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The Nd–Mn exchange interaction in $Nd_{0.7}Sr_{0.3}MnO_3$

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Abstract

The Nd–Mn exchange interaction in $Nd_{0.7}Sr_{0.3}MnO_3$ is considered by studying its influence on the ^{55}Mn spin-echo NMR lineshape and spin–spin relaxation time. It is seen that the interaction is of considerable strength well above the Nd spin ordering temperature (≈20 K), with a significant influence on the Mn (electron) spin dynamics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The rich physics of colossal magnetoresistive manganites ($R_{1-x}A_xMnO_3$, where R = rare earth and A = alkaline earth) has been the focus of experimental and theoretical research of several groups over the past ten years. Although a universally accepted origin of colossal magnetoresistance, ferromagnetic insulating and charge ordered ground states is as yet elusive, we now have an overall understanding of the major physical phenomena observed—charge and orbital order, local lattice distortions due to the Jahn–Teller effect in the insulating and metallic temperature regimes and competing magnetic interactions [1]. These dominant factors have often overshadowed the role of the magnetic moment of the rare earth ion in influencing the spin dynamics due to an R–Mn magnetic interaction at temperatures well below the Mn spin ordering temperature. Our recent study [2] of the temperature dependence of ^{55}Mn spin-echo NMR in $Nd_{1-x}Sr_xMnO_3$ revealed the significant role played by the Nd magnetic moments in the ferromagnetic state and to the best of our knowledge is the first NMR evidence of rare earth ordering in manganites. In this report we focus on the influence of the Nd–Mn exchange

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interaction on the ^{55}Mn spin-echo lineshape of $Nd_{0.7}Sr_{0.3}MnO_3$. We show for the first time that the Nd–Mn interaction has a significant impact on the spin-echo lineshape well above Nd ordering temperature. We systematically establish the existence of two Mn species that differ in the extents to which they couple with Nd spins. Using single crystals of $Nd_{0.7}Sr_{0.3}MnO_3$ we show that the Nd–Mn interaction has a discernible effect on low temperature electrical resistivity. We estimate the strength of the Nd–Mn interaction and offer a possible explanation for its strong influence on Mn spin dynamics.

2. Experimental details

Nuclear magnetic resonance in ferromagnetic materials occurs at a frequency ν given by $2\pi\nu = \gamma B_e = A\langle S\rangle/\hbar$, where γ is the nuclear gyromagnetic ratio ($\gamma/2\pi = 10.553$ MHz T^{-1} for ^{55}Mn), B_e is the effective internal magnetic field, arising mainly from hyperfine interactions, A is the hyperfine coupling constant and $\langle S\rangle$ the average Mn spin. Since $\langle S\rangle$ for a Mn^{3+} ion is 2 and 3/2 for a Mn^{4+} ion, ^{55}Mn NMR can distinguish between different Mn charge states. In ferromagnetic solids the applied rf field tilts the electronic magnetization (and hence the hyperfine field) from its equilibrium position, giving rise to a transverse component of B_e. Since $B_e \gg B_{rf}$ the effective field experienced by the nuclei is much higher than that actually applied. This 'rf enhancement' is a typical feature of NMR in ferromagnetic solids [3]. The ^{55}Mn NMR spin-echo amplitude and relaxation time measurements were performed with an untuned probe head with a 1 μs-τ-2 μs spin-echo pulse sequence with $\tau = 2$ μs using a home-built spectrometer.

The spin–spin relaxation time (T_2) was obtained by measuring the echo amplitude as a function of the delay between the two pulses. The polycrystalline $Nd_{0.7}Sr_{0.3}MnO_3$ samples used in this study were prepared by standard solid-state reaction [2]. Magnetization data were obtained using an MPMS Quantum Design SQUID magnetometer.

3. Results

In ferromagnetic metallic manganites the ^{55}Mn spin-echo spectrum is expected to exhibit a single broad peak between the Mn^{3+} ($\approx$425 MHz) and Mn^{4+} ($\approx$325 MHz) resonances [4]. The peak frequency of this signal was found to scale with the average Mn spin state ($\langle S\rangle$) [5] and therefore was attributed to the fast hopping of carriers from Mn^{3+} and Mn^{4+} which results in a hyperfine field corresponding to an averaged Mn^{3+}/Mn^{4+} state due to the double exchange interaction (DEX). However, the DEX peak has some structure between 340 and 400 MHz (figure 1), the origin of which is discussed at the end of the paper.

