temperature-dependent distribution of the hyperfine internal magnetic fields, effect of intercluster interactions which would be strongly dependent on temperature, and relaxation itself involving fluctuations of magnetic vectors of large spin clusters in directions close to an easy

direction of magnetization. In our approach, we do not use any fitting model; however, we are able to extract all general trends in the material's response to the temperature or magnetic field and then look for the most plausible explanation without being constrained by the limits of any particular fitting model.

DATA AND DISCUSSION

Superparamagnetic-Like Behavior below T_C

The Mössbauer spectra obtained at different temperatures for $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ are shown in Fig. 1a. It is to be compared with the computer simulated spectra for a regular ferromagnet given in Fig. 1b. In the latter case, the spectral extent of the magnetically split sextet which is proportional to the natural magnetization, diminishes continuously with temperature and finally collapses into a single line at T_C (= 198 K). It is obvious that the behavior of the manganite ferromagnet is anomalous in several respects (19, 20). The lines in the sextet are rather broad and they tend to become broader at higher temperatures, indicating an increase of distribution of internal hyperfine magnetic fields experienced by the Mössbauer probe with temperature, and relaxation due to collective excitations in directions close to easy directions. More importantly, the spectra consist of two components, a sextet M and a central peak (C). In a regular ferromagnet we would expect to see the C-component only above T_C. One can also observe that the central component is growing at the expense of the sextet with increasing temperature. Such behavior is typical for superparamagnetic behavior of small single domain particles with a distribution in size around an average value of 50–100 Å. Since the grain size in all our polycrystalline samples is larger that 1 μm and also that a single crystal of $La_{0.89}Ca_{0.11}Mn(^{57}Co)O_3$ also shows similar behavior (21), we attribute this behavior to magnetic clusters formed in the material itself. The manganites are fairly good ferromagnets at low temperatures, but above $T/T_C = 0.7$, the long-range ferromagnetic order starts crumbling down and spin clusters are formed with short-range order. At any specific temperature, if the available thermal energy is sufficient to overcome the anisotropy barrier, then the magnetic vector of the spin clusters can flip among the easy directions at a rate faster than the Larmor frequency of the daughter ^{57}Fe (about 10^8 s^{-1}), with the internal magnetic field at the probe averaging out to zero. The relaxed component C (which consists of an unresolved quadrupole doublet) becomes larger with temperature, as an increasing fraction of small spin clusters with high flipping rates are formed.

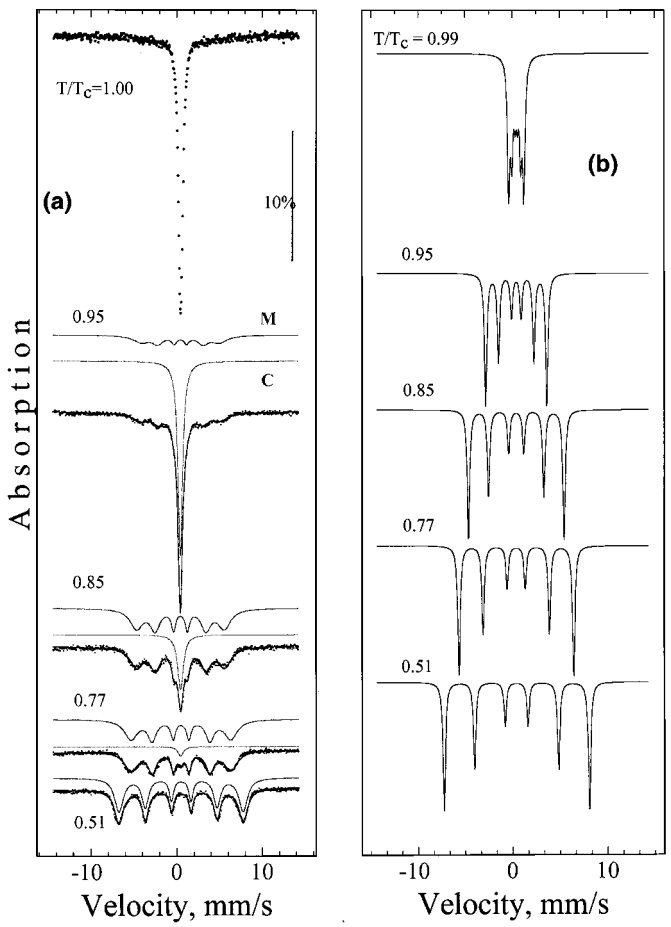

FIG. 1. (a) Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at different temperatures, $T_C = 198$ K (20). (b) Computer-simulated Mössbauer spectra of a regular ferromagnet at various temperatures.

