A ^{55}Mn nuclear magnetic resonance study of mixed-valence manganites

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Abstract. The temperature dependence of the ^{55}Mn nuclear magnetic resonance of some manganese perovskites of the form $[La_{1-x}A_x]MnO_3$ (A = Ca, Sr) for x of 1/3 is reported. The ^{55}Mn spin-echo spectra were measured in zero field and in an applied magnetic field up to 6 T for polycrystalline samples of $[La_{0.67-y}Tb_yCa_{0.33}]MnO_3$ ($y = 0, 0.1, 0.22$), $[La_{0.6}Y_{0.07}Ca_{0.33}]MnO_3$ and $[La_{0.7}Sr_{0.3}]MnO_3$. The single resonance line observed for all compounds, for temperatures between 4.2 K and 293 K, is attributed to a fast carrier motion ($<10^{-9}$ s) between the Mn^{3+} and Mn^{4+} sites resulting from the double-exchange mechanism. For some of the samples the zero-field nuclear magnetic resonance signal has been detected at temperatures far above the magnetic ordering temperature, providing direct evidence of magnetic correlations whose lifetime is greater than 10^{-5} s. The correlations can possibly be related to magnetic polarons.

1. Introduction

The alkaline-earth-doped, mixed-valence manganites of the general formula $[La_{1-x}A_x]MnO_3$, where A = alkaline-earth metal, have recently attracted a great deal of renewed interest in their magnetoresistive properties and their potential applications. The compounds exhibit many interesting phenomena related to their structural, magnetic and transport properties, including a huge negative magnetoresistance occurring around the magnetic ordering temperature [1–5]. The magnetoresistance defined as $(R(0) - R(H))/R(0)$, where $R(H)$ is the resistivity in a magnetic field H, in some materials such as $[La_{0.6}Y_{0.07}Ca_{0.33}]MnO_3$ exceeds 100.000% [6]. This behaviour has been termed 'colossal magnetoresistance' (CMR).

The magnetic properties of these compounds are governed by the superexchange and double-exchange mechanisms. The superexchange dominates in the compounds containing solely Mn^{3+} or Mn^{4+} ions, e.g. $LaMnO_3$ and $CaMnO_3$, leading to antiferromagnetic structures. Partial substitution for the trivalent rare earth with a divalent alkaline-earth metal introduces holes at the Mn^{3+} sites, i.e. produces a mixture of the Mn^{3+} and Mn^{4+} ionic states. A hopping of carriers between the Mn^{3+} and Mn^{4+} adjacent sites leads to a ferromagnetic coupling of the

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Mn spins called double exchange [7]. The ratio of the rare-earth to alkaline-earth content of 2:1 corresponds to the optimum conditions for the double-exchange mechanism and, thus, to the highest magnetic ordering temperatures (T_C). Such optimally doped perovskites, where RE = La, exhibit a metallic conductivity below T_C and an 'activated' temperature dependence of the conductivity above T_C. Existence of polarons has been indicated for cuprates [8] and manganites [9, 10]. The transport properties below T_C have been attributed to electron hopping between large magnetic polarons [11]. The existence of magnetic polarons above T_C has been suggested by small-angle neutron scattering experiments (SANS) [12, 13] and by La NMR [14].

Nuclear magnetic resonance (NMR) allows the study of the properties of magnetic materials at the microscopic level via hyperfine interactions. In zero-field NMR, the hyperfine fields, probed by the resonant response of nuclear magnetic moments at individual atomic sites, provide information on the local magnetic states. Resonance occurs at a frequency ν when $2\pi\nu = \gamma B_e$, where γ is the nuclear gyromagnetic ratio ($\gamma/2\pi = 10.553$ MHz T^{-1} for ^{55}Mn and B_e is the effective internal magnetic field, arising largely from hyperfine interactions. The ^{55}Mn NMR spectra have been reported for [La$_{1-x}$Ca$_x$]MnO$_3$ [15, 17] and [La$_{1-x}$Sr$_x$]MnO$_3$ [17] compounds at 4.2 K and 77 K. The only NMR data up to the magnetic ordering temperature was reported for [Pr$_{0.7}$Ca$_{0.15}$Sr$_0$.15]MnO$_3$ and [Pr$_{0.7}$Ba$_{0.3}$]MnO$_3$, where the temperature-driven change from localized Mn^{3+} and Mn^{4+} states to the fast-hopping regime was observed [18]. The present NMR study provides information on the state of Mn ions below the magnetic ordering temperature and the nature of magnetic clusters above it in a range of samples, including both La–Y and La–Tb systems.

