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NMR study of layered manganite $La_{1.4}Sr_{1.6}Mn_2O_7$

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Abstract

A ^{55}Mn nuclear magnetic resonance study of a layered perovskite $La_{1.4}Sr_{1.6}Mn_2O_7$ is reported. Between 4.2 K and the magnetic ordering temperature, 100 K, zero field spin echo spectra consist of signals corresponding to the double-exchange (DE) states and charge localized Mn^{3+}, Mn^{4+} states. This indicates occurrence of electronic and magnetic phase segregation into ferromagnetic metallic and ferromagnetic insulating regions. Above 100 K a DE line is observed, revealing the presence of long lived metallic clusters. The relation of results to magnetoresistive properties of the compound is discussed.

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Keywords: Nuclear magnetic resonance; Colossal magnetoresistance

Mixed valence manganites of Ruddlesden–Popper series $(RE_{1-x}A_x)_{n+1}Mn_nO_{3n+1}$ (RE = rare earth, A = alkaline earth) have recently attracted a great deal of interest caused by their unusual magnetic, electronic, structural and transport properties. $La_{1.4}Sr_{1.6}Mn_2O_7$ belongs to the $n = 2$ series of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.3$) layered perovskites. Its body centered tetragonal structure (I4/mmm space group) consists of bilayers of MnO_6 octahedra separated by $(La,Sr)_2O_2$ layers. Such a structure is responsible for highly anisotropic properties, e.g. electrical resistivity [1]. The compound exhibits metallic-like resistivity behaviour below the paramagnetic–antiferromagnetic transition temperature, T_N, of 100 K. A change to ferromagnetic structure occurs at T_C of 70 K [2]. In the low-temperature range at $B = 0$ Perring et al. proposed AF coupling between bilayers, parallel to the c-axis, with FM order within the bilayers [3]. Hole doping was found to influence dramatically the intra-layer exchange and only weakly the inter-layer interaction [4]. Colossal magnetoresistance (CMR) is observed near T_N [5]. At low temperatures, it saturates at low fields and the compound behaves like a natural spin valve [1].

In order to study the local magnetic states of manganese a ^{55}Mn nuclear magnetic resonance (NMR) experiment has been carried out. The spin echo spectra and relaxation times (T_1—spin–lattice and T_2—spin–spin) have been measured on a powder sample prepared as described in Ref. [6]. Spin echo spectra at zero external field and at temperatures between 4.2 and 293 K were obtained with a frequency swept spectrometer [7], using a two pulse sequence with pulse power adjusted to an optimum signal for each spectrum.

NMR measures the response of nuclear magnetic moments at individual atomic sites. Resonance occurs at the frequency ν when $2\pi\nu = \gamma B_e$, where γ is the nuclear gyromagnetic ratio of the isotope and B_e is the effective field, which is mostly of hyperfine origin.

The spectra below 100 K, (see Fig. 1), show three lines, which, like for cubic manganites [8], are attributed to the charge localised (CL) ferromagnetic insulating (FMI) Mn^{3+}(450 MHz), Mn^{4+}(340 MHz) and to the

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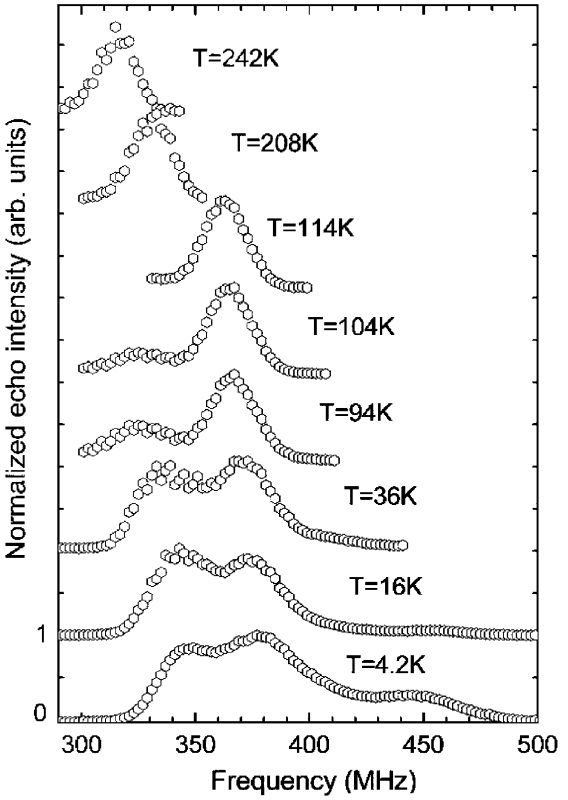