At T_C, if an external magnetic field is applied, the Mössbauer spectrum undergoes a dramatic change (Fig. 2). Even with the application of a modest field of 1.8 T, one can see that the central relaxed peak produced by small spin clusters has vanished. Our computer analysis shows that it is replaced by regular magnetically split spectra characteristic of bulk ferromagnet with internal magnetic field, $H_{int} = 278$ kOe and large magnetic clusters having $H_{int} = 160$ kOe. The relative line intensities have changed from 1:2:3 to 1:4:3 due to alignment of the magnetic moments of the ferromagnetic domains along the applied field, which is perpendicular to the direction of observation. This is a very graphic evidence of coalescence of small spin clusters to form large clusters and to give regular bulk ferromagnetic order. Since ferromagnetic order and DE hopping of electrons go hand in hand, the appearance of magnetically ordered components under the influence of a magnetic field also implies regeneration of metallicity. We have reported earlier a direct correlation between the change in the abundance of the ferromagnetic fraction and the magnetoresistivity on application of $H_{ext} = 0.6$ T (20) as well as linear dependence of the resistivity on the amount of ferromagnetic fraction in zero field in $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ based on simultaneous measurements of the (magneto)resistivity and emission spectra (22).

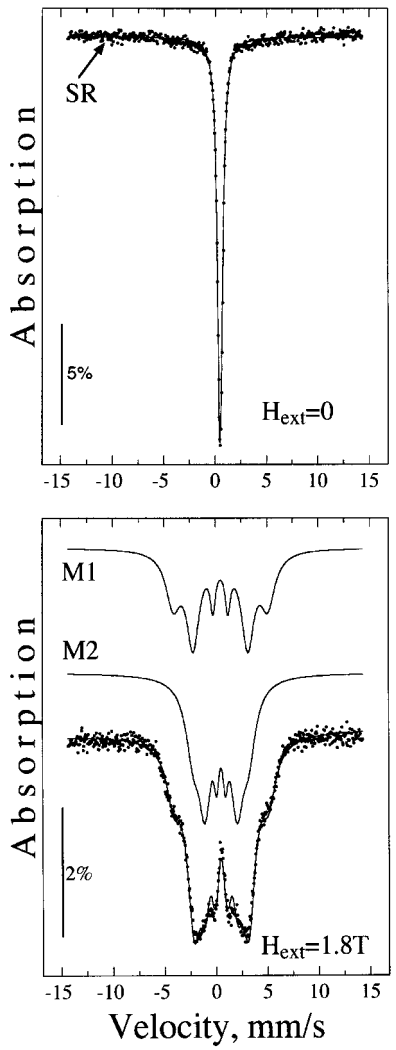

FIG. 2. Mossbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ with and without $H_{ext} = 1.8$ T at $T_C = 198$ K. The computer fits are raised for clarity.

Superparamagnetic-Like Behavior above T_C

The question arises as to the state of the so-called "paramagnetic" phase above T_C. It is widely believed that lattice distortions occur and the electrons are localized and that the conductivity is governed by hopping of lattice polarons (3–8). Our observations strongly suggest that even well above T_C, small spin clusters exist with size of about 20 Å in diameter (if approximated by a sphere) containing couple of hundred Mn atoms. A simple indication of this is the observation of magnetically split spectrum even at $T/T_C = 1.54$ on application of a modest external magnetic field (Fig. 3). A cluster of couple of hundred Mn atoms would have large enough magnetic interaction energy with even a modest field of 1.8 T to overcome the thermal randomizing of spins at room temperature. For other supporting evidence, we have to first convince ourselves that the parts per million of $^{57}Co/^{57}Fe$ substituting Mn are part of the electronic system and participating in the double exchange electron transfer. The local distortions at the site of substitution surrounded completely by Mn–O framework can change the oxidation potential of the daughter $^{57}Fe^{3+}$ so as to allow electron transfer to a neighboring Mn^{4+}. It may be underscored that for probing the magnetic behavior, ^{57}Fe does not have to be involved in the DE electron hopping. The following observations provide evidence for the minuscule amount of ^{57}Fe substituent being a full partner of Mn atoms in DE electron transfer. First, we observe a small but distinct decrease in isomer shift when Ca content is increased from 20% ($\delta = 0.49$ mm/s) to 30% ($\delta = 0.47$ mm/s) in the La–Ca–Mn–O system at 78 K. One expects the isomer shift to decrease with increasing hole density in the *d*-shell as the *s*-electron density on the ^{57}Fe nucleus would be enhanced due to diminished *d*-shielding. We should not expect a larger change because the hole has significant oxygen 2*p* character due to hybridization (23, 24). Arai *et al.* (25) have also reported a small but systematic decrease in isomer shift

