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Abstract. Emission Mössbauer effect investigations were done simultaneously with resistivity measurements on two similar samples of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$, in one of which ^{18}O was substituted for ^{16}O. Only a few parts per million of ^{57}Co were substituted for Mn with minimal perturbation of the system. For both compounds, the long range ferromagnetic spin order decreases anomalously below the transition temperature (T_c) and we observe three broad categories of electronic phases. Surprisingly, we find that ^{18}O substitution brings about a stronger exchange interaction between Mn^{3+}/Mn^{4+}, and the internal field (H_{int}) is larger than that for the ^{16}O compound at all normalized temperatures (T/T_c) observed. The stronger exchange interaction in the ^{18}O compound is in apparent contradiction with the observation that the ferromagnetism in this compound starts crumbling at a lower T/T_c, forming small spin clusters exhibiting superparamagnetic-like behaviour. However, the ^{18}O compound is more amenable to spin ordering under the influence of a magnetic field near T_c.

1. Introduction

$LaMnO_3$ is an insulating antiferromagnet. When La^{3+} is substituted by bivalent ions like Ca^{2+}, holes are introduced and the compound $La_{1-x}Ca_xMnO_3$ becomes a ferromagnetic metal for $0.18 \leqslant x < 0.5$. An electron hop 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 angle subtended by the ferromagnetically aligned Mn^{3+} and Mn^{4+} ions [1]. The transition from a ferromagnetic metal to insulating 'paramagnet' is associated with a sharp decrease in conductivity. On application of a magnetic field, the transition temperature (T_c) is raised considerably resulting in a sharp drop in resistivity near T_c. This drop in resistivity is known as the colossal magnetoresistance (CMR) [2]. The physics underlying the metal to insulator transition and the CMR are the focus of attention [3–6]. There is considerable evidence of a strong electron–phonon interaction in this system [3–8]. Zhao *et al* [9] reported a giant oxygen isotope effect in $La_{0.8}Ca_{0.2}MnO_3$. Substitution of ^{18}O for ^{16}O resulted in a decrease in T_c of >20 K. They interpret the decrease in T_c as due to reduced mobility of polarons resulting from contraction in effective width of the conduction band. Franck *et al* [10] claim that part

of the decrease in T_c may be attributed to differences in the oxygen content of the manganite samples. Nagaev [11] has proposed that the equilibrium densities of the oxygen vacancies or excess oxygen atoms depend on the mass of the oxygen atom. Kresin and Wolf [12] attribute the oxygen isotope effect to the dynamic Jahn–Teller effect on the bridging oxygen anion, which acquires a double-well structure. Several researchers have reported that the substitution of ^{18}O for ^{16}O in manganites favours the charge-ordered insulating state [13–18]. A clear understanding of the mechanism of the isotope effect would shed light on the physics underlying the ferromagnetic metal to 'paramagnetic' insulator transition.

Here we report on the enigmatic observation that at all normalized temperatures with the exception of lower temperatures, the ^{18}O compound shows a greater break-down of long range ferromagnetic order despite the fact that the exchange interactions between Mn^{3+}/Mn^{4+} are larger as depicted by the internal hyperfine magnetic fields. We also observe that on application of a magnetic field, the small magnetic clusters grow to give larger clusters with better spin ordering. This feature is more pronounced for the ^{18}O compound.

2. Experimental and data analyses

The material was prepared by conventional solid state reaction from stoichiometric amounts of La_2O_3 (which was predried at $1000\,^\circ C$ for 12 h), $CaCO_3$ and Mn_3O_4 (obtained by heating MnO_{2+x} at $1000\,^\circ C$ for 12 h). The powdered mixture was initially thermally treated at $900\,^\circ C$ in air for 12 h, followed by repeated thermal treatments at $1100\,^\circ C$ for 12 h, with periodic mixing until a single phase was seen by x-ray diffraction. The powder was annealed at $1100\,^\circ C$ for 12 h before compacting into a pellet. The pellet was annealed in air at $1350\,^\circ C$ for 20 hours. The x-ray diffractogram showed only the $La_{0.80}Ca_{0.20}MnO_3$ phase. The material was also characterized by magnetization measurements. The pellet was cut into several equal rectangular pieces measuring $13 \times 4 \times 1$ mm suitable for both resistivity and emission Mössbauer effect measurements. To obtain the Mössbauer data reported here, a few parts per million ^{57}Co were substituted for Mn in a pair of samples. The experimental procedure is discussed in an earlier publication [19]. Since Co(Fe) prefer 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 and magnetic behaviour of the dominant host material. Finally these two samples were treated with O_2, one in $^{16}O_2$ and the other in $^{18}O_2$ (1 atm) under exactly the same conditions in a parallel processing system described elsewhere [10]. The samples were gas exchanged at $950\,^\circ C$ for 10 h. This resulted in an $^{18}O_2$ bulk concentration of about 80% (by weight) which suggests near 100% substitution within the 50–100 μ from the sample surface where ^{57}Co resides. Magnetization and resistivity measurements were carried out on this pair of samples along with Mössbauer studies.

