Temperature dependence of the ESR linewidth in the paramagnetic phase ($T>T_C$) of $R_{1-x}B_xMnO_{3+\delta}$ (R=La,Pr; B=Ca,Sr)

C. Rettori, D. Rao, J. Singley, D. Kidwell, and S. B. Oseroff
San Diego State University, San Diego, California 92182

M. T. Causa
Centro Atómico Bariloche and Instituto Balseiro 8400, San Carlos de Bariloche, Argentina

J. J. Neumeier and K. J. McClellan
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

S-W. Cheong
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

S. Schultz
University of California, San Diego, California 92037
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Electron spin resonance (ESR) experiments in the paramagnetic phase of $R_{1-x}B_xMnO_{3+\delta}$ (R=La,Pr; B=Ca,Sr) show, for $1.1\ T_C \lesssim T \lesssim 2T_C$, a linear T increase of the resonance linewidth, ΔH, in powders, ceramic pellets, and single crystals. Above $\sim 2T_C$ a slowdown in the T increase of ΔH is observed. The data resemble the results found in other ferromagnetic insulators where the spin-lattice relaxation involves a single-phonon process. We find that the one-phonon process may account for the linear T dependence of the linewidth observed up to $\sim 2T_C$. A large T dependence of the resonance intensity above T_C was found in all the samples studied, suggesting the existence of *spin clusters* in these compounds over a wide range of temperature. [S0163-1829(97)05805-0]

I. INTRODUCTION

The discovery of huge negative magnetoresistance (MR), now termed colossal magnetoresistance (CMR), in the doped manganites $R_{1-x}B_xMnO_{3+\delta}$ (R=La, Pr, Nd, etc.; B=Ca, Sr, Ba, Pb) with a perovskite structure has recently become a subject of intense interest.[1] The increased interest in the study of these systems arises from the high correlation found between their structural, transport, and magnetic properties at T_C, the Curie temperature.[2] The proximity of the paramagnetic-ferromagnetic (FM) phase transition,[3] and the semiconductor-metal phase transition lead to giant MR effects at T_C.[1,2] Further improvements in the MR sensitivity, particularly at low magnetic fields and room temperatures, may make these systems suitable for commercial magnetic sensing applications.[2,3]

The structure and basic behavior of the doped manganites has been established long ago.[4] A model for the transition to a FM-metallic phase was postulated by Zener[5] and refined later by deGennes using the double-exchange (DE) mechanism. In this model the conductivity is established by an itinerant Mn d-electron hopping between Mn^{3+} and Mn^{4+} e_g states. The carriers are strongly exchange coupled to the localized electrons (FM aligned) in the d-core t_{2g} states according to Hund's rule ($S=\frac{3}{2}$). However, recent calculations[6] indicated that the DE model alone cannot quantitatively account for the measured CMR values. The formation of a spin-polaronic band in the paramagnetic phase arising from Jahn-Teller splitting of the outer $e_g$states, has been invoked to explain the experimental results.[6,7] But the true nature of the semiconducting-paramagnetic phase and the metallic-FM phase is still a subject under intense investigation.[8]

We have previously reported[9] that these systems have a strong ESR line in the paramagnetic phase ($T>T_C$). In particular, for those compounds that undergo a FM transition, the intensity of the resonance grows approximately exponentially as one approaches T_C from above. The increase in intensity is much more rapid than the T^{-1} Curie-like behavior expected for a single-ion excitation (either Mn^{3+}or Mn^{4+}), and it does not follow a $(T-\Theta)^{-1}$ Curie-Weiss law which is commonly observed for FM coupled ions. We have suggested that the *anomalous* increase in intensity is due to the formation of a complex of $Mn^{3+}-Mn^{4+}$ *spin clusters*.[9] The average effective spin **S** increases as we approach T_C. This growth reflects the increase of the number of Bohr magnetons measured in dc-magnetization experiment as T decreases.[9,10]