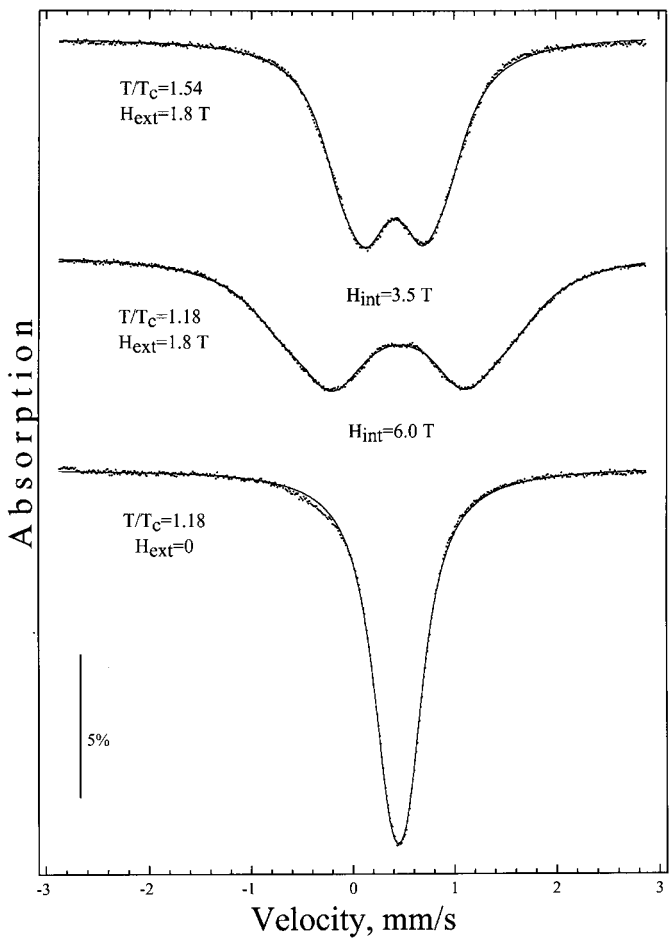

FIG. 3. Effect of $H_{ext} = 1.8$ T on the Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at $T/T_C = 1.18$ and 1.54, $T_C = 198$ K (20).

when Sr content in $La_{1-x}Sr_xMnO_3$ (doped with 1% of ^{57}Fe) is varied from 0.0 to 0.5. Simopoulos *et al.* (26, 27) observe a change in isomer shift from 0.515 to 0.463 mm/s at 4.2 K going from 33 to 50% Ca in $La_{1-x}Ca_xMnO_3$ with 1% ^{57}Fe substitution. However, these researchers believe that ^{57}Fe is part of the elecronic system only for 50% Ca substitution. The above-discussed observations show that iron, when substituted for Mn even at relatively high level of 1%, may also participate in electron hopping. Figure 4 shows a computer fit of Mössbauer spectra obtained above T_C (= 243 K) at 250 K for $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$. About 5% of Fe^{4+} (Mn^{4+}) seems to be segregated, presumably due to slowing down of the rate of electron hopping below the Mössbauer time scale of 10^{-7} s. A hole is delocalized over 3.3 Mn atoms. The distortion imposed on the probe by the Mn–O framework is rather small as the quadrupole splitting (QS) is only 0.18 mm/s, which is again indicative of the fact that the Mössbauer probe, ^{57}Fe participates in electron hopping. The Mössbauer probe senses distortions in a 10^{-7} s period. On the other hand, the very fast techniques (10^{-15} s) like EXAFS (28) and pair distribution function (PDF) (29) do show significant distortions above T_C. Neutron and X-ray diffraction average out distortions over a 10^{-12}-s period. Therefore, it stands to reason that MnO_6 octahedra are undergoing dynamic Jahn–Teller oscillations above T_C as supported by other investigations (30–32). We propose that these oscillations are induced by the slowed down electron hopping. The observation of a single major species above T_C by Mössbauer spectroscopy is supported by ESR studies by Lofland *et al.* on $La_{1-x}Sr_xMnO_3$ ($x = 0.1$, 0.2, and 0.3) (33). They find that all Mn spins contribute above T_C, indicating formation of magnetic clusters. Kapusta *et al.* (34) also report the observation of a single ^{55}Mn NMR line both below and above T_C for $[La_{1-x}A_x]MnO_3$ (A = Ca, Sr) providing direct evidence according to the authors of magnetic correlations whose lifetime is greater than 10^{-5} s.

