Topic area: **CMMSP**

An Alternative Interpretation of Mössbauer Spectra for ^{57}Fe-doped Lanthanum Calcium Manganite

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Introduction

It was known some time ago that certain insulating rare earth manganites exhibit a remarkable transition to metallic ferromagnetic behaviour when doped with divalent metal ions. More recently, the observation of "colossal magnetoresistance" associated with this transition has led to a renewed interest in these materials. The ^{57}Fe Mössbauer spectra reported here are for the generic $La_{2/3}Ca_{1/3}MnO_3$ system with a dilute 0.5 at. % concentration of enriched ^{57}Fe nuclei introduced into the Mn sub-lattice. When we first recorded these spectra, it was anticipated that they might provide insight into the hole hopping process of the "double exchange" interaction that is responsible for the ferromagnetic transition. However, attempts to interpret them in terms of local electronic fluctuation proved unsuccessful. Simopoulos *et al.* [1,2] then reported similar spectra with a 1 at. % ^{57}Fe substitution. Based on the simple magnetic hyperfine field (B_{hf}) distribution model that they used to analyse their spectra, the ^{57}Fe probe nuclei could be divided into two categories: those which were in a "paramagnetic phase" with zero (or very small) B_{hf} and those which experienced a distribution of non-zero B_{hf}. One possible explanation for this is that the paramagnetic phase corresponds to ferromagnetic regions of the Mn sub-lattice small enough that their superparamagnetic-like fluctuation rates exceed the characteristic Larmor precession frequency of the ^{57}Fe nuclei (≈60 MHz) [1-4]. With decreasing temperature, the ferromagnetic regions might then coalesce into larger regions with slower fluctuation rates so that the paramagnetic component diminishes. For the analysis presented here, we adopt a slow relaxation model that was initially developed by Bocquet *et al.* [5,6] for magnetic clusters in iron oxides and compare it with the distributed-field model. The derived Mn sub-lattice magnetisation behaviour is then compared with results reported elsewhere using ^{55}Mn NMR [7,8], neutron diffraction [2] and μ^+SR [9].

Experimental results and analysis

The single-phase, ^{57}Fe-doped specimen was prepared from a stoichiometric mix of La_2O_3, $CaCO_3$, $^{57}Fe_2O_3$ and MnO_2 via three successive solid state reactions (1250 °C in air) with intermediate grinding and pressing. DC magnetisation measurements yielded $T_C \approx 250$ K, compared with $T_C \approx 273$ K for the pure manganite [8, 9]. The T_C suppression is brought about by the antiferromagnetic coupling of the ^{57}Fe probes with the surrounding Mn lattice and is about half that reported by Simopoulos *et al.* [2] for their 1 at. % ^{57}Fe concentration. Mössbauer spectra were recorded over the temperature range of 4.2 – 300 K using a ^{57}Co**Rh** source and an absorber of 190 mg of specimen material in a 5 cm^2 holder.

At the extremes of the temperature range, the Mössbauer spectra are relatively straightforward (Figure 1). The room temperature Mössbauer spectrum is a single unresolved doublet corresponding to the single Mn site. At 4.2 K, the spectrum is a single magnetically-split sextet. The fit parameters for the room temperature and 4.2 K spectra are summarised in Table 1 where they are compared with the results of Simopoulos *et al.* [2]. The 4.2 K value of B_{hf} = 52.4 T corresponds to the high spin S = 5/2 state of Fe^{3+} (typically 51 – 54 T).

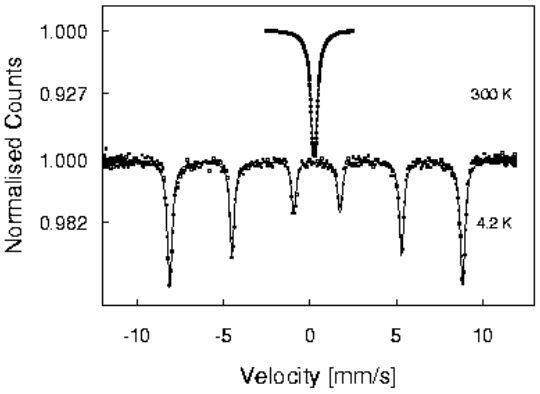

Figure 1: ^{57}Fe Mössbauer spectra for ^{57}Fe-doped $La_{2/3}Ca_{1/3}MnO_3$ at 300 K and 4.2 K.

Table 1: Mössbauer parameters (isomer shift is relative to α-Fe) from fits to $La_{2/3}Ca_{1/3}MnO_3$ spectra at room temperature and 4.2 K. Simple Lorentzian line shapes were employed.

