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Absence of small lattice polarons above the Curie temperature in magnetoresistive manganites

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It is generally believed that the electrical transport in magnetoresistive manganites above T_C is governed by small polarons associated with large lattice distortions. We present evidence which confirms the existence of magnetic clusters (polarons) associated with minimal lattice distortions above the Curie temperature. We take advantage of the fact that the Mössbauer spectra of the relatively large and slowly fluctuating magnetic polarons consist of incompletely collapsed magnetic component with extensive wings.

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Kusters *et al.*[1,2] proposed existence of magnetic polarons in manganites on the basis of spin polarized neutron scattering observations and the behavior of resistivity above the Curie temperature (T_C). Sun *et al.*[3] and Archibald *et al.*[4] examined the temperature and field dependent magnetization and came to the same conclusion. Zhang and Yang[5] gave a theoretical treatment using similar features. Lynn *et al.*[6] in their neutron scattering studies observed an anomalous strongly field dependent diffusive component which dominated as one approaches T_C from below. Heffner and co-workers[7] interpreted their observations of nonexponential muon spin relaxation, and the results of Lynn *et al.* as arising from diffusive relaxation of variable size magnetic clusters. De Teresa *et al.*[8] using a combination of volume thermal expansion (with and without an applied field), magnetic susceptibility, and small angle neutron scattering measurements, proposed the existence of magnetic polarons in a paramagnetic matrix above T_C. Viret *et al.*[9] carried out small-angle neutron scattering (SANS) measurements on a single crystal of $La_{0.75}Sr_{0.25}MnO_3$. Their observations were not consistent with the presence of spin polarons in a paramagnetic matrix. Our emission Mössbauer investigations on $La_{0.8}Ca_{0.2}MnO_3$[10,11] reveal that on application of an external magnetic field of 1.8 T at $T/T_C=1.54$, practically all the small clusters which were superparamagnetically relaxed coalesce to give much larger spin clusters with a hyperfine magnetic field of 35 kOe. Within the capability of our measurements, all the spin clusters participate and grow into larger ones. Therefore, it rules out the possibility of existence of a paramagnetic matrix as proposed by De Teresa *et al.* This is also borne out by electron spin resonance (ESR) studies of $La_{1-x}Sr_xMnO_3$ by Lofland *et al.*,[12] who observed that all the spins contribute to give a single ESR species. Kapusta *et al.*[13] also observed a single ^{55}Mn NMR peak above T_C for several manganites. These observations are consistent with the proposed existence of spin clusters where double exchange electron transfer between Mn^{3+} and Mn^{4+} occurs fairly rapidly for a single species to be detected by these techniques. Here we discuss of some additional evidence for the existence of magnetic polarons with little lattice distortion above T_C, taking advantage of the superparamagnetic relaxation characteristics of larger magnetic clusters.

In a regular situation where superparamagnetic behavior arises from small size magnetic particles with single magnetic domains, the Mössbauer spectrum at low temperatures consists of a single magnetically split sextet with narrow lines. At higher temperatures, the spectra consist of two components, a sextet and a collapsed component in the middle which grows with temperature at the expense of the magnetic counterpart. The central component arises when the available thermal energy is sufficient to flip the magnetization vector of the smaller particles along easy magnetic directions at a rate much faster than the Larmor frequency of ^{57}Fe (about $10^8\ s^{-1}$), which results in a net zero field at the ^{57}Fe nuclei. At higher temperatures, an increasing fraction of particles will have a flipping rate much faster than $10^8\ s^{-1}$. At intermediate temperatures, a large fraction of particles have flipping rate comparable to the Larmor frequency and would exhibit a characteristic evolution of line shapes with temperature. This is the typical signature of superparamagnetic behavior. For the magnetoresistive manganites studied by us, the grain size is too large (a few microns) to exhibit superparamagnetic behavior. In this case, the superparamagnetic-like behavior arises from the anomalous behavior of the ferromagnetism.[10,11] The long range ferromagnetic order starts breaking down well below T_C and smaller spin clusters are formed (Fig. 1) which survive well above T_C. The presence of spin clusters and their evolution with temperature makes magnetic behavior of manganites very different from the conventional ferromagnets and determines their transport properties and the CMR.