Figure 2 shows the temperature dependence of the spin–spin relaxation time T_2 measured at the peak frequencies of the two DEX peaks. Below 80 K the spin–spin relaxation time decreases—unlike the behaviour expected in a ferromagnet—and a prominent minimum of T_2 is observed around 10 K. No deviation from an exponential decay of the echo amplitude was observed during measurement of T_2. Hence the measured T_2 is not due to local nuclear-spin diffusion and reflects electron dynamics.

The temperature dependence of the T_2 can be understood using neutron diffraction measurements by Junghwan *et al* [6] that reveal the ordering of the Nd moments below 20 K, resulting in a canting of the Mn spins away from the b-axis below 15 K. This was associated with a strong Nd–Mn exchange coupling. The decrease in T_2 observed below 80 K points to the presence of hyperfine field fluctuations at the position of the Mn nuclei, which cease below 10 K, resulting in a minimum in T_2. Since a decrease in T_2 below T_C has not been observed in the La-based manganites [7], we conclude that the hyperfine field fluctuations arise as a result of the Nd–Mn exchange interaction (involving electron spins). The minimum in T_2 around 10 K

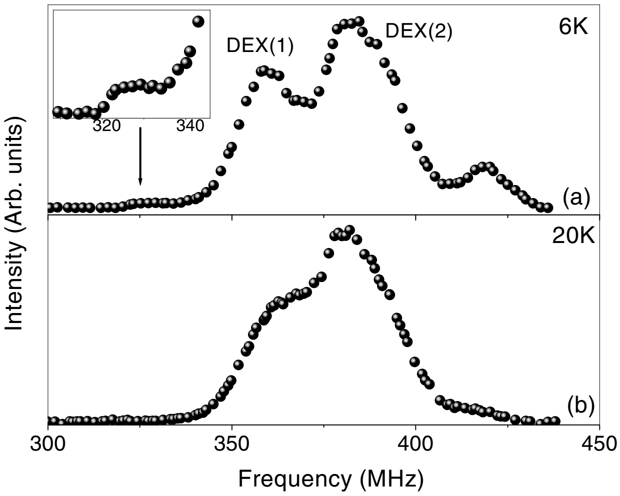

Figure 1. The spin-echo lineshape at 6 and 20 K for $Nd_{0.7}Sr_{0.3}MnO_3$.

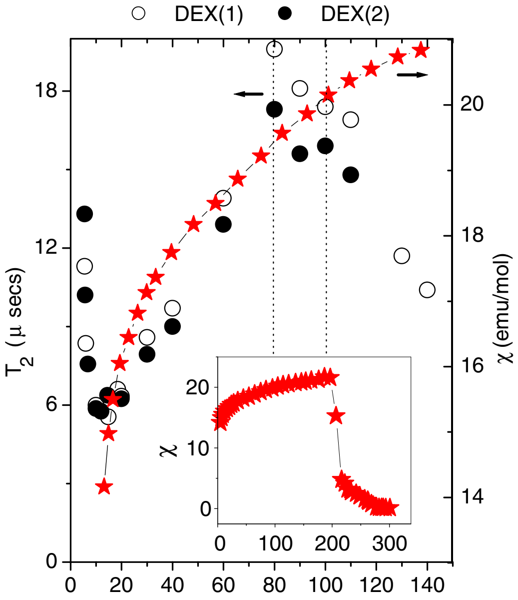

Figure 2. Temperature dependence of T_2 for the two DEX peaks. The low temperature susceptibility (stars) is also plotted. The susceptibility up to 300 K is shown in the inset. The dotted vertical lines aid comparison with figures 3 and 4.

is thus attributed to the canting of the Mn spins as a result of the Nd–Mn interaction. A marked dip in the zero-field cooled susceptibility which coincides with the T_2 minimum (right axis and inset of figure 2(b)) strongly supports this scenario. The observation of a broad and shallow T_2 minimum suggests that Nd spins could order through a gradual spin-freezing process and that the Nd–Mn interaction extends well above the Nd ordering temperature (20 K). The slow variation of T_2 below 140 K may be attributed to the Boltzmann population of the Nd crystal field levels.

