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Effects of quenched disorder on Griffiths phase and EPR line width in La$_{0.67-2x}$Nd$_{2x}$Ca$_{0.33-x}$Sr$_x$MnO$_3$ manganites

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It is widely accepted that there is Griffiths phase (GP) present in the paramagnetic phase in doped manganites. We studied the effect of quenched disorder on the region of GP in connection with the temperature dependence of the line width (ΔH) of the electron paramagnetic resonance (EPR) in La$_{0.67-2x}$Nd$_{2x}$Ca$_{0.33-x}$Sr$_x$MnO$_3$ ($x = 0$, 0.1, 0.15, 0.2 and 0.25). With this approach it is found that $\Delta H(T)$, the minimum in the line width (ΔH_{min}) and T_{min} are reproduced. With increasing values of the quenched disorder the values of ΔH_{min} are found to increase. A numerical relation that correlates the temperature range in which GP exists and the cation size disorder is obtained and found to be in agreement with some reported data.

1 Introduction In the 1950s Zener [1] developed the double exchange mechanism (DEX) to correlate the ferromagnetic ground state and the electronic transport properties of the perovskite manganites Ln$_{1-x}$A$_x$MnO$_3$ (Ln = La^{3+}, Nd^{3+}, etc. and A = Sr^{2+}, Ca^{2+}, etc.). In the 1990s the colossal magnetoresistance (CMR) in the vicinity of the ferromagnetic metal to paramagnetic insulator transition temperature (T_C) of the pervoskite manganites was observed and has been a central topic of research in the field of condensed matter physics [2]. However, it is found that DEX alone is insufficient to elucidate the complicated properties of the CMR. Additional effects, e.g. lattice distortion, phase separation and intrinsic inhomogeneity, are reported to play additional important roles in these materials [3]. Recently mixed phase tendencies (formation of spin clusters) in CMR systems have been widely accepted to be the emerging picture to unravel the CMR mechanism(s) [4]. Intrinsic inhomogeneity was determined in (La$_{0.4}$Eu$_{0.6}$)$_{0.7}$Pb$_{0.3}$MnO$_3$ single crystals by means of electron paramagnetic resonance (EPR) [5]. It was observed that at a temperature ($T^* = T_{min}$) well above T_C, ferromagnetic clusters appear which in turn produce magnetic fluc-

tuations. These results are in line with those reported for La$_{1-x}$Sr$_x$MnO$_3$ [6] where it was reported that there is a novel triangular phase regime which is characterized by the existence of ferromagnetic entities in paramagnetic phase far above T_C. The nature of this phase could be interpreted in terms of a Griffiths singularity arising due to the presence of quenched disorder (QD) in the orthorhombic phase of these types of materials. Griffiths [7] showed that the essential singularities would develop in a temperature range $T_C(P) < T < T_G$, where P is the disorder parameter and T_G is the new transition temperature scale corresponding to T_C [1]. The phase in this temperature range is termed the 'Griffiths phase' which is characterized by a random distribution of dilute magnetic entities and slow spin dynamics [8]. In manganites the QD is caused by the random distribution of the ions in the pervoskite A-site in Ln$_{1-x}$A$_x$MnO$_3$ (Ln = La^{3+}, Nd^{3+}, etc. and A = Sr^{2+}, Ca^{2+}, etc.). The magnitude of the QD can be evaluated by the variance of the ionic radii of the cations Ln and A respectively. The QD has a role in smearing out the first-order transition between competing phases which induces inhomogeneities inherent to CMR. Among the techniques used

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to determine the spin clustering and inhomogeneity is EPR, which is a very sensitive tool for investigating the interaction of magnetic origin and spin correlations. From the EPR line width ($\Delta H(T)$), it is possible to find clues to the coupling strength, spin relaxation and susceptibility. Oseroff et al. [9] have shown that CMR manganites produce unusual linear $\Delta H(T)$ above T_C and presented evidence of spin clustering in the paramagnetic phase. The linear $\Delta H(T)$ and minimum in $\Delta H(T)$ just above T_C are unclear and the conventional models are questioned.

Recently, by constructing a relation between susceptibility and relaxation time of spin using the Langavin equation, without inclusion of the effect of spin clustering, Hu [10] was able to produce qualitatively a theoretical $\Delta H(T)$ with a minimum at a temperature T^* just above T_C. The temperature dependence of $\Delta H(T)$ has been reproduced qualitatively, but the values of $\Delta H(T)$ were found to be five times larger than those reported experimentally.