Our evidence for the existence of spin clusters (magnetic polarons) is twofold, first the coexistence of a magnetically split sextet with a central collapsed peak (Fig. 1) and secondly under the influence of a modest external field the central collapsed peak vanishes and converts into a magnetically split sextet characteristic of large spin clusters.[10,11,14,15] However, the evolution of line shapes with temperature typical of

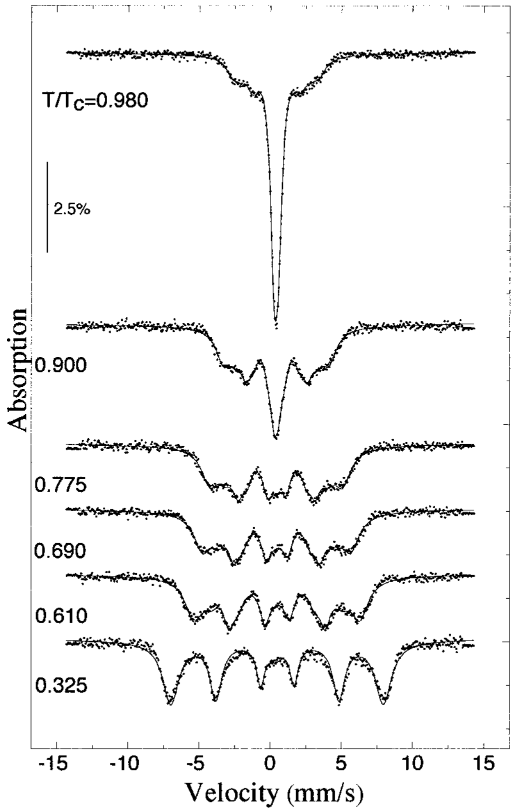

FIG. 1. Mössbauer spectra of $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ at different temperatures, $T_C = 243$ K.

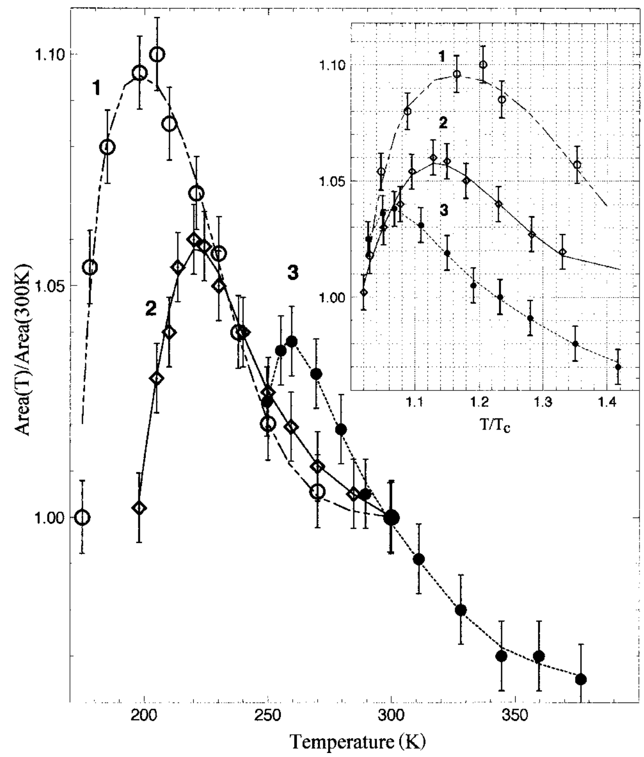

FIG. 2. Normalized area of the Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)^{16}O_3$, $La_{0.8}Ca_{0.2}Mn(^{57}Co)^{18}O_3$, and $La_{0.7}Ca_{0.3}Mn(^{57}Co)O_3$ in narrow velocity span as a function of temperature, and also as a function of T/T_C (inset).

superparamagnetic relaxation are masked to a large extent for the following reasons. First, broadening of the sextet lines occurs not only due to collective excitations of spin clusters between directions close to the easy direction, but due to the fact that the spins in smaller clusters are not well aligned. Second, it is the intrinsic property of magnetoresistive manganites that as the temperature approaches T_C from below, more and more spin clusters are generated presumably due to distortions introduced by Ca^{2+} substitution and defect cationic vacancies. They do not preexist as in the case of small particles. Third, there is strong interaction between the clusters due to their close vicinity, which is likely to vary with temperature. Fourth, a fraction of the material exhibits bulklike ferromagnetism even near T_C and so in a certain sense, the ''blocking temperature'' (the temperature at which the magnetic vectors of all the particles fluctuate faster than the Larmor frequency and result in a net zero field at the Mössbauer nuclei) coincides with the Curie temperature. These four features are responsible for a distinctive behavior which deviates in some respects from regular superparamagnetism. In view of the above, one can argue against our interpretations and suggest that the central peak (Fig. 1) belongs to a paramagnetic rather than a superparamagnetically relaxed species. This question has acquired considerable importance because in the former case we expect small lattice polarons with Mn^{3+}/Mn^{4+} charge separation to dominate the scene above T_C, whereas in the latter case magnetic clusters (polarons).[16,17] To distinguish clearly between the two possibilities, we adopted the following procedure. One can expect that a fraction of the spin clusters (polarons) above T_C would be relatively large and fluctuating slowly with relaxation time close to 10^{-9} s. The Mössbauer spectra for these clusters will consist of a centrally collapsed component along with a very wide component with extensive wings.[18,19] It is easy to lose such a broad component in the background during computer analysis, while the central part will incorrectly form part of the almost completely relaxed component belonging to the major fraction of smaller spin clusters. If large slowly fluctuating ferromagnetic clusters do exist above T_C, they could be detected by reducing the energy scale to accommodate only the collapsed component presented by a single line (unresolved quadrupole split doublet). Then if one follows the behavior of its area while approaching T_C from above, it becomes possible to detect even subtle changes in the amount of incompletely relaxed magnetically split fraction which will manifest itself through the loss of the area while measuring only the collapsed part which can be done with $\pm 1\%$ accuracy in the narrow velocity range. Experimental results presented below unambiguously show that this is indeed the case.