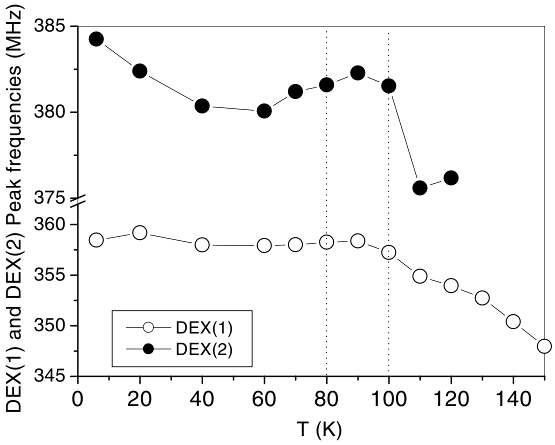

Figure 3. Temperature dependence of DEX(1) and DEX(2) peak frequencies. The dotted vertical lines aid comparison with figures 2 and 4.

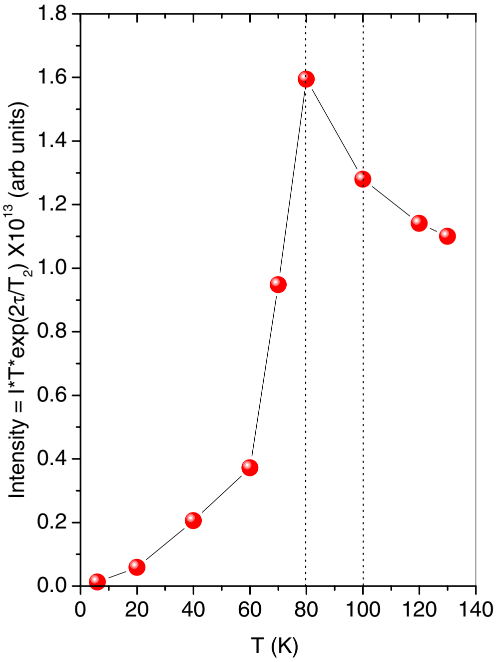

Figure 4. Sum of the intensities of the two DEX peaks. The solid lines guide the eye. The dotted vertical lines aid comparison with figures 2 and 3.

The shape of the spin-echo spectrum provides further evidence of the Nd–Mn interaction. The temperature dependence of the two DEX peaks is plotted in figure 3. Comparing figures 2 and 3 it is seen that the onset of the decrease in T_2 coincides with distinct changes in peak frequencies of the DEX peaks—the high frequency DEX peak exhibits a marked shift in frequency accompanied by a change in slope in the temperature dependence of the low frequency DEX peak frequency. This suggests that the Nd–Mn interaction has a significant influence on the temperature evolution of the two DEX peaks.

The sum of the intensity of the two DEX peaks ($I_{\mathrm{DEX}}(T)$) is plotted as a function of temperature in figure 4. It is seen that the decrease in intensity coincides with the decrease in T_2. A decrease in spin-echo spectral intensity points to a decrease in rf enhancement. This in turn points to fluctuations in the hyperfine field and hence the magnetization of the Mn