The temperature dependence of $\Delta H(T)$ is usually related to the magnetic susceptibility and longitudinal and transverse relaxation times of the system under study. From an analysis of experimental data Causa et al. [11] correlated the magnetic susceptibility with $\Delta H(T)$ as $\chi^{-1}(C(T - \theta)/T)$, where C is the Curie constant and θ is the Curie–Weiss constant. Those authors achieved good results in the temperature range far above T_C. In CMR manganites the values of C are reported to be large and χ^{-1} deviates near T_C [12]. The latter observation has been related to formation of Griffiths phase in the neighbourhood of T_C. This enhanced magnetic susceptibility was not taken into consideration in the model of Hu [10].

In this paper, we present an analysis of the experimental data for the temperature dependence of the EPR line width for the compounds $La_{0.67–2x}Nd_{2x}Ca_{0.33–x}Sr_xMnO_3$ ($x = 0.0, 0.1, 0.15, 0.2$ and 0.25) in which QD is created in the A-site. We propose that the formation of Griffiths phase due to QD is an important factor for interpreting the unusual line width broadening.

2 Experimental Polycrystalline samples were prepared following the conventional ceramic route and characterized by X-ray powder diffraction (XRD) using a Philips X-Pro (Cu $K_{\alpha 1}$) diffractometer. The details of the sample preparations and magnetization measurements by means of SQUID are given in [13]. The magnetic susceptibility above room temperature was measured using an EG and G vibrating sample magnetometer up to 700 K at 500 Oe. The EPR measurements were obtained from 80 K up to 575 K using a Varian spectrometer operating in the X-band at 9.5 GHz. The samples were cut and ground to a spherical shape of diameter not more than 1 mm.

3 Results and discussion The Rietveld refinement of the XRD data showed that all the samples are single phase and their crystal structure is orthorhombic with space group Pnma. The inverse of the high-temperature magnetic susceptibility for a selected sample is shown in Fig. 1a while the inverse of the magnetic moment measured by SQUID is shown in Fig. 1b. On approaching T_C from above, there is a downturn in $\chi^{-1}(T)$ near T_C. The values of the Curie constant obtained from the straight line are in the range $6–10$ emu K mol^{-1} Oe^{-1} which are large compared to theory, and generally this is related to the formation and presence of spin clusters up to temperatures well above T_C [9].

The EPR spectra of the samples showed single lines with Lorentzian line shape:

$$Y = Y_{max} \frac{2\Gamma^2(H - H_r)}{[\Gamma^2 + (H - H_r)^2]^2}, \tag{1}$$

where H is the applied magnetic field, H_r the resonance field, Y_{max} the maximum intensity and Γ the half width at full maximum. The peak-to-peak line width $\Delta H(T)$ is determined from $\Delta H = (2/\sqrt{3})\Gamma$. The line width of the EPR signal $\Delta H(T)$ was plotted versus temperature, as shown in Fig. 2. As the temperature decreases $\Delta H(T)$ shows a linear decrease down to approximately 400 K then increases rap-
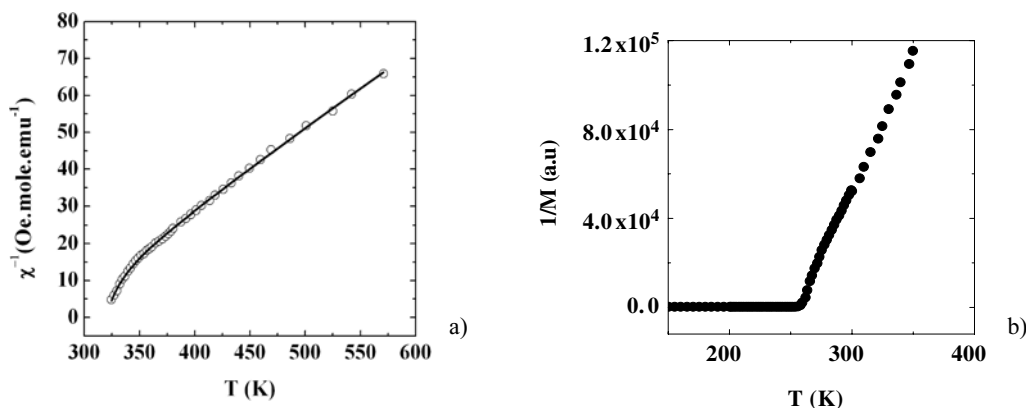
Figure 1 a) Inverse of the magnetic susceptibility as a function of temperature for the sample $La_{0.23}Nd_{0.4}Ca_{0.13}Sr_{0.2}MnO_3$; the solid line is the fit for magnetic susceptibility in Griffiths phase. b) Inverse magnetic moment of the same sample shows a kink around 300 K.
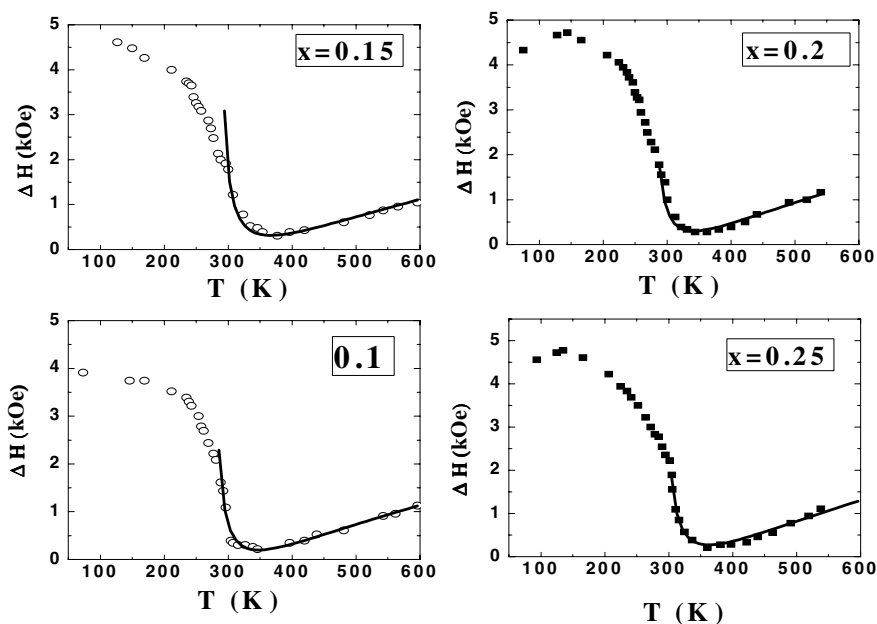
Figure 2 Results of the line width fitting to Eq. (6) for some selected samples of $La_{0.67-2x}Nd_{2x}Ca_{0.33-x}Sr_xMnO_3$.