To perform precise comparative Mössbauer effect study of ^{16}O- and ^{18}O-containing samples over a range of temperatures and magnetic fields, a special experimental set-up (schematically shown in figure 1) was designed to permit simultaneous measurement for both samples. A standard gas flow cryostat (from APD Cryogenics) was modified by addition of an extended sample holder (shown on the right hand side in figure 1) allowing both samples to be kept under exactly the same conditions and to perform four probe resistivity measurements while collecting the Mössbauer data. Relatively high magnetic field from the compact LakeShore EM4-CV electromagnet was achieved using a miniature sample holder with only 13 mm diameter vacuum chamber. As a drawback of this, sample temperature could not be lowered below 100 K, while a standard sensor at the heat exchanger showed 77 K. Therefore the sensor was used only for controlling the temperature. The actual temperature of the samples was measured with a differential thermocouple with the cold end placed in close
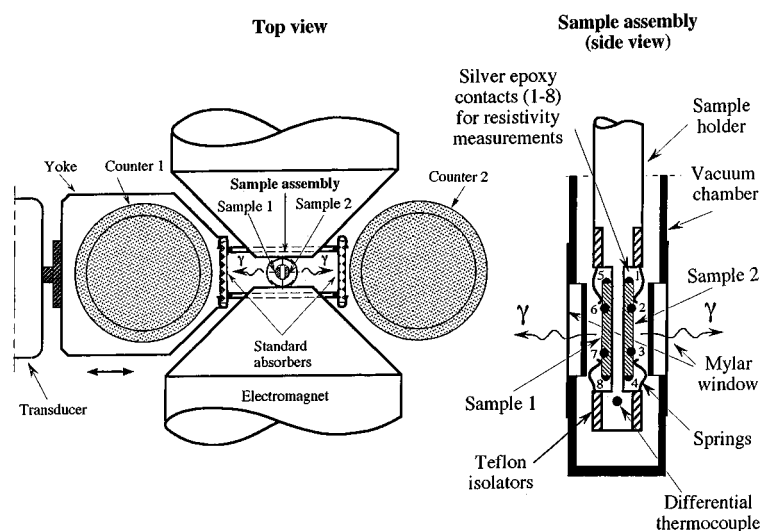
Figure 1. Experimental set-up for simultaneous Mössbauer and resistivity measurements for both ^{16}O and ^{18}O substituted La$_{0.8}$Ca$_{0.2}$Mn(^{57}Co)O$_3$.

proximity to the samples and the other end kept outside at 0 °C. Surfaces of the copper sample holder were electrically insulated from the samples by thin layers of epoxy mixed with copper powder for better thermal conductivity. Highly conducting silver epoxy contacts were used to provide all the wiring for resistivity measurements (figure 1, right hand side). A dual constant acceleration spectrometer was used to provide simultaneous Mössbauer effect measurements of the two samples in exactly identical conditions. To accomplish this the velocity transducer was equipped with a special light weight non-magnetic yoke moving two standard absorbers placed on the opposite sides of a ring-shaped frame inside which a sample assembly could be inserted from the top and sit between the magnet's poles with a minimal gap (see figure 1, left hand side). The dual spectrometer comprised the two identical radiation registration blocks powered from the same source and two PCs with PCA cards both synchronized from the Electronic Drive generator (ED-600 from Ranger Scientific) which produced channel advance and address reset pulses.