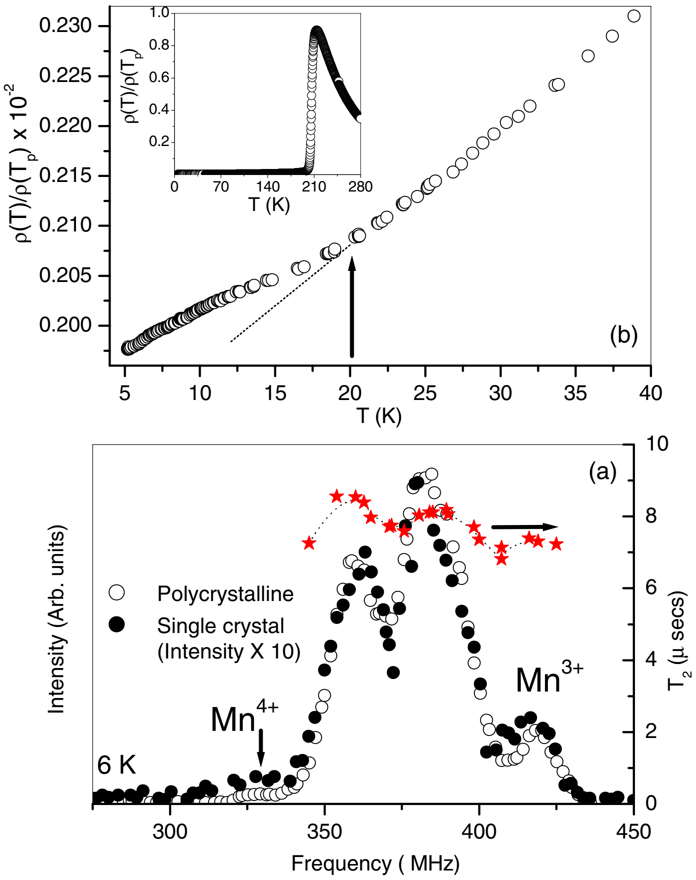

Figure 5. (a) The spin-echo lineshape at 6 K for single and polycrystalline samples of $Nd_{0.7}Sr_{0.3}MnO_3$. The frequency dependence of T_2 for the polycrystalline sample is also shown (right axis). (b) Low temperature resistivity. The inset shows the metal–insulator transition.

(electron) spins. Thus figures 1–4 clearly suggest that the Nd–Mn interaction has a significant influence on the Mn (electron) spin dynamics.

The influence of the Nd–Mn interaction on the spin-echo line shape is clearly seen when $Nd_{0.7}Sr_{0.3}MnO_3$ is heated to 20 from 6 K (figures 1(a) and (b)). The Mn^{4+} signal observed as a weak shoulder at 6 K is absent at 20 K. The Mn^{3+} peak observed at 6 K is seen only as a shoulder at 20 K. The DEX peaks appear less resolved at 20 K compared to 6 K. The appearance of the Mn^{3+} and Mn^{4+} signals at 6 K (figure 1(a)) points to localization of a fraction of charge carriers. This may be linked to the canting of Mn spins below 15 K.

Single crystals are necessary in order to check if the Nd–Mn interaction has an effect on electrical transport since the resistivity in polycrystalline manganites exhibits an upturn at low temperatures irrespective of composition or A-site substituent [8] because of (grain connectivity dependent) Coulomb blockade effects [9]. ^{55}Mn spin-echo NMR and resistivity measurements were performed on a single crystal of $Nd_{0.7}Sr_{0.3}MnO_3$ grown in an infrared image furnace by the floating zone technique [10].

It is seen from figure 5(a) that the single crystal and polycrystalline samples have nearly identical spin-echo spectra at 6 K with Mn^{3+} and Mn^{4+} peaks. Above 6 K the spin-echo

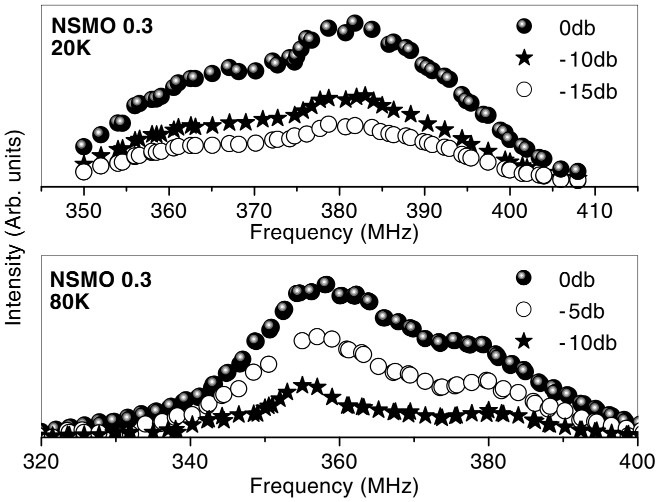

Figure 6. Rf power level dependence of the spin-echo spectrum at 20 and 80 K for $Nd_{0.7}Sr_{0.3}MnO_3$.

spectrum was not observable due to poor rf penetration into the single crystal. Low temperature resistivity measurements on single crystals of $Nd_{0.7}Sr_{0.3}MnO_3$ show that below 20 K there is a change in slope in the resistivity (figure 5(b)). Extrapolating the resistivity above 20 K to lower temperatures (dotted line in figure 5(b)) suggests that there is a small but discernible increase in the resistivity just above the T_2 minimum. This is likely to be related to the canting of Mn spins below the Nd ordering temperature.