2. Experimental procedure

A series of swept-frequency, spin-echo, nuclear magnetic resonance measurements was carried out on polycrystalline powder samples, using an automated, computer-controlled spectrometer [19]. This spectrometer has a flat frequency response from 10 MHz to 1000 MHz, providing a far better dynamic range than in other studies of related systems [16]. Measurements were made in zero magnetic field and in applied fields of up to 6 T at temperatures between 4.2 K and 293 K. Spin-echo spectra were obtained by measuring the integrated echo intensity versus frequency. A two-pulse sequence, consisting of two radio-frequency pulses, 1 μs and 2 μs (or 0.2 μs and 0.4 μs) in length, separated by $\tau = 7$ μs, was used. The magnetic properties of the samples studied are shown in table 1 [11, 20–22].

3. Results

The ^{55}Mn NMR spin-echo spectra obtained at various temperatures for [La$_{0.67}$Ca$_{0.33}$]MnO$_3$ and [La$_{0.45}$Tb$_{0.22}$Ca$_{0.33}$]MnO$_3$ are presented in figure 1. The spectra show a single resonance line for all of the samples at all temperatures. Central frequencies and linewidths obtained from fitting the resonance lines with a Gaussian curve are collected in the table 1. The values of B_e obtained from central frequencies using a conversion factor of 10.552 MHz T^{-1} are also given in table 1. The single line in the ^{55}Mn NMR spectra found in these compounds was attributed to a fast hopping of the carriers between the Mn^{3+} and Mn^{4+} sites, resulting from the double-exchange interaction [15]. The single line indicates that the hopping time for hops between neighbouring Mn^{3+} and Mn^{4+} sites, τ_h, is much shorter than the period of the Larmor precession of the Mn nuclear spins, τ_L, which is of the order of 10^{-9} s, so the nuclear spins see a 'motionally' averaged hyperfine field corresponding to an averaged Mn^{3+}/Mn^{4+} state. For a value of τ_h comparable to or larger than τ_L, one would expect a

Table 1. Magnetic data, temperatures of NMR measurements T, linewidths Γ, central frequencies v_0 and hyperfine fields B_e.

	T (K)	Γ (MHz)	v_0 (MHz)	B_e (T)
$[La_{0.7}Sr_{0.3}]MnO_3$	293	17	274.1	26.1
Ferromagnetic	198	18	343.3	32.7
$T_C = 370$ K [11]	77	20	375.6	35.8
	4.2	22	382.7	36.4
$[La_{0.67}Ca_{0.33}]MnO_3$	250	21	280.2	26.7
Ferromagnetic	198	28	325.2	31.0
$T_C = 270$ K (this work)	77	20	373.1	35.5
	4.2	20	381.0	36.3
$[La_{0.57}Tb_{0.1}Ca_{0.33}]MnO_3$	212	22	305.5	29.1
Ferromagnetic	198	18	315.9	30.1
$T_C = 160$ K (this work)	77	25	371.1	35.3
	4.2	22	379.4	36.1
$[La_{0.45}Tb_{0.22}Ca_{0.33}]MnO_3$	165	20	336.5	32.0
Spin glass	77	26	372.4	35.5
$T_g = 44$ K [22]	4.2	22	379.4	36.1
$[La_{0.6}Y_{0.07}Ca_{0.33}]MnO_3$	165.0	40	327.2	31.0
Ferromagnetic	150	40	337.7	32.0
$T_C = 160$ K (this work)	77	34	370.9	35.3
	4.2	31	381.2	36.3

broadening of the line or, eventually, separate Mn^{3+} and Mn^{4+} resonances, as has recently been observed for $[Pr_{0.7}Ba_{0.3}]MnO_3$ [18]. The single, averaged Mn state, deduced from the present NMR measurements, is consistent with the recent results of an x-ray diffraction study of $[La_{0.67-y}Tb_yCa_{0.33}]MnO_3$ where no evidence for the existence of Mn^{3+} and Mn^{4+} was found [20].

