Nanoscale magnetism in the chalcogenide spinel $FeCr_2S_4$: Common origin of colossal magnetoresistivity

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Most of the models purporting to explain the intriguing observation of colossal magnetoresistivity (CMR) in manganites invoke double exchange (DE) electron transfer between Mn^{3+} and Mn^{4+} ions, and coupling between the itinerant electrons and the dynamic Jahn-Teller (J-T) lattice distortions. Here we report using Mössbauer spectroscopy some very revealing commonalities in the magnetic behavior of $FeCr_2S_4$, which is representative of systems that do not exhibit DE electron transfer nor J-T distortions. These observations shed light on the origin of intrinsic CMR in general.

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Doped manganites, $Ln_{1-x}M_xMnO_3$, where Ln=La, Pr, and others, and M=Ca, Sr, and others, are fascinating materials, which are the focus of extensive studies.[1–4] They have a perovskite-type crystal structure, where Mn ions are surrounded by six oxygen anions that are shared by other Mn ions in a three-dimensional network, while the Ln/M ions occupy the spaces between these octahedra. When, for instance, Ca^{2+} is substituted for La^{3+}, the compound $La_{1-x}M_xMnO_3$, a prototypical manganite, becomes a ferromagnetic metal for $0.18<x<0.5$. The electron hopping between Mn^{3+} and Mn^{4+} occurs via $O^{=}$ by a simultaneous jump from Mn^{3+} to $O^{=}$ and from the latter to Mn^{4+}. This double exchange (DE) event is facilitated when the two hopping electrons have the same spin polarization, a requirement that is met when Mn ions are ordered ferromagnetically.[1–4] Surprisingly, application of a magnetic field near T_C results in a large decrease in resistivity due to regeneration of metallicity, an effect known as the colossal magnetoresistivity (CMR). The essential ingredients behind the intriguing phase transitions and the CMR are believed to be the synergistically intertwined DE and ferromagnetism, and the strong interaction between the itinerant electrons and the lattice.[1–4] Several models have invoked the concept that the electron carries with it the Jahn-Teller (J-T) distortion of the MnO_6 octahedron. The greater the distortion, the more localized the charge carriers, and this deformation either diminishes considerably or vanishes in the metallic state below T_C.

On the other hand there are some systems such as the chalcogenide spinel $FeCr_2S_4$,[5–11] and the pyrochlore $Tl_2Mn_2O_7$,[12–15] which exhibit magnetoresistivity, without the involvement of DE electron transfer between aliovalent ions or J-T distortions. Here we seek with the help of a local microscopic Mössbauer probe, commonalities between widely different magnetoresistive systems. Our investigations shed light on the origin of bulk magnetoresistivity in general.

$FeCr_2S_4$ is a *p*-type semiconducting ferrimagnet[16,17] with Curie temperature about 170 K. The formal charges are Fe^{2+}, Cr^{3+}, and S^{2-} with considerable covalent character.[18,19] Fe^{2+} occupies tetrahedral sites and Cr^{3+} octahedral ones. They are aligned antiferromagnetically. Double exchange electron transfer is ruled out.[9] However, weak dynamic Jahn-Teller distortions of the Fe^{2+} tetrahedra have been invoked at temperatures above 10 K, but without any clear experimental evidence.[20–25] Haacke and Beegle[16] on the basis of anomalous thermoelectric power observations near T_C have proposed the existence of magnetic short-range order above T_C.

Our Mössbauer studies give insight into the magnetic behavior of $FeCr_2S_4$ vis-à-vis the DE/J-T mixed-valence manganites. Samples of $FeCr_2S_4$ used for these investigations are from the same batch for which Ramirez *et al.*[8] have reported their measurements for magnetization, thermopower, and CMR. The Mössbauer spectra at selected temperatures with a computer fit are shown in Fig. 1. We can fit the spectra with a magnetically split sextet and a central component. One can observe that at low temperatures only a magnetically split sextet is observed. However, as the temperature is raised and approaches T_C, the central component grows at the expense of the sextet. The coexistence of magnetically split sextet(s)

