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Magnetic clusters in $Nd_{1-x}Sr_xMnO_3$ $(0.3 \leqslant x \leqslant 0.5)$: An electron-spin resonance study

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The paramagnetic electron-spin resonance (ESR) linewidth of polycrystalline $Nd_{1-x}Sr_xMnO_3$ ($x = 0.3$, 0.33, 0.4, and 0.5) increases in a quasilinear manner up to 400 K due to the formation of paramagnetic clusters, which is also confirmed by the observation of an activated behavior of the ESR intensity above T_C. Upon cooling, a pair of ferromagnetic resonance lines appear well above the magnetic transition temperature (T_C, T_N) in all cases. This suggests the presence of ferromagnetic clusters at a temperature $T^* > T_C$. The two-line structure below T^* is discussed in terms of phase separation and formation of magnetic clusters and their coexistence with a charge-ordered phase for $x > 0.4$. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Electron-spin resonance (ESR) is a powerful microscopic probe that reveals the charge state, site symmetry, g value, internal magnetic fields and their distribution, the interactions among the ions and the lattice, magnetic ordering and relaxation processes, etc. Even though there have been several reports of ESR studies[1] in the colossal magnetoresistive manganites, there have so far been only few reports of ESR on $Nd_{1-x}Sr_xMnO_3$ (NSMO) compounds.[2] We report here a systematic X-band ESR investigation on polycrystalline $Nd_{1-x}Sr_xMnO_3$ ($x = 0.3$, 0.33, 0.4, and 0.5) in the temperature range 100–400 K.

II. EXPERIMENT

Polycrystalline $Nd_{1-x}Sr_xMnO_3$ ($x = 0.3$, 0.33, 0.4, and 0.5) samples were prepared by mixing stoichiometric amounts of Nd_2O_3, $SrCO_3$, and MnO_2 and calcining at 1200 °C for 24 h. This procedure was repeated three times, after which the powder was pelletized and sintered at 1500 °C for 4 h. The samples were characterized by x-ray diffraction, dc electrical resistivity, and magnetization measurements.[3]

ESR measurements were performed with an X-band Varian™ E-112 continuous wave-spectrometer equipped with a continuous nitrogen gas-flow cryostat in the temperature range between 100 and 400 K. Approximately 1–2 μg of loosely packed fine powder was used for the measurement. A platinum resistance thermometer (PT-100) and a heater, which are kept below the sample, were used to measure and control the temperature from 100 to 400 K. 2,2-diphenyl(picryl hydrazyl) was used as the g marker.

III. RESULTS AND DISCUSSION

In all samples, a single ESR line was observed in the paramagnetic state, with $g \sim 1.99 \pm 0.1$ up to 400 K. This line splits into two lines at low temperatures. Figures 1(a)–1(d) show the ESR spectra of NSMO 0.3, 0.33, 0.4, and 0.5 at various temperatures. It is well known that g is isotropic and nearly equal to 1.994 for Mn^{4+} in an octahedral crystal field, while Mn^{3+} ($3d^3$ with $S = 3/2$) is unlikely to have an observable ESR signal since it has a large zero-field splitting and short spin-lattice relaxation time.[4]

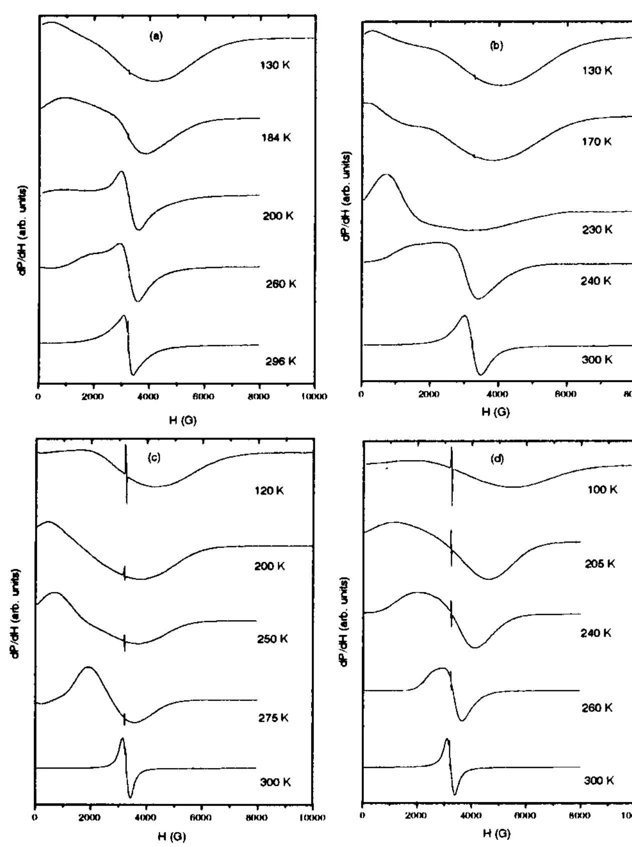

FIG. 1. ESR spectra of NSMO (a) 0.3, (b) 0.33, (c) 0.4, and (d) 0.5 for various temperatures.