Standard K$_4$[Fe(CN)$_6$] pellets containing 0.20 mg cm^{-2} of ^{57}Fe were used as standard absorbers. Mössbauer effect measurements were performed in the temperature range 100–300 K and in external magnetic fields up to 1.8 T. The statistics for each spectrum below T_c was about 10^6 counts per channel, and the resistivity was checked repeatedly during the data collection. This allowed direct comparison of the resistivity values with Mössbauer effect parameters at the same temperature. Temperature stability was about ±0.2 K and the accuracy of the temperature determination was ±2 K at all temperatures.

The observed spectra in the 100 K < T < T_c range are complex (see, for example, figure 2) and their computer analyses were accomplished in several stages depending on the nature of desired information, including fitting of additional runs in expanded scales and different external magnetic fields. The shape of the magnetically split component and its evolution with temperature have been discussed earlier [19]. The distribution in hyperfine internal fields is quite symmetrical which allows us to approximate the magnetic component by individual sextet(s) with broadened lines and obtain meaningful information [19]. In a preliminary fit, the intensities of the different lines of the magnetically split spectra as well as

their line widths were estimated with a good accuracy by approximation of the experimental spectra as a superposition of three doublets instead of a sextet, and a singlet (or doublet with small quadrupole splitting, Q_s) representing the 'paramagnetic component'. This helps in feeding information to the final fitting program which yields the hyperfine parameters, i.e. internal magnetic field H_{int}, Q_s (if any) and the associated angle Θ between the major axis of the electric field gradient (EFG) and the direction of the magnetization and the centre (isomer) shift, at different temperatures [19].

3. Observations and discussion

In figures 2 and 3, we depict the Mössbauer spectra of $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ at an intermediate temperature and in the vicinity of T_c respectively, with and without application of an external magnetic field (H_{ext}). From the spectra obtained without H_{ext} in figures 2 and 3, one can see that a central peak grows at the expense of the magnetically split sextet(s) with increasing temperature; the bulk ferromagnetic order breaks down and small spin clusters are formed, which interact with each other quite strongly as reported earlier [19]. If at any specific temperature the available thermal energy, kT is sufficient to overcome the anisotropic barrier, then the magnetic vector of the cluster can oscillate between the two easy directions at a frequency higher than the Larmor frequency of the excited ^{57}Fe ($\sim 10^8$ s^{-1}) and the net magnetic field experienced by the nucleus could be zero. If there is some distribution in cluster size, and/or the bulk ferromagnet continues to form fresh clusters as temperature increases,
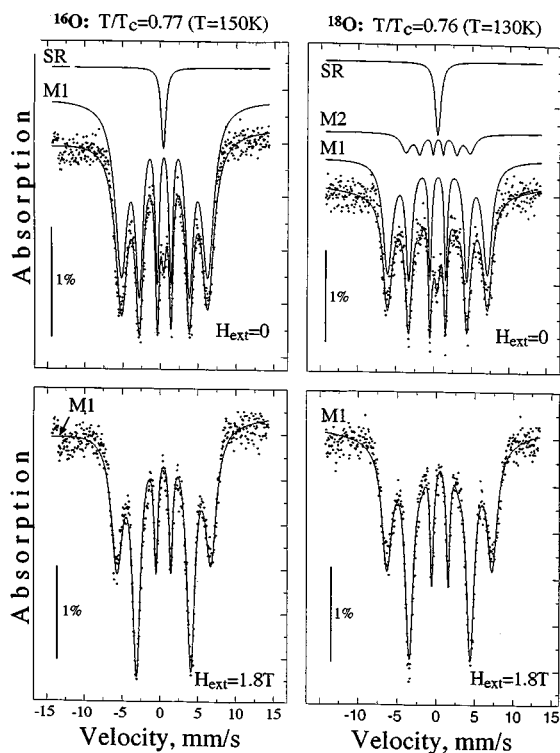