idly near T_C after a minimum at T_{min}. Similar trends were reported previously [5, 11, 14].

Interpretation and discussion of the variation of the EPR line width of manganites would be incomplete without understanding of the effect and the nature of the spin clustering on the magnetic susceptibility and the longitudinal and transverse relaxation times in the paramagnetic phase of manganites. Attempts were made [11, 14] to elucidate the variation of the EPR line width of these materials in connection with the magnetic ordering near T_C. Yaun et al. [14] by considering the formation of Griffiths phase gave an explanation of the variation of $\Delta H(T)$ in the range from T_C up to T_{min} by fitting their experimental data using the following equation:

$$\Delta H \approx a + bf(T). \qquad (2)$$

Here $f(T)$ is the volume fraction of the ferromagnetic clusters which is assumed to vary as the magnetization and is approximated as

$$f(T) = m = B_J\left(\frac{3J}{J+1}\frac{m+h}{t}\right), \qquad (3)$$

where B_J is the Brillouin function. Equation (2) was seen to be valid in a very limited range as the Griffiths phase does not occur at very high temperature.

In Eq. (2) the effect on the spin correlation caused by DEX interaction is not considered. The effect of DEX on the EPR line width was examined theoretically by Hu [10], within constrains of Schwinger bosons where he made a rigorous derivation, from fundamental formalism, of the EPR line width in DEX systems. He calculated the transverse relaxation time above T_C and was able to reproduce the minima ΔH_{min} and the upturn below T_{min} was found to be intrinsic. The cause of the upturn is related to diver-

gence of the function $\ln(1-z)$ defined in the following equation:

$$\Delta H = -4\frac{G^2+F^2}{k_B T_C}\left(\frac{S-x/2}{g_{3/2}(1)}\right)^2\left(\frac{T}{T_C}\right)^2\ln(1-z), \qquad (4)$$

where G and F are constants. At low temperature this equation reduces to

$$\Delta H \propto -\ln\left(\frac{T}{T_C}-1\right). \qquad (5)$$

Nevertheless, the calculated ΔH_{min} is large compared with the reported experimental values.

Recent experimental studies [15] have proved the simultaneous presence of longitudinal (T_1) and transverse (T_2) relaxation times near T_C. Far above T_C and the critical region the relaxation times are equal ($T_1 = T_2$) due to fast fluctuations of internal fields. Near T_C a breakdown of this equality was measured and found to take place in the range from T_C up to approximately ($T_C + 100$) K. In this range the values of T_1 are found to be smaller by 2 to 3 order of magnitude than T_2 [20] as a result of the divergence of χ near the Curie temperature due to formation of spin clusters and Griffiths phase.