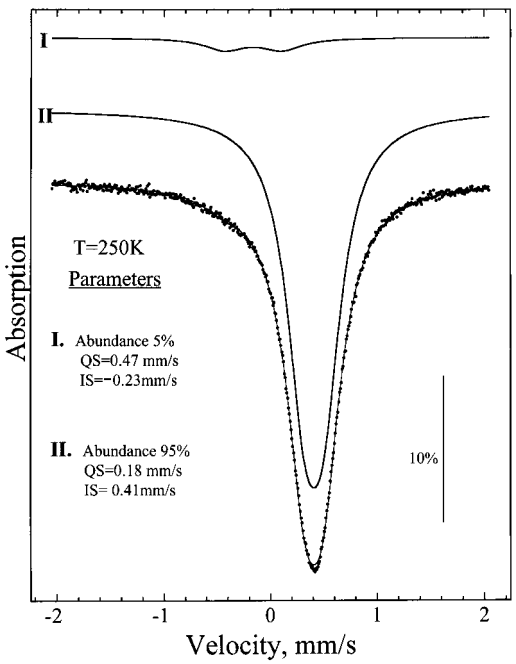

FIG. 4. Computer fit of Mössbauer spectra of $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ at 250 K (T_C = 243 K). QS, quadrupole splitting; IS, isomer shift.

De Teresa and coworkers (35) have proposed the existence of magnetic polarons above T_C in $(La_{1-x}A_x)_{2/3}MnO_3$ (A = Y or Tb) using a combination of volume thermal expansion (with and without applied field), magnetic susceptibility, and small angle scattering measurements (SANS). They attributed CMR in these compounds to the presence of magnetic polarons dispersed in a paramagnetic matrix. Viret *et al.* (36) carried out SANS measurements on a single crystal of $La_{0.75}Sr_{0.25}MnO_3$. Their interpretation was not consistent with the presence of spin polarons in a paramagnetic matrix. Our observations given in Figs. 2 and 3 suggest that all the spin clusters participate and grow into larger ones. In conclusion, our studies (19–22, 37, 38) show that the anomalous superparamagnetic-like behavior observed in ferromagnetic manganites where long-range magnetic order breaks down to give small magnetic clusters below T_C, and that they survive well above T_C, is an intrinsic characteristic of manganites. Superparamagnetic-like behavior below T_C has also been reported in Mössbauer studies of some other compounds, e.g., $YFeO_3$ (39), FeF_3 (39), and magnetically dilute systems (40).

Model

Now the question arises as to how the long-range ferromagnetic order breaks down and small magnetic clusters/polarons (with very little lattice distortions) are formed below T_C. Moreover, in manganites, the spin–spin correlation is particularly strong and magnetic clusters exist up to $2T_C$ (20, 35, 37, 38). This is in sharp contrast to the behavior of regular ferromagnets like Fe and Ni, where magnetic coherence is observed only up to $1.1T_C$, and there is no evidence of formation of magnetic clusters below T_C. Our model, which rationalizes the superparamagnetic-like behavior below T_C, is based on the large anharmonicity in oscillations of the Mn–O–Mn moiety (22, 41–45). The anomalous decrease in the total area of the Mössbauer spectra below T_C is evident from Fig. 5. The magnitude of the Mössbauer area is indicative of how strongly the Mössbauer probe is bound to the Mn–O–Mn network. A sharp decrease below T_C strongly suggests softening of the phonon spectra due to the anharmonic stretching of Mn–O bonds and the enhanced amplitude of torsional oscillations of the Mn–O octahedra. The anomalous increase in Mn–O bond lengths, the bending of the Mn–O–Mn moiety, and the enhanced Debye-Waller factors for Mn and O atoms below T_C have also been observed by X-ray and neutron