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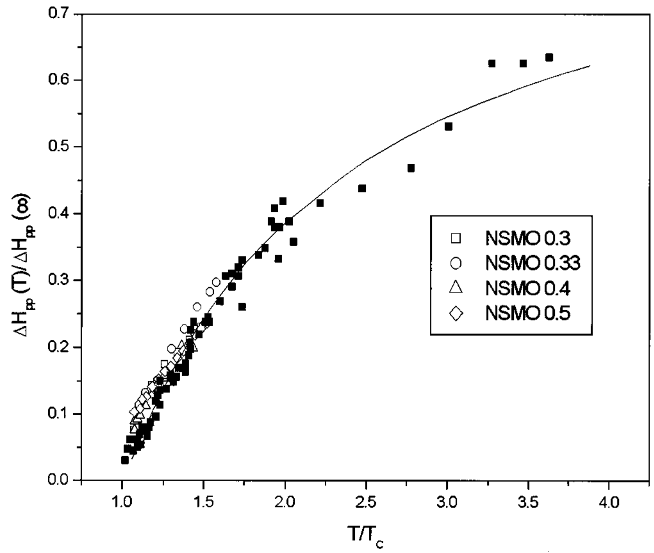

FIG. 2. Plot of $\Delta H_{pp}(T)/\Delta H_{pp}(\infty)$ vs T/T_C. Open symbols are for NSMO; closed symbols are for $R_{0.67}A_{0.33}MnO_3$ (R=La, Pr and A=Ca, Sr) reproduced from Ref. 5; solid line is the universal curve.

The paramagnetic linewidth of all the samples increases in a quasilinear manner with increase of temperature. This behavior could be described by an equation of the form[5]

$$\Delta H_{pp}(T)=\Delta H_{pp}(\infty)\left[\frac{C}{T\chi}\right], \quad (1)$$

where C/T is the single ion (Curie) susceptibility, χ is the measured paramagnetic susceptibility of a magnetically coupled clusters, and $\Delta H_{pp}(\infty)$ is the linewidth expected at temperatures high enough for the dc susceptibility to follow a Curie–Weiss law. This behavior is similar to that observed by Causa *et al.* in $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.67}Sr_{0.33}MnO_3$, and $Pr_{0.67}Sr_{0.33}MnO_3$.[5] Figure 2 shows the linewidths in the paramagnetic state for all the samples which are plotted accordingly on the *universal* curve in a normalized state, T/T^*. Values of $\Delta H_{pp}(\infty)$ shown in Table I are of the same order as of those obtained for La– and Pr–Sr manganites.[5] The ESR linewidth thus reflects the importance of magnetic clustering even in the paramagnetic state. A similar behavior was also inferred from H^2 dependence of magnetoresistance above T_C.[3,6]

The double-integrated intensity of the paramagnetic line decreases exponentially as the temperature increases above room temperature for all samples. The intensity can be fit to the Arrhenius equation of the form[7]

$$I=I_0 \exp(\Delta E/k_B T), \quad (2)$$

TABLE I. Values of the $\Delta H_{pp}(\infty)$, ΔE, T_C, and T^* [see Eqs. (1) and (2) and Fig. 4].

X	$\Delta H_{pp}(\infty)$ (G)	ΔE (eV)	T_C (K)	T^* (K)
0.3	5200	0.04	207	260
0.33	3500	0.12	235	254
0.4	2900	0.10	273	279
0.5	2500	0.06	248	267

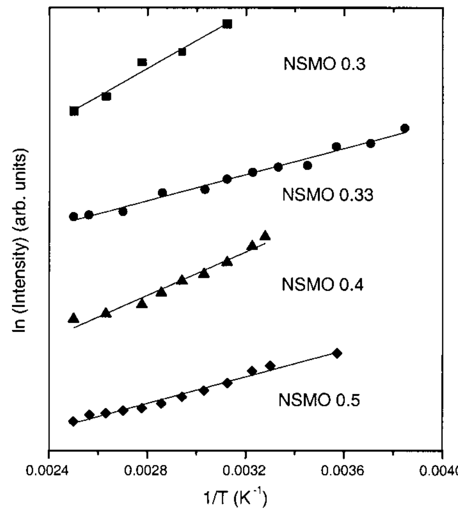

FIG. 3. Plot of ln(ESR intensity) in the paramagnetic state vs inverse of the temperature.

where ΔE is the activation energy for dissociation of the paramagnetic spin clusters. Figure 3 shows the plots of ln-(intensity) versus temperature for all the samples over the paramagnetic temperature range. Table I shows the calculated values of ΔE for NSMO that lie between 0.04 and 0.12 eV. They are less than the values found for $La_{0.67}Ca_{0.33}MnO_3$[7] and for $La_{0.5}Pb_{0.5}MnO_3$.[8]