In this paper we have extended our previous work[9] to a larger number of systems of the $R_{1-x}B_xMnO_{3+\delta}$ (R=La,Pr; B=Ca,Sr; $0\leqslant x\leqslant 0.5$) family in the form of powders, ceramic pellets, and single crystals. We have studied the T dependence of the linewidth, ΔH, for $T\gtrsim 1.1T_C$. We find that, for $1.1T_C \lesssim T \lesssim 2T_C$, ΔH increases linearly with T over a large range of x. Such behavior is unusual for materials that, as in our case, are semiconductors or insulators. Above $\sim 2T_C$ a slowdown in the slope of ΔH is found. We attempt to describe our results in terms of a single-phonon spin-lattice

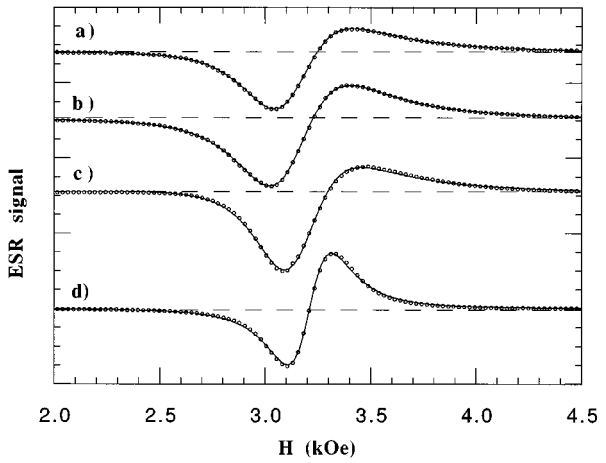

FIG. 1. X-band, 9.2 GHz, ESR spectra taken at 320 K (a) $Pr_{0.625}Sr_{0.375}MnO_{3+\delta}$ single crystal; (b) $La_{0.78}Ca_{0.22}MnO_{3+\delta}$ single crystal; (c) $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ ceramic pellet; and (d) $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ powder from ceramic pellet in (c). The solid lines are the best fit of the experimental spectra to Dysonian [(a)–(c)] and Lorentzian line shapes (d).

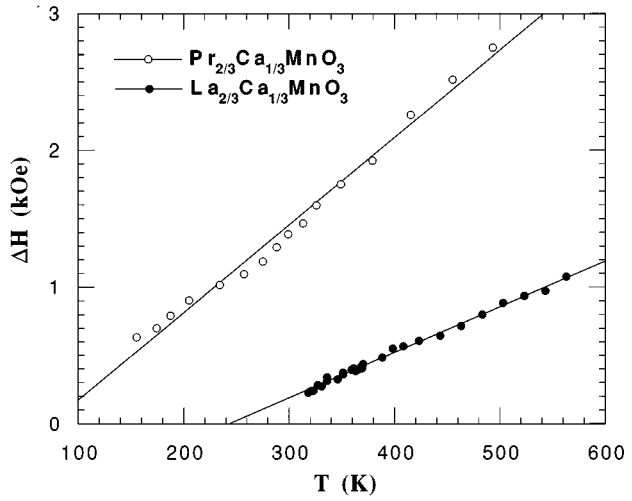

FIG. 2. X-band, 9.2 GHz, ESR linewidth for powder samples of $Pr_{0.67}Ca_{0.33}MnO_{3+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$. The solid lines are the best fit to $\Delta H = a + bT$, for $1.1T_C \lesssim T \lesssim 2T_C$. The values of b are given in Tables I and II.

relaxation mechanism. The data are well fit over the studied T range, provided we use the experimental susceptibility.