Figure 2. Computer analysed Mössbauer spectra of ^{16}O and ^{18}O substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ with and without $H_{ext} = 1.8$ T well below T_c.
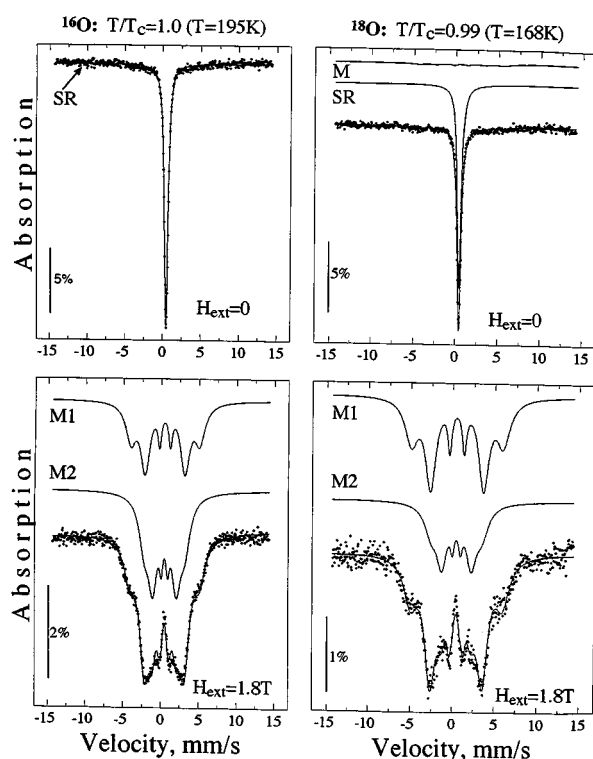
Figure 3. Computer analysed Mössbauer spectra of ^{16}O and ^{18}O substituted La$_{0.8}$Ca$_{0.2}$Mn(^{57}Co)O$_3$ with and without $H_{ext} = 1.8$ T at $T/T_c \approx 1$.

the central peak representing the superparamagnetically relaxed component will grow at the expense of the bulk. The size of the spin clusters is determined by the degree of delocalization of the holes.

The ferromagnetic metal to 'paramagnetic' insulator transition temperatures (T_c) were determined by observing the temperature at which the magnetically split sextet vanishes completely. The observed T_c values for the ^{18}O and ^{16}O compound were 170 and 195 K. The resistivity measurements supported these estimates.

The Mössbauer spectra for the ^{16}O substituted compound can be fitted with only a central peak and a single sextet, except perhaps near T_c. On the other hand, the spectra for the ^{18}O compound require a fit with two sextets apart from the central peak, except at low temperatures (figures 2, 3 and figure 2 of [19]). On application of $H_{ext} = 1.8$ T, the central peak, arising from superparamagnetic relaxation of the small spin clusters, vanishes completely. In the ^{18}O compound, the spin clusters convert to give regular bulk ferromagnetism with completely delocalized holes (M1) and an intermediate size clusters with poorly ordered spins and thereby exhibiting a smaller H_{int} (M2). On the other hand, in the ^{16}O compound, only the bulk ferromagnetic component is observed under the influence of H_{ext}, except when $T/T_c > 0.80$. Moreover, H_{int} for components belonging to intermediate size clusters as well as that for the regular bulk ferromagnet increases by application of $H_{ext} = 1.8$ T due to an improved ordering of spins (figures 2 and 3).

How does one rationalize these observations? Apparently, the long range ferromagnetic interactions are breaking down in large sections of La$_{0.8}$Ca$_{0.2}$MnO$_3$ material even below T_c.
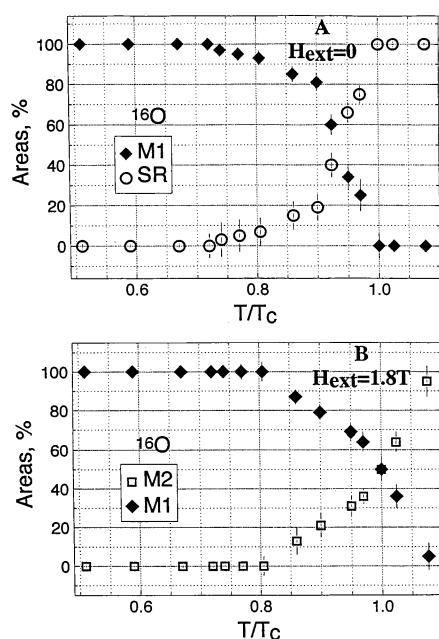
Figure 4. The abundances (areas) of small spin clusters (with superparamagnetically relaxed peaks), bulk ferromagnetic (M1) and intermediate size cluster (M2) components as a function of T/T_c for the ^{16}O substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ (A) with zero field; (B) with an external field of 1.8 T.

