

Evidence for collective spin dynamics above the ordering temperature in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$

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(Received 25 August 1995; revised manuscript received 22 November 1995)

We have measured the temperature dependence of the electron paramagnetic resonance (EPR) of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ for $0.0 \leq x \leq 1$ at 9.2 and 35 GHz from 270 to 800 K. We vary δ by oxygen and argon annealing. We observe that the intensity of the EPR line decreases exponentially for T above the ordering temperature T_c , with an activation energy which varies with x and δ . We find that the EPR data below ~ 600 K cannot be attributed to an individual Mn ion of any valency, i.e., Mn^{2+} , Mn^{3+} , or Mn^{4+} for all annealing conditions. The theoretical models of these "colossal" magnetoresistance compounds has not yet focused on the ground-state spin properties, and an interpretation of these data is therefore still lacking. We suggest that the explanation of these EPR data may provide useful tests of the correct model of the magnetization and magnetotransport properties in these compounds. The maximum EPR intensity per formula unit (for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ air annealed, $T_c \sim 270$ K) corresponds to correlated moments with an effective spin of ~ 30 at $T = 280$ K.

INTRODUCTION

The recent demonstration of a huge magnetoresistive response, now termed colossal magnetoresistance (CMR), in the perovskite manganites $R_{1-x}B_x\text{MnO}_{3+\delta}$ ($R = \text{La, Pr, Nd}$, $B = \text{Ca, Sr, Ba, Pb}$) has attracted much attention.¹ Stoichiometric LaMnO_3 is a semiconductor that orders antiferromagnetically and changes to a magnetic ferromagnet phase for $0.2 \leq x \leq 0.5$.² It had been proposed many years ago that the ferromagnetism (FM) of this class of compounds could be explained on the basis of Zener's model of double exchange between pairs of Mn^{3+} and Mn^{4+} .³ Experimentally the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio can be modified by changing either the doping level x or the oxygen content, i.e., δ , thereby producing an important variable to test the theory.⁴ However, the use of the double exchange model to explain all the features associated with CMR has been questioned recently, and alternative mechanisms have been proposed. Inoue and Maekada,⁵ making use of a mean-field approximation, conclude that the antiferromagnetism of LaMnO_3 changes to a spiral spin state, and not to a canted state as predicted by double exchange. Furukawa⁶ has suggested a mechanism of spin disorder scattering to explain CMR in the Mn oxides. Millis, Littlewood, and Shraiman⁷ concluded that double exchange alone cannot explain the experimental data, and propose that a strong electron-phonon interaction plays a crucial role. In summary, the issue of what is the correct model to explain the magnetotransport properties in these systems is still not understood.

We have measured the temperature dependence ($T_c \leq T \leq 3T_c$) of the electron paramagnetic resonance (EPR) at 9.2 and 35 GHz, for ceramic powder samples of

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$, varying both x and δ . We find a large EPR signal, which decreases exponentially at temperatures above the ordering temperature T_c . We attribute this observation to short-range ferromagnetic ordering above T_c and suggest that an explanation of these data may provide new insights into the nature of the magnetic entities that govern the unusual magnetoresistive properties at $\sim T_c$.

The most common Mn ion that is measured via EPR is Mn^{2+} , which is generally accepted as not being present in these compounds. (As we shall demonstrate, a single $S = \frac{5}{2}$ ion is incompatible with our data.) Of the two accepted ion species in these systems: (i) Mn^{3+} ($3d^4$ with $S = 2$) is unlikely to have an observable EPR signal as it exhibits a large zero-field splitting. To our knowledge, there is only one report about Mn^{3+} ever being seen by EPR.⁸ (ii) Mn^{4+} (a $3d^3$ with $S = \frac{3}{2}$) has been reported to give an EPR signal but only for a few compounds, and generally at low temperature.⁹ As we shall show, the EPR data we observe are inconsistent with either Mn^{3+} or Mn^{4+} , and we can only conclude that the EPR signals are a consequence of some complex magnetic entity made of a collection of Mn^{3+} and Mn^{4+} ions. Further theoretical and experimental effort will be needed to identify the correct description for the ground-state spin system.

EXPERIMENTAL PROCEDURE

The samples were prepared by standard ceramic methods, heating stoichiometric mixtures of La_2O_3 , CaCO_3 , and MnO_2 at 1200 °C for 24 h. The powders were ground and reheated several times. The powders were pelletized and then heated in air for another 24 h at the same temperature, and

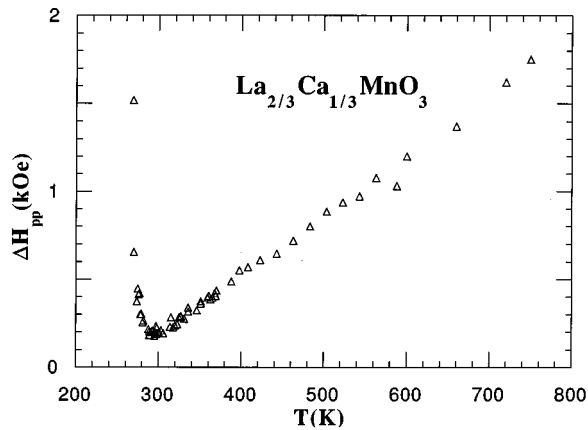


FIG. 1. The peak-to-peak EPR linewidth ΔH_{pp} for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ with a T_c of ~ 270 K as a function of T measured at 9.2 GHz.