II. EXPERIMENTAL DETAILS

Ceramic samples were prepared by standard ceramic methods, heating stoichiometric mixtures of the corresponding oxides as described in Ref. 9. The oxygen content was modified by subsequent annealing in oxygen or argon atmospheres. For $x \lesssim 0.33$ the oxidation was accomplished by annealing in a flowing O_2 atmosphere for 24 h between 900 °C and 1400 °C. The reduction was achieved by annealing the samples in a flowing Ar atmosphere (using Zr or Ti as getters) between 800 °C and 1000 °C for 24 h. The change in oxygen content, for $x=0$ and 0.33, was determined by thermogravimetry with an accuracy of ± 0.02. Single crystals of $La_{0.83}Sr_{0.17}MnO_{3+\delta}$ and $La_{0.78}Ca_{0.22}MnO_{3+\delta}$ were grown by the optical float zone method. Typical rotation rates for both the seed crystal and feed rod were 50 rpm and the crystals were grown at a rate of 6 mm/h. The $Pr_{0.625}Sr_{0.375}MnO_{3+\delta}$ single crystal was also grown by the floating zone method, using a lamp-image furnace.[11] The structure and phase purity were checked by x-ray diffraction. The resonance measurements were performed in conventional ESR spectrometers locked to the cavity and using field modulation. The spectrometers operate at 9.2 GHz between 100 and 800 K and at 35 GHz between 77 and 300 K. The samples used in our ESR measurements were single crystals and ceramic pellets of about $1\times2\times2$ mm^3, or particles of about 5 μm in diameter, obtained by filing and sieving the ceramic pellets.

III. EXPERIMENTAL RESULTS

Figure 1 shows the ESR lines measured at the X band (9.2 GHz) and $T \gtrsim 1.1T_C$ for four of the roughly 100 samples studied in this work. For single crystals and ceramic pellets, with dimensions larger than the skin depth ($\gtrsim$100 μm), Dysonian line shapes (admixture of absorption and dispersion) with $A/B \approx 2.3$ were observed over the temperature range reported (A and B are the heights of the low- and high-field Dysonian resonance peaks, respectively).[12] These values correspond to the diffusionless limit in Dyson's theory.[12] Therefore, our resonances are similar to those of localized magnetic moments in conducting hosts. For powdered samples, with particle size smaller than the skin depth, the resonance shows the normal expected Lorentzian shape. The solid lines in Fig. 1 are the best fit of the experimental spectra to Dysonian and Lorentzian line shapes.[12]

Figures 2 and 3 show, respectively, the T dependence of ΔH for powdered $R_{1-x}Ca_xMnO_{3+\delta}$ and single crystal $R_{1-x}Sr_xMnO_{3+\delta}$ (R=Pr,La) samples for $1.1T_C \lesssim T \lesssim 2T_C$. In all cases a linear T dependence of the linewidth, $\Delta H = a + bT$, was observed. Within the accuracy of the experiments, the g values are T independent and consistent at 9 and 35

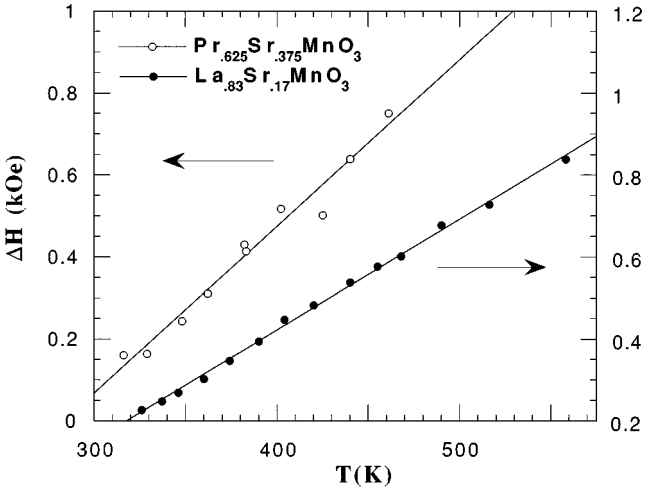

FIG. 3. X-band, 9.2 GHz, ESR linewidth for single crystals of $Pr_{0.625}Sr_{0.375}MnO_{3+\delta}$ and $La_{0.83}Sr_{0.17}MnO_{3+\delta}$. The solid lines are the best fit to $\Delta H = a + bT$, for $1.1T_C \lesssim T \lesssim 2T_C$. The values of b are given in Tables I and II.