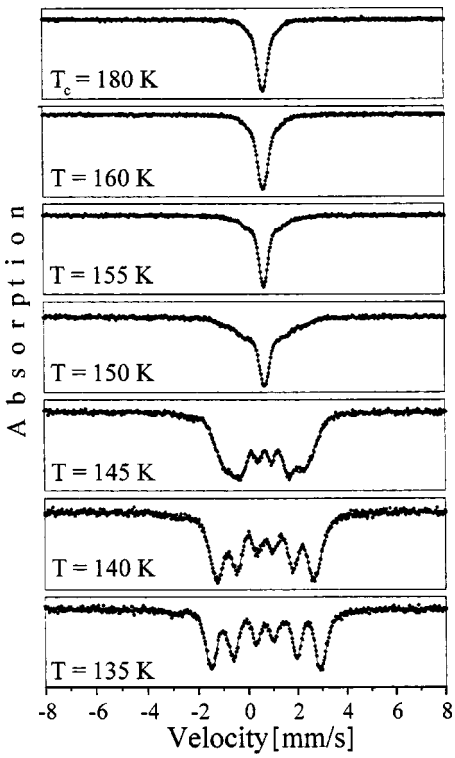

FIG. 1. ^{57}Fe Mössbauer spectra of $FeCr_2S_4$ taken at selected temperatures above and below the magnetic ordering temperature ($T_c = 170$ K).

and the relaxed central component is an indication of superparamagnetic behavior. It is generally associated with the presence of nanoscale single magnetic domain particles.[26,27] Since the grain size of our material is relatively large (>1 μm), this behavior can be attributed to the breakdown of long-range magnetic order and the formation of nanoscale magnetic clusters. As the temperature approaches T_C more and more clusters are formed. If the available thermal energy in kT is larger than the magnetic anisotropic barrier, the magnetic axis of each cluster would fluctuate between the two orientations of the easy directions at a rate faster than the Larmor frequency of the daughter ^{57m}Fe($\sim 10^8$ Hz), then the net magnetic field experienced by the nuclei would be

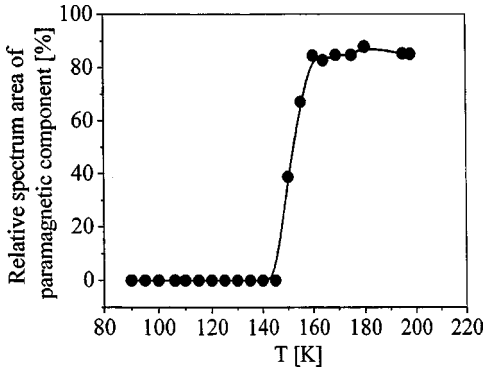

FIG. 2. The relative spectrum area of the superparamagnetically relaxed component as a function of temperature. The uncertainty of the displayed values is below 3%.

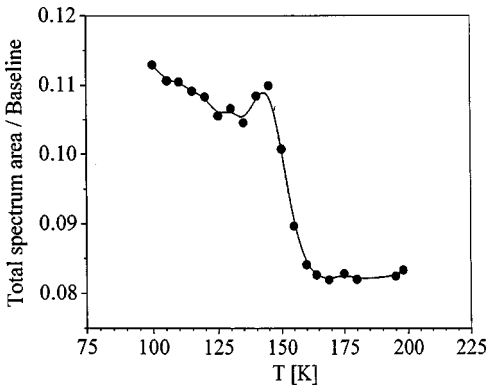

FIG. 3. Plot of normalized total area under the ^{57}Fe Mössbauer spectra of $FeCr_2S_4$ as a function of temperature.

zero, and the magnetically split sextet would collapse to give a central line (Fig. 1). Similar Mössbauer observations were made for manganites.[28,29] This behavior was attributed to the intrinsic nature of the manganites and interpreted as due to the breakdown of long-range ferromagnetic order with the formation of nanoscale magnetic clusters with fairly strong short-range interactions.[30–33] The breakdown of long-range order for manganites starts occurring even below T_C. Similar behavior is observed for $FeCr_2S_4$ in Figs. 1 and 2.