In some sections of the material, the electron DE hopping is restricted to small regions resulting in superparamagnetic-like behaviour. The broadening of the spectral lines also suggests that the spins are not ordered well; the smaller the spin clusters with limited delocalization of electrons and lower rate of DE hopping, the less the degree of spin ordering. When an external magnetic field is applied, the regions of spin order and electron delocalization grow in size and the rate of DE hopping also increases synergetically. The question arises as to what causes the spin disorder and break-up of the long range ferromagnetic order below T_c? The abnormal thermal expansion of manganites [20–22], the occurrence of nonlinear temperature dependence in the oxygen rms displacements and the anomalous increase in the Mn–O bond lengths with temperature below T_c [22–24] are clearly indicative of the high degree of anharmonicity associated with vibrations of the Mn–O–Mn moiety. The anomalous stretching of Mn–O bonds would result in decrease of hybridization and exchange interaction associated with diminished frequency of DE electron hopping. An increase of the amplitude of torsional oscillations between neighbouring Mn–O octahedra would also contribute toward slowing down the rate of electron hopping as the electron hop between neighbouring spins will occur only with appropriate configurations acquired statistically as a result of thermal fluctuations [25]. This picture leads to a very interesting phenomenon, the regions of manganite exhibiting superparamagnetic-like behaviour of small spin clusters are mobile and would change position continuously with thermal fluctuations in local phonon density. This is akin to a dynamic stripe. Application of an external magnetic field suppresses the spin disorder and thereby enhances the rate of DE hopping and increases the exchange interactions.

The area (abundance) of the components belonging to small spin clusters exhibiting superparamagnetic behaviour, as well as that of the sextets for ^{16}O and ^{18}O compounds with
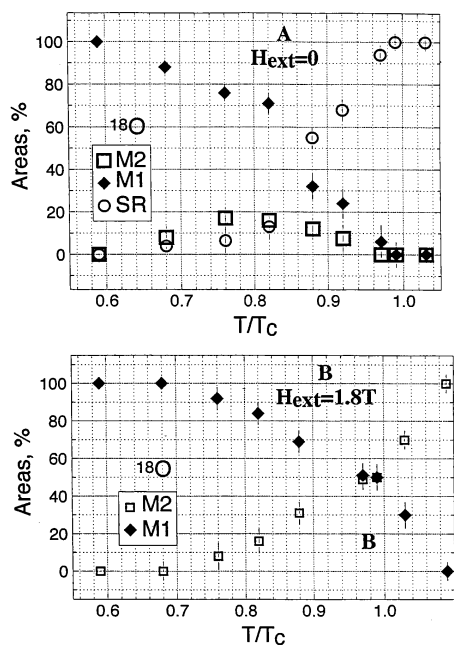
Figure 5. The abundances (areas) of small spin clusters (with superparamagnetically relaxed peaks), bulk ferromagnetic (M1) and intermediate size clusters (M2) components as a function of T/T_c for the ^{18}O substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ (A) with zero field; (B) with an external field of 1.8 T.
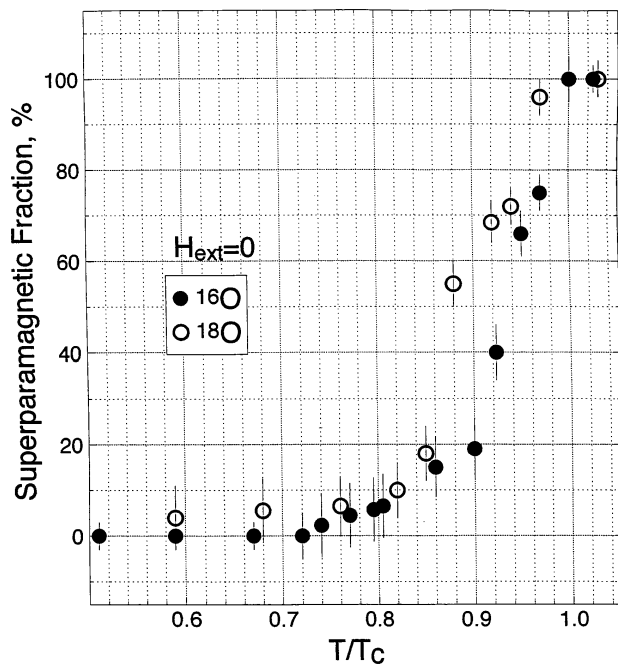