Atsarkin et al. [15] showed that a best fit for the data of the relaxation time T_1 was obtained if it was left to vary as $[(T/T_C) - 1]^{0.5}$. It is now possible to deduce from these observations and the calculations of Hu that there is more than one mechanism responsible for the broadening of the EPR line width starting from the Curie temperature. By combining Hu's model with the findings of Atsarkin et al. we may write the temperature dependence of the EPR line width as follows:

$$\Delta H = A\sqrt{\frac{T}{T_C}} + B\left(\frac{T}{T_C}-1\right)^\alpha - C\ln\left(\frac{T}{T_C}-1\right). \qquad (6)$$

Table 1 The fitting parameters obtained using Eq. (6).

| x	A	α	B	C	T_C (K)	T_{min} (K)	ΔT (K)
0.00	−8.64	0.50	13.14	2.30	265	312	47
0.10	−8.78	0.49	13.40	2.31	281	336	55
0.15	−8.99	0.49	13.80	2.46	289	348	59
0.20	−8.78	0.49	13.62	2.30	290	358	68
0.25	−8.86	0.50	13.80	2.37	296	372	76

The first term on the right-hand side is the line width due to the transverse relaxation time at high temperature; the second is the line width due to the longitudinal relaxation time near T_C; and the third is the line width due to transverse relaxation near T_C. Here A, B, C and α are fitting parameters.

Fitting of Eq. (6) is found to be in good agreement with our data for the present samples, where the upturn below ΔH_{min} and T_{min} were reproduced. The results of the fittings are shown is Fig. 2. The fitting parameters are given in Table 1. It is worth mentioning here that attempts were made to fit the data without including the term

$$B\left(\frac{T}{T_C} - 1\right)^\alpha ,$$

but they failed to reproduce quantitatively the observed line width. Interestingly enough, all the fitting parameters, except T_C, are almost equal. The value of the exponent α almost equals 0.5 in all the samples reproducing its value obtained by Atsarkin et al. This is consistent with the fact that all the samples have the same mixed valence state of Mn^{3+}/Mn^{4+}. Thus the variation of in T_{min} may be directly related to the effect of the QD on T_C. The Griffiths phase region, $T_C < T < T_{min} = T_G$, is seen to expand as σ^2 increases which is shown in the linear plots of $\Delta T = T_G - T_C$ versus σ^2, as depicted in Fig. 3. The linear relation is of the form

$$\Delta T = m\sigma^2 + A = 1.5 \times 10^3 \sigma^2 + 44.85 . \tag{7}$$
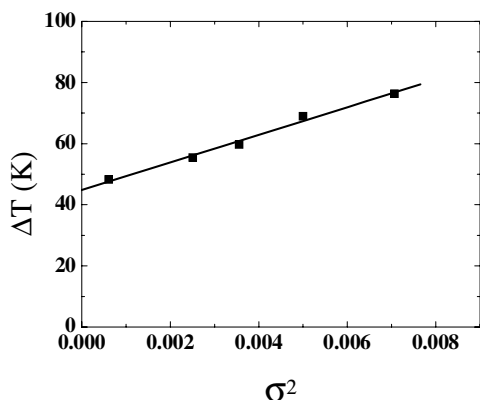
Figure 3 Temperature difference $\Delta T = T_C - T_{min}$ as a function of the cation size disorder. The straight line is the linear fit given by Eq. (7).

A value of $\Delta T = 44.85$ at $\sigma^2 = 0$ may be due to the constraints imposed in the model of Hu, in addition to other lattice distortions, e.g. the Jahn−Teller effect. Thus with knowing the Curie temperature and the QD parameter of any manganite the temperature at which Griffiths phase sets in can be estimated using Eq. (7). Variation of T_{min} is reported by Ulyanov et al. [16] in $La_{0.7}Ca_{0.3-x}Ba_xMnO_3$ for $x = 0$, 0.15 and 0.3 and by Yuan et al. [14] in $(La_{1-x}Y_x)_{0.67}Ca_{0.33}MnO_3$ at $x = 0$. T_{min} values shown in the curves of Ulyanov et al. are slightly different from the estimated values of ΔT using Eq. (7) but the data of Yuan agree when $x = 0$.

4 Conclusions EPR experiments were performed on $La_{0.67-2x}Nd_{2x}Ca_{0.33-x}Sr_xMnO_3$ ($x = 0$, 0.1, 0.15, 0.2 and 0.25) manganites. Inclusion of quenched disorder expressed by the cation size mismatch in the analysis of the EPR data is found to be essential, where the formation of spin clusters is related to the unusual line width broadening near the ferromagnetic transition temperature. With this approach it is found that $\Delta H(T)$, the minimum in the line width (ΔH_{min}) and T_{min} are reproduced throughout the studied temperature range in the paramagnetic phase. A numerical relation to estimate the temperature region in which Griffiths phase exists has been obtained and found to be in agreement with reported data. Further work on the effect of concentration at different valence states is required to verify and refine Eq. (7).

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