4. Discussion

The origin of the two DEX lines is considered next. We first show that the two DEX lines do not arise from differences in rf enhancement. This can be seen from the near independence of the spin-echo lineshape on the power of the applied rf field (figure 6). If the lineshape does change with power of the applied field then it is likely that the two peaks have different rf enhancement factors [11]. If this is the case, since rf enhancement is produced by the coherent oscillation of electron spins, then it is possible that the two DEX peaks originate from spatially resolved ferromagnetic regions (possibly with different electronic properties), as was seen in $La_{0.67}Ca_{0.33}MnO_3$ [12]. However, such a possibility can be eliminated for $Nd_{0.7}Sr_{0.3}MnO_3$, since figure 6 suggests that both peaks have similar rf enhancement factors. The frequency dependence of the spin–spin relaxation time for the polycrystalline sample is also plotted in figure 5(a). Although it follows the lineshape at 6 K, T_2 values at the DEX peak frequencies are nearly the same. This suggests that the Suhl–Nakamura interaction—an indirect coupling between like nuclear spins and the excitation/absorption of electronic spin waves via the hyperfine interaction, resulting in the displacement of the NMR peak frequency upon lowering the temperature [13]—is not likely to be the main mechanism of spin–spin relaxation at low temperatures and hence not responsible for the observed temperature dependence of the DEX peaks (figure 3).

There is a clear correspondence between the onset of the decrease in T_2, distinct changes in the temperature dependence of the DEX peak frequencies, and crucially the decrease in temperature dependence of the DEX intensity. The decrease in $I_{DEX}(T)$ is the direct evidence that the Nd–Mn interaction is of considerable strength well above the Nd spin ordering temperature with a significant influence on the Mn (electron) spin dynamics. The distinctly different temperature evolution of the DEX peak frequencies, when the Nd-spin ordering temperature is approached from above, points to the existence of two Mn species that differ in the extent to which they couple with Nd spins. However, it is not possible to conclude whether this inhomogeneous distribution of Nd–Mn interaction strengths is because of hyperfine field fluctuations or because of an intrinsic electronic phase separation (that may result in two Mn spin species).

We suggest that the observed coupling between Nd and Mn moments may arise from the strong hybridization of the Mn 3d and Nd 4f states with the O 2p states recently observed from high resolution resonant photoemission studies on $Nd_{0.5}Sr_{0.5}MnO_3$ [14]. Thus the valence band structure is influenced by the 4f states.

The strength of the Nd–Mn interaction is proportional to the energy difference between the Zeeman-split levels of the ground state doublet of Nd^{3+}. This is ≈0.93 meV for $Nd_{0.67}Sr_{0.33}MnO_3$ obtained from the analysis of the Schottky peak in specific heat data [15]. Among the parameters that determine the physics of manganites like the hopping matrix element for e_g holes ($t \approx 0.2$ eV), the static Jahn–Teller energy ($E_{JT} \approx 0.25$ eV) etc, the Nd–Mn interaction strength is comparable in magnitude to the antiferromagnetic superexchange coupling between t_{2g} spin ($J_{AF} \approx 2$ meV). The present study shows that, though small in magnitude, the Nd–Mn interaction strength significantly influences the Mn spin dynamics in NdSr manganites, just as J_{AF} is found to influence the magnetic ground state for all alkaline earth doping concentrations [1].

Manganites with other rare earths also exhibit interesting properties at low temperatures. For example, Pr moments have been reported to order below 60 K from neutron measurements in PCMO [16]. ^{55}Mn spin-echo studies on $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ reveal a ‘plateau’ between 20 and 50 K in $1/T_1(T)$ [17]—a relatively less pronounced manifestation of the rare earth–Mn coupling. However, the Pr ordering temperature (≈60 K) is higher than the Nd ordering temperature (≈20 K). The reason for this is currently unclear.

Thus a detailed study of the low temperature microscopic magnetism in several rare earth manganites is necessary to understand the influence of the effective molecular field of the Mn spins on the rare earth crystal field levels and how the rare earth–Mn interaction affects the Mn spin dynamics. We hope that the present study will incite interest towards this end.

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