Figure 6. The abundance of superparamagnetic-like small spin clusters for ^{16}O and ^{18}O substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ as a function of T/T_c.
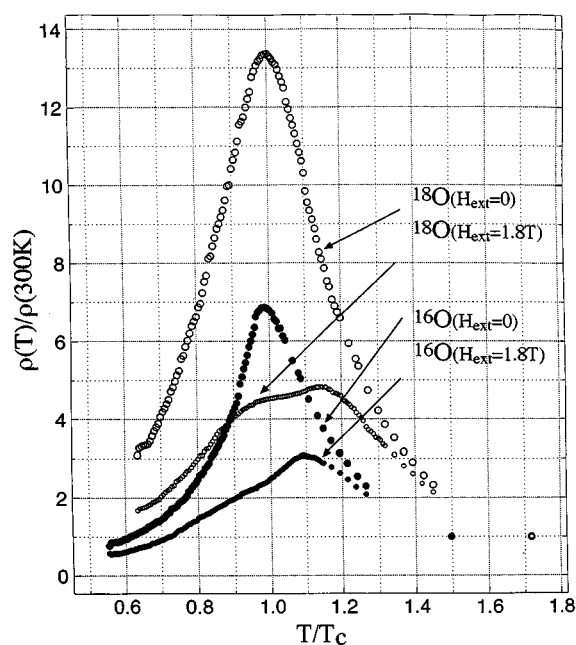
Figure 7. The resistivity of ^{16}O and ^{18}O substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ as a function of T/T_c.

and without H_{ext}, are plotted in figures 4 and 5, respectively. From figure 4, one can see that for the ^{16}O compound, at $T/T_c = 0.95$, the abundance of the collapsed component is about 66%, and on application of H_{ext} 31% of units go to form intermediate size clusters (M2) and the remaining 35% of units consolidate to exhibit bulk ferromagnetism (M1). Similarly, for the ^{18}O compound, the collapsed component constitutes about 94% at $T/T_c = 0.97$ (figure 5). Application of $H_{ext} = 1.8$ T causes roughly half of the small spin clusters to consolidate to give bulk ferromagnetism (M1) and the other half forms intermediate size clusters (M2). The abundance of the superparamagnetic-like component for ^{16}O and ^{18}O compounds is plotted as a function of T/T_c in figure 6. Surprisingly, in the ^{18}O compound, the ferromagnetism starts crumbling at a lower T/T_c than for ^{16}O. For instance, at $T/T_c = 0.925$, about 68% of the ^{18}O substituted compound breaks down into small clusters as compared to only 40% for the ^{16}O counterpart. These findings are consistent with the observation of higher resistivity for the ^{18}O substituted compound versus ^{16}O for the same T/T_c (refer to figure 7): the larger the concentration of small spin clusters, the higher the expected resistivity. The ^{18}O compound also exhibits a larger magnetoresistivity than the ^{16}O.

The observations summarized in figure 6 are in apparent contradiction with the fact that the H_{int} at any T/T_c is always larger for the ^{18}O compound as compared to the ^{16}O one (figure 8). This indicates a stronger exchange interaction for the ^{18}O substituted compound as compared to the ^{16}O compound, a surprising observation.

However, the ^{18}O compound is more amenable to the influence of an external field at or above T_c (figures 9 and 10). The internal field of the intermediate size clusters formed by consolidation of small size superparamagnetically relaxed clusters under the influence of $H_{ext} = 1.8$ T is plotted against T/T_c in figure 10. For instance, at $T/T_c = 1.1$, the induced value of H_{int} for the ^{18}O compound is about 16 T as compared to 8.3 T for ^{16}O (figures 9 and 10).
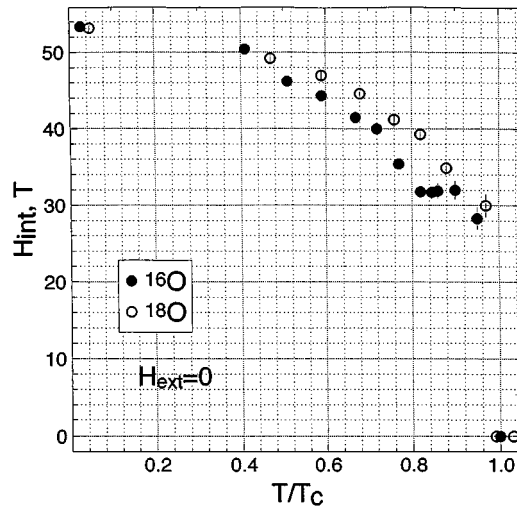
Figure 8. The plots of internal hyperfine fields H_{int} on the ^{57}Fe nucleus for ^{16}O and ^{18}O substituted La$_{0.8}$Ca$_{0.2}$Mn(^{57}Co)O$_3$ as a function of T/T_c.