The total area of the Mössbauer spectra, which represents the fraction of recoil-free events, is determined by the mean-square amplitude of vibration and it tells us how strongly the Mössbauer probe is bound to its neighbors.[34] The total area is plotted as a function of temperature in Fig. 3. It clearly shows softening of the lattice in the range 145–165 K, which corresponds with the temperature range in which the breakdown of the long-range magnetic order occurs [Figs. 1 and 2 (Ref. 35)]. It is interesting to note that the maximum for CMR is observed at about 170 K,[8,10] where the breakdown into nanoscale clusters is completed. If an external magnetic field is applied during a Mössbauer run above T_C, a well-defined magnetically split sextet is generated (Fig. 4). It is a graphic demonstration of the magnetic clusters aligning themselves and coalescing to exhibit long-range magnetic order and diminished resistivity. Similar behavior has been observed for $La_{1-x}Ca_xMnO_3$ ($x = 0.1$, 0.2, and 0.3) and the pyrochlore $Tl_2Mn_2O_7$.[28,30–33]

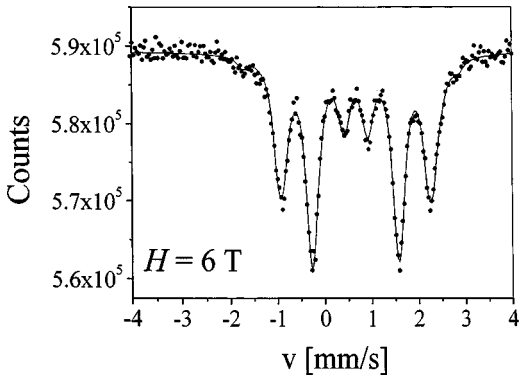

FIG. 4. ^{57}Fe Mössbauer spectrum of $FeCr_2S_4$ recorded at $T = 186.5$ K in an external magnetic field of $H = 6$ T. Zero velocity corresponds to the isomer shift of α iron.

It may be mentioned that the role of magnetic clusters in colossal magnetoresistive manganites was pursued vigorously in the early days by Kusters and co-workers.[37,38] More recently, De Teresa *et al.*[39] building on the work of Lynn *et al.*[40] and Sun *et al.*[41] proposed existence of magnetic polarons dispersed in a paramagnetic matrix above T_C in $(La_{1-x}A_x)_{2/3}MnO_3$ (A=Y or Tb). They used a combination of volume thermal expansion (with and without field), magnetic susceptibility, and small-angle neutron-scattering measurements. However, our observations and interpretation differ in some important aspects. Our observations of the nanoscale spin clusters growing under the influence of external magnetic field is very dramatic and revealing. All the spins in each cluster participate and grow into larger ones. It is the intrinsic behavior of the material that the long-range order has been replaced by a short-range one in contrast to the picture of nanoscale spin clusters dispersed in a paramagnetic matrix.[39] In a similar fashion, Uehara *et al.*[42] and Burgy *et al.*[43] have proposed percolative phase separations consisting of ferromagnetic (FM) and antiferromagnetic (AF) (or CO) clusters. However, we do not observe any AF clusters in $La_{1-x}Ca_xMnO_3$ (x=0.1, 0.2, and 0.3) (Refs. 28, 30–33, and 36) nor in chalcospinels. Moreover, our model is more general and encompasses the ones invoking a mixture of FM-AF magnetic clusters. Whether AF clusters are present or not, rapidly fluctuating ferromagnetic clusters (where holes are completely delocalized over each ferromagnetic cluster) would also constitute an insulating phase. One does not have to necessarily invoke the presence of insulating AF clusters (they would certainly be present near 0.5 dopings). Electron transfer would be slowed down considerably as it would be possible for electrons to hop only between neighboring clusters with the same orientation.[30–33,36,42,44]

In general, it seems that the softening of phonons presumably arises from anharmonic oscillations which in turn cause stretching of bonds and larger amplitude of torsional oscillations. This results in diminished exchange interactions. Consequently, the long-range magnetic order breaks down and a new electronic phase consisting of rapidly fluctuating nanoscale magnetic clusters is formed. However, under the influence of an external magnetic field, the spin clusters align and coalesce to give long-range order, which exhibits lowering of resistivity and regeneration of ferromagnetism.

On the basis of the afore-discussed observations, one can infer that in many respects colossal magnetoresistive pyrochlores[31] and chalcospinels demonstrate behavior similar to manganites, namely, (i) the long-range ferromagnetic order breaks down gradually when approaching T_C from below with formation of nanoscale spin clusters (ii) nanoscale spin clusters survive well above T_C, and (iii) application of an external magnetic field well above T_C results in coalescence of nanoscale rapidly fluctuating clusters, restoration of bulklike ferromagnetism, and lowering of resistivity. These common features among widely different magnetoresistive materials suggest that the observation of nanoscale spin clusters is a prerequisite for observation of intrinsic negative magnetoresistivity.

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