The spin-echo spectra of the $La_{0.67}Ca_{0.33}MnO_3$ and $[La_{0.57}Tb_{0.1}Ca_{0.33}]MnO_3$ samples at 4.2 K have also been measured in an applied magnetic field of up to 6 T. In the applied field a single resonance line was observed for both compounds. The line revealed a shift towards lower frequencies, indicating an antiparallel orientation of the manganese hyperfine field with respect to the magnetization for both samples and no satellite lines were observed. The linewidths were close to those for zero-field spectra indicating a negligible anisotropy of the hyperfine interactions, and the slope of the central frequencies versus applied magnetic field was very close to that expected from the ^{55}Mn gyromagnetic ratio for an internal (hyperfine) field antiparallel to the applied field. The antiparallel orientation of the hyperfine field with respect to the Mn magnetic moment indicates that the polarization of the core electrons by the spin of the parent atom is the dominant contribution to the manganese hyperfine field. From the theoretical calculations for manganese intermetallics, a value of the hyperfine coupling constant for the core polarization with the Mn spin moment of 10 T/μ_B has been obtained [23] Using this value we arrive at a Mn magnetic moment value of 3.8 μ_B which is very close to that of 3.67–3.7 μ_B expected from the Mn^{3+}/Mn^{4+} ratio deduced from the content of the trivalent lanthanide and divalent alkaline-earth metal. This result indicates that the other contributions to the hyperfine field, i.e. the contribution from polarization of the valence electrons and from an unquenched orbital moment, are probably negligibly small.
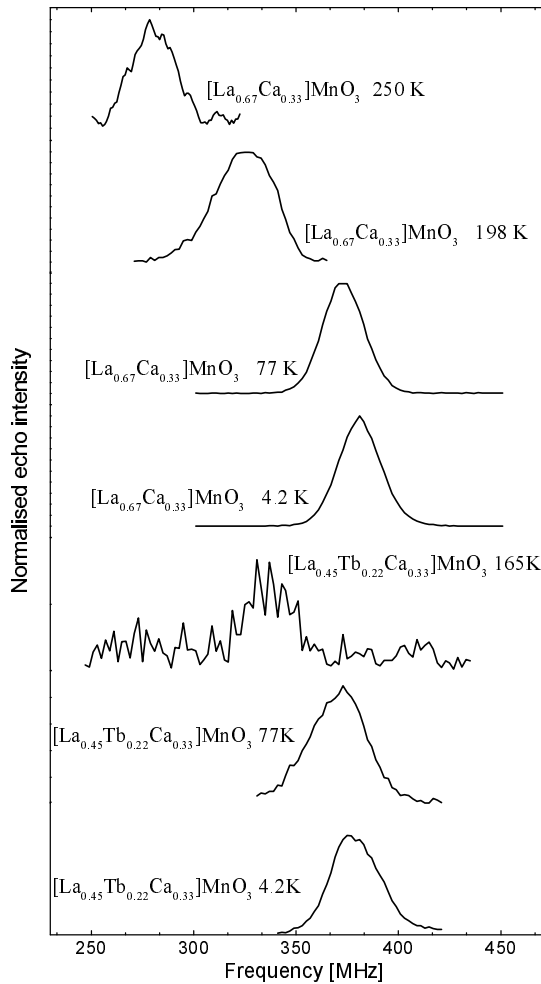
Figure 1. The ^{55}Mn spin-echo spectra of [La$_{0.67}$Ca$_{0.33}$]MnO$_3$ and [La$_{0.45}$Tb$_{0.22}$Ca$_{0.33}$]MnO$_3$.