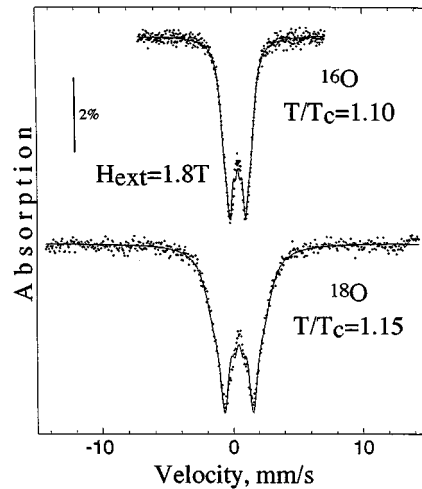**Figure 9.** Demonstration of the different degree of consolidation of small spin clusters under the influence of H_{ext} = 1.8 T above transition temperatures in ^{16}O and ^{18}O substituted La$_{0.8}$Ca$_{0.2}$Mn(^{57}Co)O$_3$.

A very interesting correlation between CMR and consolidation of small spin clusters under the influence of a magnetic field [19] can be discerned by comparing figures 4, 5 and 7. At $T/T_c \geqslant 1.1$, H_{ext} induces only relatively short range order (as only intermediate size spin clusters (M2) are generated) reducing the resistivity but preserving semiconductor-like behaviour due to the spread in the orientation of spins in the clusters and more so between them. At $T/T_c \geqslant 1.1$, small clusters start to form interconnected ferromagnetic filaments (M1) and the resistivity behaviour changes to metallic.

In summary, we observe three broad categories of electronic phases in La$_{0.8}$Ca$_{0.2}$MnO$_3$ below T_c [26], namely bulk-like (M1), intermediate size spin clusters (M2) and small spin
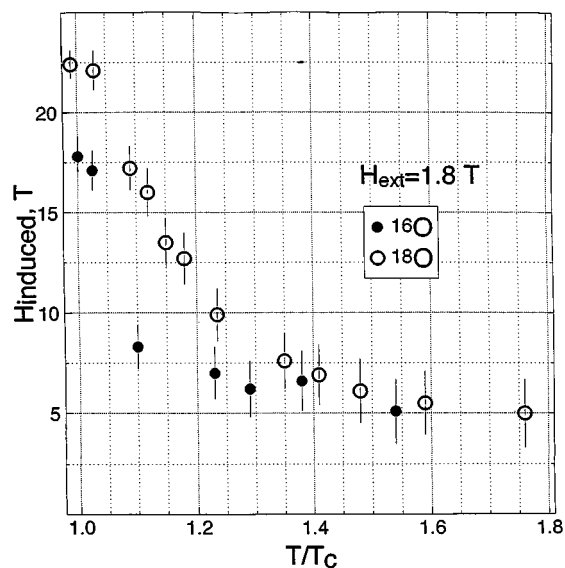
Figure 10. A plot of magnitudes of the internal magnetic fields on the ^{57}Fe nucleus due to the consolidation of small spin clusters under influence of $H_{ext} = 1.8$ T above transition temperatures in ^{16}O and ^{18}O substituted $La_{0.8}Ca_{0.2}Mn(^{57}Co)O_3$ as a function of T/T_c.

clusters which exhibit superparamagnetic behaviour [19, 27, 28]. They may be regarded as spin polarons of differing dimensions. These spin clusters arise presumably due to the anharmonic nature of vibrations in the Mn–O–Mn moiety. The stretched bonds and the higher amplitudes of torsional vibrations lead to slower DE electron hopping resulting in crumbling of long range ferromagnetic order and the formation of small spin clusters. These spin clusters are expected to be highly mobile due to local fluctuations in phonon density akin to dynamic stripes. We observe quite unexpectedly that the ^{18}O compound exhibits stronger exchange interactions as compared to the ^{16}O one at all T/T_c in the range of our measurements and concomitantly exhibits poorer spin ordering with formation of a larger fraction of small spin clusters with superparamagnetic-like behaviour below T_c.

Acknowledgments

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