Fig. 1. ^{55}Mn NMR spin echo spectra of $La_{1.4}Sr_{1.6}Mn_2O_7$.

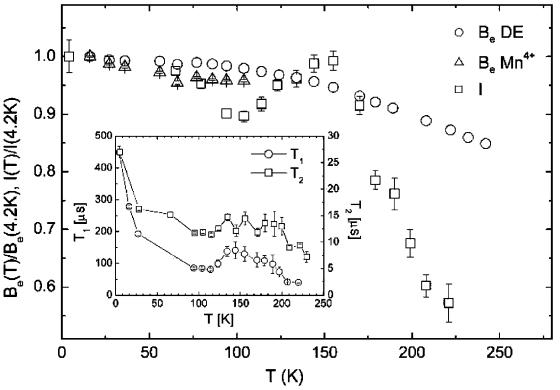

Fig. 2. Temperature dependence of the reduced hyperfine field $B_e(T)/B_e(4.2\ K)$ of the DE and Mn^{4+} lines and the normalized intensity of the DE line, $I(T)/I(4.2\ K)$. Inset: temperature dependence of T_1 and T_2 of the DE line.

double-exchange (DE) states (380 MHz) at 4.2 K, respectively. The DE line corresponds to ferromagnetic metallic (FMM) regions and an averaged Mn ionic state due to the DE driven electron (hole) hopping. This line is still observed above T_N, similarly to that in some cubic perovskites, e.g. $(La,Tb)_{0.67}Ca_{0.33}MnO_3$ [9]. The effect indicates the presence of FMM clusters in the paramagnetic phase, i.e. reveals a superparamagnetic-like behaviour.

The disappearance of the Mn^{3+} line with increasing temperature is caused by the much faster decrease of T_2 in comparison with that of Mn^{4+} or DE lines. The coexistence of CL and charge delocalized states denotes the presence of electronic and magnetic phase segregation.

The relaxation times T_1 and T_2 decrease with increasing temperature for both CL and DE lines up to 100 K (see inset in Fig. 2). For the DE line above 100 K, both relaxation times slightly increase up to 150 K and again decrease above 150 K. As the FMI states become paramagnetic at about 100 K, a minimum in the relaxation times around this temperature indicates the interplay of magnetic fluctuations between metallic and insulating regions.

Reduced values of the hyperfine fields, $B_e(T)/B_e(4.2\ K)$ of the DE and Mn^{4+} lines are shown in Fig. 2. The value for the DE line decreases merely by 30% between 4.2 and 293 K, which indicates almost fully saturated Mn magnetisation in the FMM regions in this temperature range. The hyperfine field corresponding to the FMI regions decreases faster with increasing temperature indicating a stronger temperature dependence of Mn magnetisation and, correspondingly, a weaker magnetic coupling. The DE line intensity corrected for the NMR enhancement factor, nuclear relaxation and the population of nuclear levels shows a minimum at 100 K and a smooth decrease above 150 K. The occurrence of a minimum, similar to that in the relaxation times, is another indication of the interplay of magnetic fluctuations between metallic and insulating regions.

In summary, the ^{55}Mn NMR results on $La_{1.4}Sr_{1.6}Mn_2O_7$ show the occurrence of phase segregation into FMM and FMI regions below T_N, which coincides with melting of the FMI phase. A large amount of FMM clusters is observed up to temperatures three times higher than T_N. The Mn magnetization, within the clusters, is only slightly lower than its fully saturated value. Fluctuations of these clusters caused by melting of the FMI phase are possibly responsible for the CMR observed around 100 K.

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