TABLE I. ESR parameters for $La_{1-x}(Ca,Sr)_xMnO_{3+\delta}$. b was obtained from the linear increase of ΔH between about $1.1T_C$ and $2T_C$.

x	T_C (K)	g	ΔH $(T\approx 1.1T_C)$ (Oe)	b (Oe/K)
0.0[a,b]	250(5)	2.01(2)	330(40)	2.6(3)
0.02(Ca)[b]	270(10)	2.02(4)	700(80)	2.7(3)
0.10(Ca)[b]	270(10)	2.02(4)	720(80)	2.8(3)
0.22(Ca)[c]	200(5)	1.99(2)	250(30)	2.9(3)
0.25(Ca)[b]	270(10)	2.00(2)	300(30)	2.4(3)
0.33(Ca)[b]	285(5)	2.01(2)	260(30)	3.2(3)
0.45(Ca)[b]	270(10)	2.01(2)	280(30)	2.9(3)
0.50(Ca)[b]	230(10)	2.00(2)	300(30)	3.2(3)
0.17(Sr)[c]	275(5)	2.00(2)	280(30)	2.7(3)

[a] $\delta\approx 0.1$.
[b] Powder.
[c] Single crystal.

GHz. The ESR parameters for the single-crystal and ceramic pellet samples are presented in Tables I and II for representative samples.

None of the studied samples showed thermal hysteresis. Note that most of the data presented in this paper were taken in the paramagnetic region, with T_C determined from magnetization data. For $T\lesssim 1.1T_C$ the interaction between the localized magnetic moments and the increasing demagnetization effects become significant. There are field shifts, increased broadenings, and sometimes even splittings of the resonance lines. For example, below $T\approx 1.1T_C$, the single crystals showed anisotropic g values, linewidths, and A/B ratios. However, for $T\gtrsim 1.1T_C$, no anisotropies were observed in any of the samples studied. Complimentary Q-band (35.5 GHz) measurements on the same samples showed basically the same line shape with no more than a 20% increase in the linewidth. This assured us that the observed resonances are basically homogeneous. If a distribution of g values does exist, its contribution to ΔH is small.

IV. ANALYSIS AND DISCUSSION

As mentioned above, it is surprising that in semiconductor compounds the ESR linewidth increases linearly with T up to such high temperatures. Seehra *et al.*[13] have already pointed out that a phonon modulation of the Dzialoshinsky-

TABLE II. ESR parameters for $Pr_{1-x}(Ca,Sr)_xMnO_{3+\delta}$. b was obtained from the linear increase of ΔH between about $1.1T_C$ and $2T_C$.

x	T_C (K)	g	ΔH $(T\approx 1.1T_C)$ (Oe)	b (Oe/K)
0.0[a,b]		2.03(8)	1400(150)	14(3)
0.33(Ca)[b]	120(20)	2.02(8)	1400(150)	7.5(7)
0.33(Sr)[b]	305(10)	2.02(3)	420(50)	5.5(5)
0.375(Sr)[c]	305(10)	2.03(3)	280(30)	5.7(5)

[a] $\delta\approx 0.1$.
[b] Powder.
[c] Single crystal.

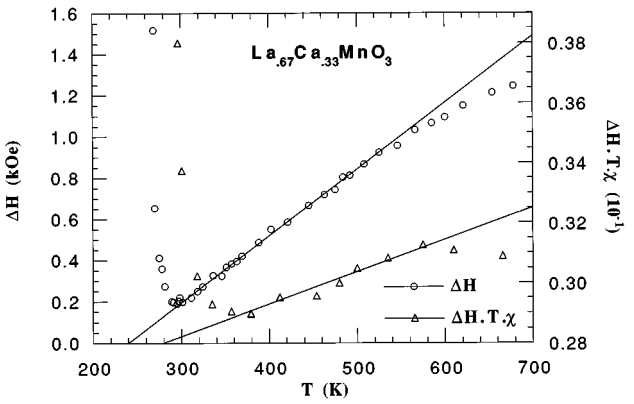

FIG. 4. Experimental ESR linewidth, $\Delta H(T)$, for a powder sample of $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ (open circles) at 9.2 GHz. The values of $\Delta H(T)T\chi(T)$ (open triangles) were obtained using the experimental $\chi(T)$ for the same sample.