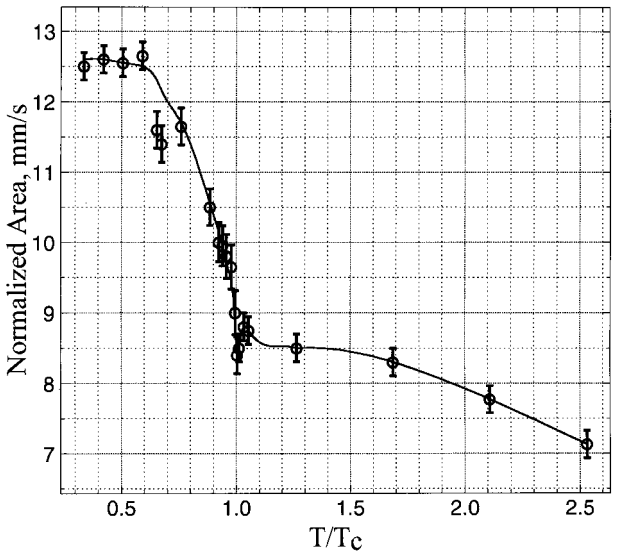

FIG. 5. Plot of normalized total area under the Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ as a function of temperature. The solid line is a guide for the eyes.

diffraction studies (32, 41–45). The localized distortions resulting from aliovalent substitution can also enhance the anharmonicity of vibrations in the vicinity. These changes will affect the exchange interactions as well as the rate of electron hopping; i.e., the two features are intertwined. The probability of hopping by double exchange via $O^=$ is the highest when both hopping electrons have the same spin orientation, requiring Mn^{3+} and its partner Mn^{4+} to be ordered ferromagnetically. For instance, if the amplitude of the torsional oscillations increase with temperature, the rate of electron hopping will decrease as the neighboring spins will have to wait until thermal fluctuations allow them the correct configuration for a double exchange hop (Franck-Condon factor). Therefore, with increasing temperature below T_C, the long-range ferromagnetic order breaks down and intermediate size and small superparamagnetically relaxed clusters are formed. The intermediate size spin clusters will have poorer spin ordering and diminished exchange interactions with a wider distribution, which results in broadening of the Mössbauer sextet lines. Collective superparamagnetic relaxation, involving fluctuations of magnetic vectors of larger spin clusters in directions close to an easy direction of magnetization, would also contribute to broadening of lines. It is worthy of note that a specific spin does not belong to the same spin cluster all the time. It is a dynamic process; larger spin clusters are formed at the expense of smaller ones and vice versa (38). The time scale for these changes has to be slower than the Larmor period of ^{57}Fe ($\sim 10^{-8}$ s); otherwise the magnetically split sextet would be obliterated. However, there are still strong intercluster exchange interactions. The rapidly fluctuating small spin clusters which exhibit superparamagnetic-like behavior will cause scattering of charge carriers. On application of an external magnetic field below and above T_C, the small spin clusters coalesce to form larger clusters which exhibit magnetically split sextet(s) (Figs. 2 and 3). If the clusters are large enough to exhibit conductivity by percolation, CMR will be observed (20, 22, 46). The magnitude of CMR near T_C will naturally be higher, where the material is more amenable to dramatic changes in the presence of an external field.

We can conclude from our studies on several polycrystalline and single-crystal perovskite manganites undergoing double exchange electron hopping that the formation of ferromagnetic spin clusters exhibiting superparamagnetic-like behavior below and above T_C is primarily responsible for the bulk CMR. Now we propose to address the question of whether superparamagnetic-like behavior is a prerequisite for observing CMR even in materials that do not exhibit DE electron transfer—like the pyrochlore $Tl_2Mn_2O_7$.