4. Discussion

A striking feature of our measurements is that the 'magnetic signal' corresponding to a nonvanishing hyperfine field at the Mn nucleus exists for [La$_{0.45}$Tb$_{0.22}$Ca$_{0.33}$]MnO$_3$ at the temperature 165 K, far above the spin-glass temperature, $T_g = 44$ K [22]. It is also present at the temperature of 212 K for ferromagnetic [La$_{0.57}$Tb$_{0.1}$Ca$_{0.33}$]MnO$_3$ which has a magnetic ordering temperature $T_C = 160$ K and at 165 K for ferromagnetic [La$_{0.6}$Y$_{0.07}$Ca$_{0.33}$]MnO$_3$ with $T_C = 160$ K. The hyperfine field which reflects the magnitude of the local magnetization decreases only slightly with temperature, retaining for some samples more than 80% of its low-temperature value at T_C or T_g, figure 2, whereas in normal ferromagnets it tends to zero on approaching T_C and no zero-field signal is observed above T_C. The persistence of this signal at elevated temperatures indicates the presence of unusual magnetic correlations extending to temperatures much higher than T_g or T_C and corresponding to the clusters of Mn spins coupled by the double-exchange interaction. This observation is consistent with the results of a recent neutron scattering experiment on [La$_{0.67}$Ca$_{0.33}$]MnO$_3$ where it was found that the spin stiffness
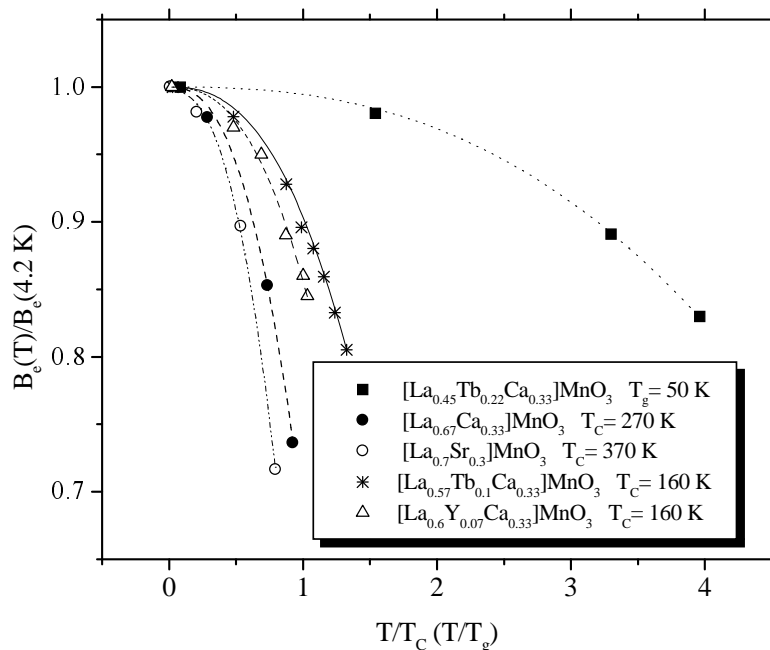
Figure 2. The temperature dependence of the reduced hyperfine field $B_e(T)/B_e(4.2\,\text{K})$ for selected samples.

coefficient D does not vanish at T_C, maintaining half of its low-temperature value [24]. It was confirmed by the AC susceptibility measurements that the samples were single phase, with no trace of an impurity phase with a higher magnetic ordering temperature. The temperature dependence of the NMR signal intensity approximately follows the temperature dependence of the bulk magnetization, figure 3, which excludes the possibility of an impurity phase as the origin of the magnetic signal above T_C. Also the key NMR parameters such as T_1, T_2 and linewidths marked in figure 3 do not show any significant changes related to a critical behaviour on crossing T_C. This shows that the magnetic behaviour in the ferromagnetic regions above T_C is identical to the magnetic behaviour of the whole sample below T_C, and that therefore the high-temperature signal does not arise from spurious magnetic phases.

The lifetime of these correlations, τ_c can be evaluated at $\tau_c \geqslant 10^{-5}$ s, which is a necessary condition for obtaining the NMR spin-echo signal in a magnetic field produced by correlated magnetic moments. Such anomalously long correlation times have also been observed in the μSR measurements above T_C [25]. These correlations would correspond to those expected for magnetic polarons. In a recent SANS experiment [13], it was deduced that the size of the magnetic polarons above T_C was in the range between 8 and 20 Å. A lack of detectable oscillation of the asymmetry parameter in the μSR measurements above T_C can possibly be explained by a small relative population of polarons which is approximately proportional to the temperature dependence of the reduced magnetization. From our NMR results it can be concluded that in the systems studied in the present work the higher T_C corresponds to a more rapid decrease of polaron population and/or their lifetimes at T_C on increasing the temperature. For these reasons and due to the short relaxation times T_2 at high temperatures, we were not able to measure a signal above T_C for [La$_{0.7}$Sr$_{0.3}$]MnO$_3$ and [La$_{0.67}$Ca$_{0.33}$]MnO$_3$.