Upon cooling, it is found that in all cases, a pair of ferromagnetic resonance lines appear at a temperature T^* which is well above the Curie temperature T_C, indicating that the ferromagnetic correlations start and magnetic clusters are formed well above the magnetic transition temperature. Our ESR study shows that there is a temperature interval in which clusters exist above the temperature, corresponding to truly long-range ferromagnetic order. Figure 4 shows a plot of T^* and T_C, and T_N versus composition

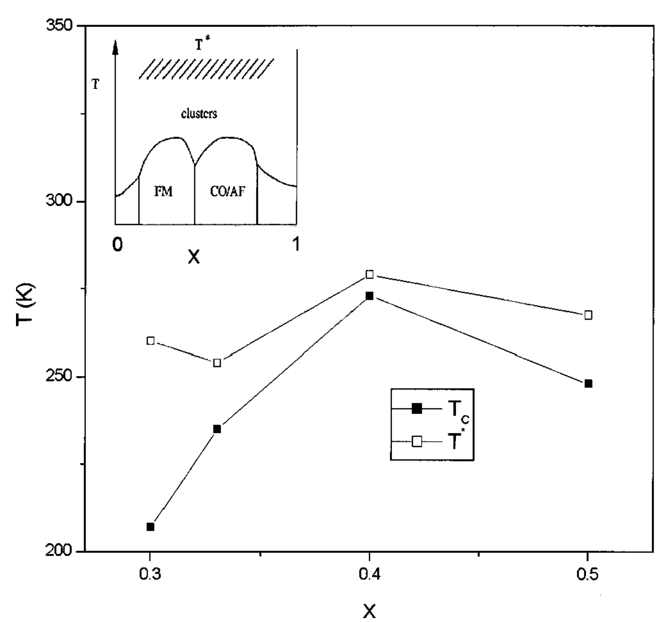

FIG. 4. Plot of T^* and T_C vs temperature. Inset shows the conjectured temperature interval for cluster formation in manganites from Ref. 9.

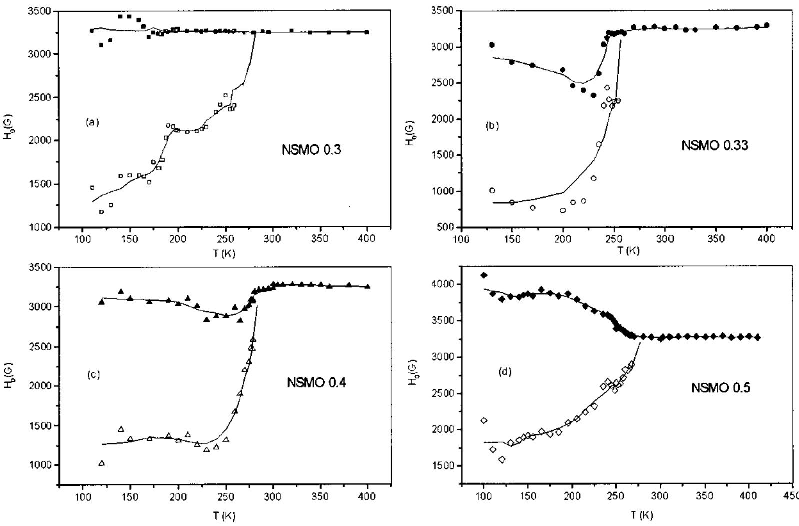

FIG. 5. Plot of resonance fields of high (H1) and low (H2) field lines of NSMO (a) 0.3, (b) 0.33, (c) 0.4, and (d) 0.5 vs temperature. Straight lines are guides to the eye.

x, with an inset showing the prediction from Dagotto *et al.*[9] A similar observation was made by Searle and Wang in $LaPbMnO_3$.[10]

The deviation of T^* from T_C is relatively small in NSMO 0.4, which has the highest T_C. For $x>0.4$, the clustering could be due to the charge/orbital ordering, while for $x<0.4$, it could be due to carrier localization at Mn^{3+} sites. T^* is much higher than T_C in case of NSMO 0.3 and this is reflected in the magnetization behavior also, in the form of a shoulder around 260 K.[3]

The ESR spectra below T^* were fitted to two Lorentzians and Figs. 5(a)–5(d) show the resonance fields for both the lines for all the samples. The two-line structure below T^* may be due to the existence of ferromagnetic clusters of different mobility each of which contributes a different internal field and consequently has a different resonance field. This is also evidenced by ^{55}Mn NMR investigations.[3] In NSMO 0.3, the high-field line stays at the paramagnetic value down to about 170 K. In NSMO 0.5, which is ferromagnetic below T_C and charge-ordered antiferromagnetic below the Néel temperature T_N, the ferromagnetic clusters appear to coexist with the *charge-ordered phase* below T^*. A similar two line structure has also been observed in the charge-ordered phase of $La_{0.5}Ca_{0.5}MnO_3$.[11]

In conclusion, the ESR linewidth and the intensity above T_C provide evidence for clustering of spins. At a characteristic temperature T^*, which is well above T_C, the line splits into two in the magnetically ordered phase, indicating the existence of two types of phase-segregated regions. Further work is in progress to elucidate the details of this phase separation.

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