Superparamagnetic-Like Behavior in Systems Not Showing Double Exchange

The pyrochlore, $Tl_2Mn_2O_7$, shows CMR without Mn^{3+}/Mn^{4+} DE. Structural analysis from powder neutron and single crystal X-ray diffraction data indicate formal oxidation states close to that of $Tl_2^{3+}Mn_2^{4+}O_7$ (47). The local spin density approximation (48) and the tight bonding band calculations (49) show that the Fermi surface is derived from strongly mixed combinations of Tl, Mn, and O orbitals. It is interesting to note that Lynn *et al.* (50) did not see the central diffusive component to the neutron scattering fluctuation spectrum in sharp contrast to the $La_{1-x}(Ca, BaSr)_xMnO_3$ system. This central diffusive component was interpreted as a signature of magnetic clusters/polarons. However, our preliminary emission Mössbauer investigations do show evidence of superparamagnetically relaxed magnetic clusters (51).

The emission Mössbauer spectra of $Tl_2Mn_2(^{57}Co)O_7$ at 78 and 120 K without H_{ext} and at 120 K with $H_{ext} = 1.8$ T are shown in Fig. 6. The incorporation of ^{57}Co at the Mn site was incomplete as we were constrained not to heat the compound above 400°C (in sealed gold foil). Of the total activity, 31% was incorporated at the Mn site and is seen as a magnetically split sextet in Fig. 5a. When the temperature is raised to 120 K, 16% units of the sextet vanishes and converts into superparamagnetically relaxed magnetic clusters (Fig. 6b). When an external field of 1.8 T is applied at 120 K, then 6% units of magnetic clusters coalesce to form large clusters with better alignment of spins. The sextet not only increases in intensity from 15 to 21%, but the internal field increases dramatically from 180 to 300 kOe, clearly indicating the growth of spin clusters.

Lang *et al.* (52) have reported the Mössbauer spectra of the CMR chalcospinel $Fe_{0.5}Cu_{0.5}Cr_2S_4$ at temperatures

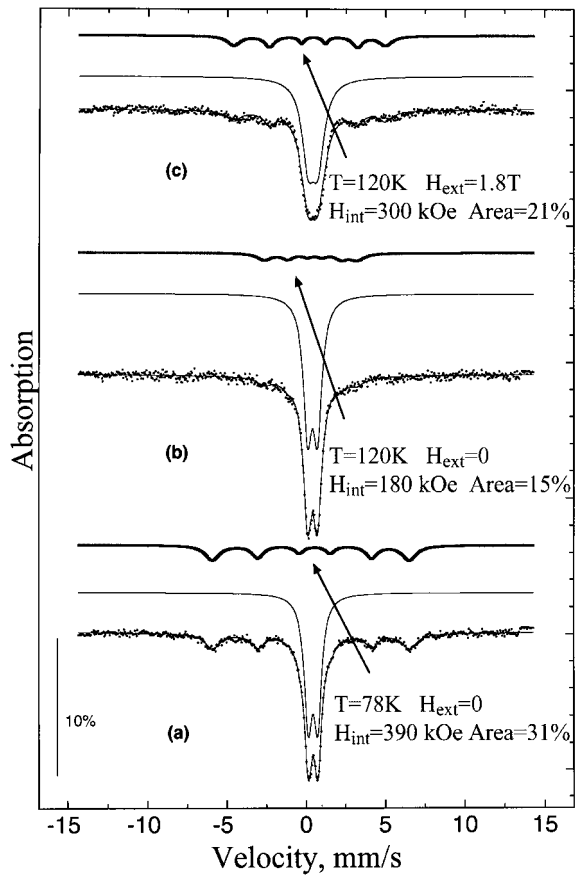

FIG. 6. Mössbauer spectra of the pyrochlore, $Tl_2Mn_2(^{57}Co)O_7$ ($T_C \sim 123$ K), at 78 and 120 K with and without an external magnetic field of 1.8 T. Only 31% of ^{57}Co has substituted at the Mn site.

ranging from 4 to 300 K. The authors observe the coexistence of a central peak and a sextet at all temperatures below 300 K. The central peak increases in intensity at the expense of the sextet as the temperature is increased. The authors do not give any specific reason for this behavior. We would like to attribute it to superparamagnetic-like behavior of spin clusters, which increases as one approaches T_C.

One can infer that the existence of small ferromagnetic spin clusters exhibiting superparamagnetic-like behavior near T_C can also account for bulk magnetoresistivity in systems without DE electron transfer.

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