T [K]	B_{hf} [T]	½e^2qQ [mm/s]	δ [mm/s]	Γ_{FWHM} [mm/s]	
300		0.16(2)	0.409(4)	0.38(2)	0.5 at. %
		0.184(3)	0.368(2)	0.378(2)	1 at.%[2]
4.2	52.7(1)	-0.03(1)	0.50(4)	0.25(3)	0.5 at. %
	53.1(1)	-0.036(2)	0.515(1)	0.374(4)	1 at. %[2]

In the intermediate temperature range, the magnetic spectrum is seen to collapse with increasing temperature (Figure 2 on the next page). The line broadening is typical of electronic relaxation processes except for the fact that it is strongly asymmetric. This asymmetry is reflected in the shape of the B_{hf} distributions that result (Figure 2a) when the spectra are fitted using the P(B) approach of Le Caer and Dubois [10]. In each case, the probability increases gradually with B_{hf} value, peaks at the modal B_{hf} value, and then cuts off sharply. The "paramagnetic" phase is also evident as a probability peak in the vicinity of zero B_{hf}. The modal B_{hf} value and the percentage of paramagnetic phase component are presented as a function of temperature in Figure 3. Note that the first order perturbation approach adopted by Le Caer and Dubois is least reliable for temperatures close to T_C where the magnetic and quadrupole interaction strengths are comparable.

On the basis of a close similarity between the present spectra and spectra reported for certain iron oxides [5,6], we propose that the same slow relaxation model employed by those authors is suitable for the present work. ^{55}Mn NMR studies [7] imply hole hopping rates of the order of 400 MHz, fast compared with the NMR and Mössbauer time scales. Hence each ^{57}Fe nucleus is expected to experience a B_{hf} proportional to the probe's average local electronic moment. The local moment is, in turn, determined by both the temperature and the strength of the Fe^{3+} ion's exchange interaction with its surrounding Mn sub-lattice. However, slow fluctuation of a large magnetic "cluster" in which the probe is located means that the B_{hf} presents a Boltzmann distribution of z-components. This leads to a distribution of B_{hf} similar to that fitted by the P(B) approach. The fitted theory curves are shown in Figure 2b and the temperature dependences of the maximum B_{hf} value and the percentage of the paramagnetic phase component are included in Figure 3. The maximum B_{hf} is seen to be slightly larger than the modal value obtained by the distributed-field approach.

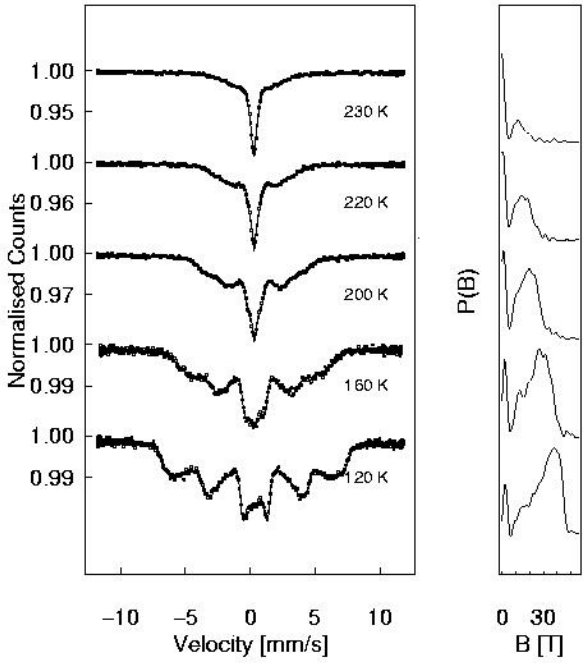

Figure 2a: P(B) approach fits (solid curves) to selected intermediate temperature Mössbauer spectra for ^{57}Fe-doped $La_{2/3}Ca_{1/3}MnO_3$.

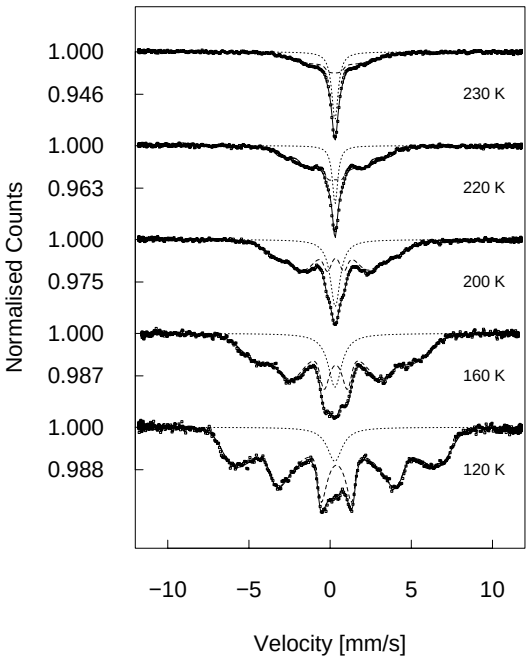

Figure 2b: Cluster model [5, 6] fits for the same selected intermediate temperature Mössbauer spectra.