Measurements were carried out mainly on two samples of polycrystalline $La_{0.8}Ca_{0.2}MnO_3$ manganite with ^{16}O and ^{18}O substitutions using a setup described earlier in Ref. 15 which allows simultaneous measurements of Mössbauer effect and resistivity on these two samples under identical conditions to seek correlation between them. Figure 2 presents the temperature dependence of the areas of each of the two samples of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ above the Curie temperature measured in a narrow energy range of about ± 5 linewidths of the collapsed component ($LW = 0.38$ mm/s). The total area under the Mössbauer spectrum is determined by the fraction of recoil-free events, which, in turn, depends on the mean amplitude of vibration. Therefore, the total area of the Mössbauer spectrum normally decreases monotonically as a function of temperature. This is not the case for the three polycrystalline manganites shown in Fig. 2, each of them shows an increase in area with temperature, with a maximum at some characteristic temperature well above T_C and followed by a rapid drop in area. Since no anomalies have been reported in the above temperature range,[20,21] this area loss has to be interpreted as a manifestation of growing number of slowly fluctuating ferromagnetic spin clusters. This fraction of the spectra appears as partially relaxed and magnetically split with broad wings, and therefore contributes to the component that is lost because it does not fit into the experimentally adjusted narrow window. The following features observed in Fig. 2 are noteworthy: The lower the Curie temperature the wider the temperature range in which these relatively large spin clusters occur. Also, the maximum is higher indicating a larger loss in area, which indicates a much higher concentration of larger spin clusters. The maximum for ^{18}O sample ($T_C = 170$ K) is seen at $T/T_C > 1.18$, for ^{16}O ($T_C = 195$ K) at T/T_C of about 1.14, and for the 30% Ca sample ($T_C = 243$ K) it is around $T/T_C = 1.07$. At higher temperatures, the larger spin clusters break up into smaller ones fluctuating faster than the Larmor frequency, which results in a net zero field at the nuclei, and their broad winged spectrum collapses into the central peak.

The presence of large spin clusters which constitute big islands of metal-like material would certainly affect the magnetic[3,4,7] as well as transport properties above T_C.[22,23] It can perhaps explain the deviation in hopping conduction when approaching T_C from above reported in Refs. 22 and 23. Analysis of our conductivity measurements shows that deviations start approximately in the same temperature region where we observe the appearance of large spin clusters. Our earlier work[10,11,14,15,20,21] and the present one clearly show the occurrence of magnetic clusters well above T_C and their role in observation of CMR. Now the question arises whether the magnetic polarons are associated with considerable lattice distortions as is generally believed.[16,17] The Mössbauer spectrum above T_C for several Ca doped manganites consists of a major quadrupole split doublet[20,21] with a splitting of only 0.18 mm/s. This shows minimal distortion of the Mn-O octahedra. It is true that the daughter $^{57}Fe^{3+}$ do not undergo Jahn-Teller distortion. However, if the ^{57}Fe-O octahedron was surrounded by segregated Mn^{3+} (a Jahn-Teller ion) and Mn^{4+} (with shorter bonds) ions, it would certainly be distorted. So our observations do not support the existence of small lattice polarons above T_C. Chun *et al.*[24] have also come to the same conclusion recently.

It may be mentioned that the large distortions observed above T_C using extended x-ray-absorption fine structure (EXAFS),[25–27] and pair-distribution function analysis[28,29] with resolution time $\sim 10^{-16}$ s, and the smaller distortions observed by neutron scattering with the time scale $\sim 10^{-12}$ s,[30–33] are just a manifestation of the fact that the rate of DE electron hopping between Mn^{3+} and Mn^{4+} in the manganite cluster has decreased due to poorer spin alignment, and that one can capture the distortions of the dynamic Jahn-Teller motions. On the other hand, Mössbauer spectroscopy with a time scale of 10^{-7} s sees very minor distortions because of the averaging effect.

In conclusion, we find additional evidence for the existence of spin clusters associated with minimal lattice distortions above the Curie temperature in manganites by detecting relatively large and therefore slowly fluctuating spin clusters in the proximity of T_C.

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