The very recent SANS experiment on a [La$_{0.75}$Sr$_{0.25}$]MnO$_3$ single-crystalline sample up to
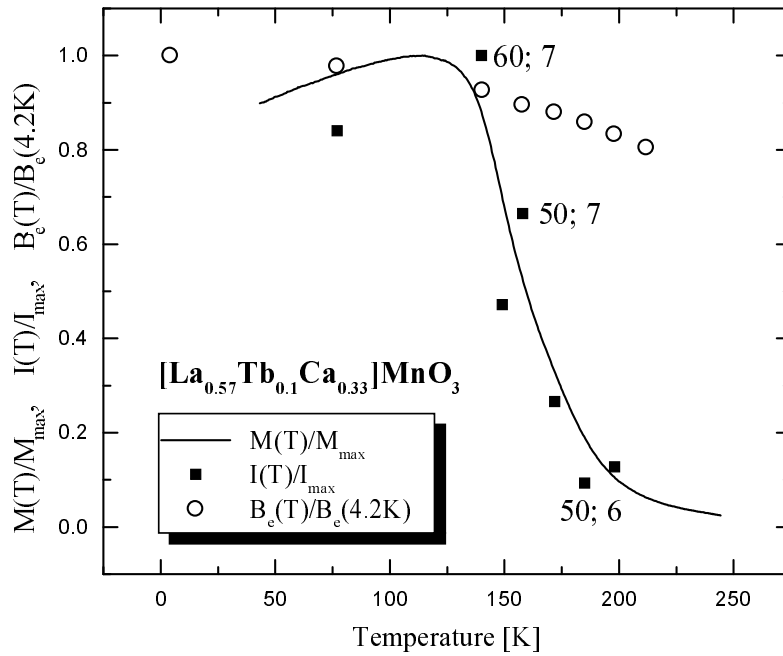
Figure 3. The temperature dependence of the reduced magnetization of the sample at 50 Oe, $M(T)/M_{max}$, the reduced ^{55}Mn hyperfine field, $B_e(T)/B_e(4.2\,\text{K})$, and the reduced intensity of the ^{55}Mn NMR signal (corrected for the transverse relaxation and the temperature dependence of the paramagnetic nuclear magnetization), I/I_{max}, for $[\text{La}_{0.57}\text{Tb}_{0.1}\text{Ca}_{0.33}]\text{MnO}_3$.

450 K showed the existence of magnetic correlations above $T_C = 345\,\text{K}$ which are incompatible with magnetic polarons [26]. This discrepancy can be attributed to the anomalous behaviour of the Sr-containing material which for $[\text{La}_{0.67}\text{Sr}_{0.33}]\text{MnO}_3$ does not show activated conductivity up to about 500 K, far above T_C, in contrast to the Ca-containing samples [27].

A 'motionally narrowed' single line in the NMR spectra of all of the samples and at all temperatures indicates that the ferromagnetic double exchange is the dominant nearest-neighbour magnetic interaction irrespective of the magnetic state of the sample (ferromagnetic, spin cluster or paramagnetic). However, it has been shown theoretically [28] that the occurrence of the double-exchange interaction alone is not sufficient for the material to attain metallic conductivity at low temperatures. An example of this is shown by the compound $[\text{La}_{0.45}\text{Tb}_{0.22}\text{Ca}_{0.33}]\text{MnO}_3$ which behaves as a semiconductor both above and below T_g. In view of the present NMR results, the spin-glass state which was attributed to a competition of the FM and AFM interactions [20–22] can be described as a cluster glass, consisting of frozen clusters of spins coupled within the clusters by the double-exchange interaction.

The temperature variation of the hyperfine field in a magnetic material usually approximately follows the temperature dependence of the magnetization. Thus, the changes of B_e with temperature can be attributed to the temperature variation of the value of the manganese magnetic moment on the NMR timescale, μ_{Mn}. The reduced values of B_e, $B_e(T)/B_e(4.2\,\text{K})$, are plotted as a function of the reduced temperature, figure 2, and fitted with a power function. The best fits have been obtained for a $T^{5/2}$-dependence. This shows that $B_e(\mu_{\text{Mn}})$ does not vanish at T_C and retains nearly 90% of its low-temperature value at T_C for $[\text{La}_{0.57}\text{Tb}_{0.1}\text{Ca}_{0.33}]\text{MnO}_3$ and at $3T_g$ for $[\text{La}_{0.45}\text{Tb}_{0.22}\text{Ca}_{0.33}]\text{MnO}_3$. Despite large differences in magnetic ordering temperature of the materials, $B_e(\mu_{\text{Mn}})$ changes gradually with temperature in a similar way,

table 1, irrespective of the magnetic state, i.e. ferromagnetic, cluster glass or magnetic clusters in the paramagnetic state. It is worth noting, however, that the samples with lower magnetic ordering temperatures exhibit slightly faster decreases of $B_e(\mu_{Mn})$ with increasing temperature, reflecting the smaller strength of the double-exchange interaction.

5. Conclusions

The observation of the zero-field NMR signal at temperatures above the magnetic ordering temperatures provides good evidence for the existence of clusters of neighbouring manganese spins, exchange coupled by a rapidly hopping electron as expected for the double-exchange interaction. The lifetime of the clusters is long (exceeding 10^{-5} s) and there are no changes in the key characteristics of the NMR spectra (other than a change in the signal intensity) as the samples are taken through the magnetic ordering temperature. The existence of magnetic polarons above the ordering temperature may provide an explanation for these phenomena.

Acknowledgments

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