Moriya antisymmetric exchange interaction between superexchange AFM coupled ions leads to a T-dependent ESR linewidth in the paramagnetic region. In particular, a linear term was predicted for the one-phonon process. Huber and Seehra[14] reported that, for a FM compound and $T\gg T_C$, it may also be expected an asymptotic linear T dependence of ΔH associated to a one-phonon process. They expressed the linewidth, in the case of isotropic behavior, as

$$\Delta H(T)=\frac{C}{T\chi(T)}[K(T)+f(\epsilon)], \tag{1}$$

where C is the Curie constant and $\chi(T)$ the susceptibility. $K(T)$and $f(\epsilon)$, with $\epsilon=(T-T_C)/T_C$, represent the noncritical and critical contributions to $\Delta H(T)$, respectively. As $f(\epsilon)$ is only important in the neighborhood of T_C it is expected that, for $T\gg T_C$, $\Delta H(T)$ follows the T dependence of $K(T)$. When only spin-spin interaction is present, $\Delta H(T)$ approaches a constant value for $T\to\infty$[$K(T)$ = const and $T\chi(T)\to C$].[13,14]

In Fig. 4 we present, for one of our $La_{0.67}Ca_{0.33}MnO_3$ samples, the experimental $\Delta H(T)$ in an extended temperature range. The low-temperature linewidth shows a fast broadening below $T\approx 300$ K. Above $T\approx 560$ K, a decrease in the thermal broadening rate is observed. For the analysis of these data, in Fig. 4 we also show $\Delta H(T)T\chi(T)$ as a function of T. $\Delta H(T)$ and $\chi(T)$ are the measured linewidth and magnetic susceptibility, respectively. From this plot and Eq. (1) we suggest that the low-temperature increase of $\Delta H(T)T\chi(T)$ is due to the critical contribution near T_C, and the linear term between $1.1T_C$ and $2T_C$ the noncritical contribution due to the one-phonon relaxation process. The decrease in the thermal broadening rate at temperatures above $T\approx 560$ K may be associated with the Debye temperature of these systems, $\theta_D\approx 500$ K.[15]

Although the analysis given above accounts for the linear T dependence of $\Delta H(T)$, we want to point out that the mechanism, as formulated by Huber and Seehra, may not be the complete explanation for the manganites. Similar calculations for the spin-lattice relaxation, involving the DE inter-

action between the Mn^{3+} and Mn^{4+} ions being modulated by a dynamic Jahn-Teller effect[16], may be more appropriate for our case.

The data given in Tables I and II show g values close to that of the free electron (2.0023) suggesting that the orbital contribution to the ground-state wave function is relatively small. Systematic larger b values are found for the Pr-based compounds. That may indicate that extra lifetime broadenings are present in these compounds. Exchange, dipolar, larger lattice distortions, and/or Jahn-Teller fluctuations may couple the Pr^{3+} and Mn^{3+}-Mn^{4+} spin systems to allow for the larger b values found in the Pr-based compounds.[16,17]

For the powdered samples studied in this work, we found an activation energy ($\Delta E \lesssim 0.2$ eV) for the increase in the resonance line intensity, as T decreases. This behavior is in agreement with the increase of the Curie constant found in magnetization measurements when T approaches T_C in the paramagnetic phase.

V. CONCLUSIONS

For these FM manganites, the broadening of the ESR lines above T_C has been already observed.[9,18] In this work we show that the linewidth increases linearly with T between $1.1T_C$ and $2T_C$. Above that $2T_C$ a slowdown is found. Although more systematic experimental studies would be required to relate the linewidth and spin-lattice relaxation, the one-phonon process calculated by Huber and Seehra[14] may account for the linear T dependence of the measured linewidth. We feel that a mechanism involving a phonon-modulated DE interaction via dynamic Jahn-Teller fluctuations,[16] may be more appropriate for the manganite compounds. We suggest that a calculation involving these mechanisms is needed at this stage.

Finally, the strength and thermally activated–like increase of the resonance intensity observed in these samples agrees with our previous work.[9] Therefore, a complex of Mn^{3+}-Mn^{4+} *spin clusters* of increasing total average spin **S** as T approaches T_C in the paramagnetic phase should be responsible for the observed resonance in these systems. It has been recently suggested in zero-field muon-spin relaxation experiments[19] that the *spin system* may develop in a ''glass state'' near and below T_C. However, for the ESR data presented here, we did not find any significant differences between zero-field cooling and field cooling.

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