Discussion and conclusion

The slow-relaxation, cluster model approach is seen to provide very similar results to those of the distributed-field approach. However, there is now a physical basis for the spectrum analysis. It is worthwhile to compare the probe B_{hf} results thus derived with magnetisation data obtained using other measurement techniques. First, we follow the lead of Hannoyer *et al.* [11] and consider the trivalent ^{57}Fe probes as magnetic impurities in the Mn host sub-lattice. Assuming S = 5/2, g = 2 for Fe^{3+}, it is then possible to estimate the exchange field, B_{ex}, that is required to induce the observed B_{hf} (assuming that B_{hf} is proportional to the induced electronic moment). The exchange field is expected to follow the Mn sub-lattice magnetisation more closely than the raw B_{hf} data. The reduced exchange field, $B_{ex}/B_{ex}(sat)$, is presented in Figure 4 as a function of the reduced temperature, T/T_C. Also included in Figure 4 are the reduced Mn moment (determined by neutron diffraction [2]), ^{55}Mn moment (determined by NMR [8]) and μ^+SR resonance frequency [9] data for undoped specimens.

The present data are in closest agreement with the μ^+SR data. However, these two sets of data lie below the curves for neutron diffraction and ^{55}Mn which, in turn, are in close agreement with one another. It appears that the two indirect probes of the Mn sub-lattice give a low estimate of the Mn magnetisation. It is possible that the B_{ex} at the Fe probes does not follow the bulk Mn magnetisation but rather a local magnetisation that is dragged down by the presence of the (antiferromagnetically-coupled) probe itself. A similar mechanism for the μ^+SR probe is not immediately obvious, although the nature of the interstitial site(s) of the muons may play a role. One problem is that the doped specimen exhibits a lower T_C. Small variations in stoichiometry and thermal history might also be responsible for different behaviour of the other specimens. It would be interesting to repeat all four measurement techniques on the same 0.5 at. % Fe-doped specimen.

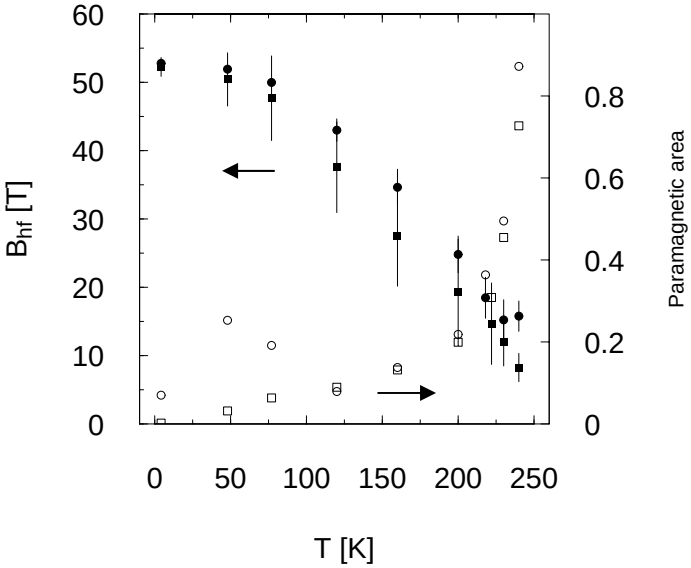

Figure 3: Temperature dependence of B_{hf} together with the fractional area of the paramagnetic component (■□ P(B) approach; ●○ cluster model approach)

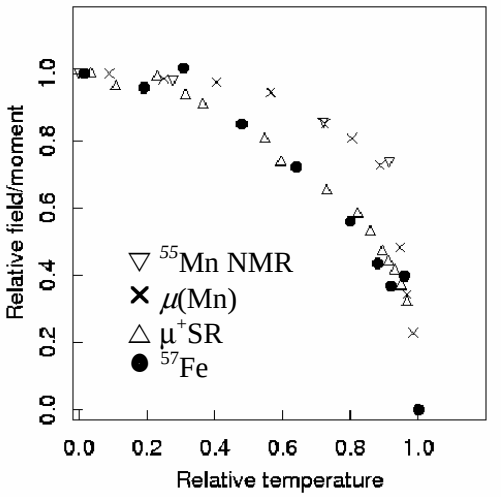

Figure 4: Reduced Mn sub-lattice data as a function of reduced temperature (▽ ^{55}Mn NMR T_C = 270 K [7]; × μ(Mn) neutron diffraction, T_C = 270 K [2]; △ μ^+SR, T_C = 274 K [9]; ● ^{57}Fe, T_C = 250 K cluster fit, this work).

Conclusion

In conclusion, the relaxation spectra recorded for ^{57}Fe probes in $La_{2/3}Ca_{1/3}MnO_3$ can be fitted with a cluster model approach. It would appear that the local electronic fluctuations due to the double exchange hole hopping process are too fast to be observed by ^{57}Fe Mössbauer spectroscopy. Instead, the relaxation effects in the Mössbauer spectrum are probably due to the slower fluctuation of larger ferromagnetic regions of the Mn sub-lattice.

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