then cooled at 100 °C/h. When a change in the oxygen content was desired, the pellets were annealed in an oxygen or an argon atmosphere. Depending on the Ca doping, the increase of oxygen was accomplished for low x , by annealing in an O_2 atmosphere for 24 h, between 900 and 1250 °C. The reduction of oxygen was achieved by annealing in an Ar atmosphere, using Zr as a getter, at 1200 °C for 24 h. The oxygen content, for $x=0$ and 0.33, was determined by thermogravimetry. The structure and phase purity were checked by x-ray diffraction. The electrical resistivity was measured using a four-probe method between 15 and 300 K on sintered pellets. The magnetization was measured with a vibrating sample magnetometer. The resonance measurements were performed using conventional EPR spectrometers, operating at 9.2 GHz between 100 and 800 K, and at 35 GHz between 77 and 300 K. The samples used in our EPR measurements were particles of but 2–5 μm obtained by filing and sieving the pellets. The powder samples were sealed in quartz tubes in a similar atmosphere as that with which they were annealed. The strength of the EPR signal is such that for the compounds with the most intense signals, no more than 1 mg of sample was used at 9.2 GHz and 100 μg at 35 GHz to avoid saturating the spectrometers.

EXPERIMENTAL RESULTS

In all the systems studied, for $T > T_c$, an EPR line with a gyromagnetic factor $g \sim 2.0$ was measured up to ~ 800 K. As shown in Fig. 1 as T approaches T_c from above, the linewidth of the resonance goes through a minimum, and then increases abruptly near T_c . Below T_c , the resonance shifts to lower field, and our studies in that regime will be reported elsewhere.

In Fig. 2 we show the resonance lines measured at 300 K and 9.2 GHz for $\text{LaMnO}_{3+\delta}$ samples annealed in oxygen, air, and argon, with $\delta=0.2, 0.12,$ and 0.02 , respectively. In Fig. 2, as in the rest of this paper, the amplitudes of the resonance lines have been normalized, including compensation for the change of the Q of the cavity with temperature and sample. The scaling factor used for each case was chosen, so the resonance lines have a comparable peak-to-peak height. We note, that if the resonance lines shown in Fig. 2

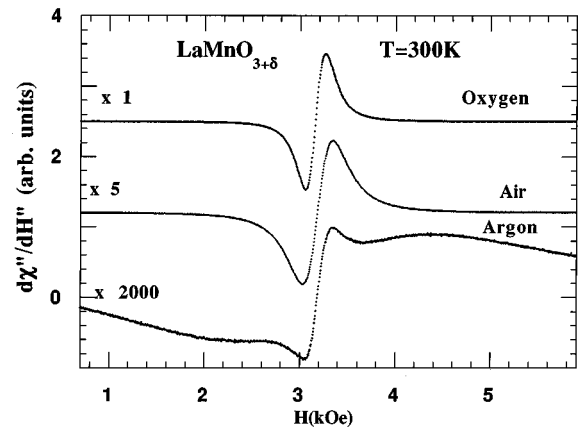


FIG. 2. EPR lines measured at 300 K and 9.2 GHz for $\text{LaMnO}_{3+\delta}$ samples annealed in oxygen, air, and argon, with $\delta=0.2, 0.12,$ and 0.02 , respectively. The amplitudes of the resonance lines have been normalized. The scaling factor used was chosen so the resonance lines have a comparable peak-to-peak height. If the resonance lines shown were solely due to Mn^{3+} , their intensity should increase as δ decreases, contrary to what is observed.

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In Fig. 3, the EPR lines for $\text{LaMnO}_{3.02}$, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, and CaMnO_3 are shown. It can be that the origin of these signals cannot be solely associated with Mn^{4+} , because in that case, CaMnO_3 would have the most intense signal, contrary to what is observed.

As mentioned earlier, the presence of Mn^{2+} is easy to detect via EPR. It has been suggested that as a result of thermally excited disproportionation¹⁰ in these compounds two Mn^{3+} ions might transform into Mn^{2+} and Mn^{4+} pairs. If that would be the case, we should expect the most intense signal for the LaMnO_3 argon-annealed sample. As can be seen in Figs. 2 and 3 the opposite occurs. Above 500 K in $\text{LaMnO}_{3.02}$ we do observe some EPR features which may be attributed to Mn^{2+} . We estimate that the total intensity if there is Mn^{2+} is only $\sim 1\text{--}2\%$ of the total Mn. For T

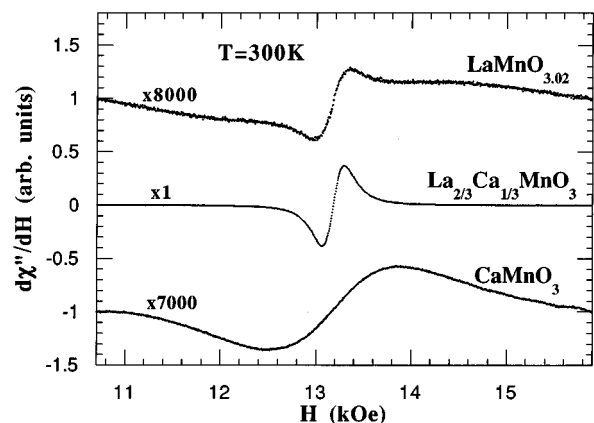


FIG. 3. EPR lines for $\text{LaMnO}_{3.02}$, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, and CaMnO_3 measured at 300 K and 35 GHz. The origin of the signals cannot be solely associated with Mn^{4+} , because in that case CaMnO_3 would have the most intense signal, contrary to what is observed.

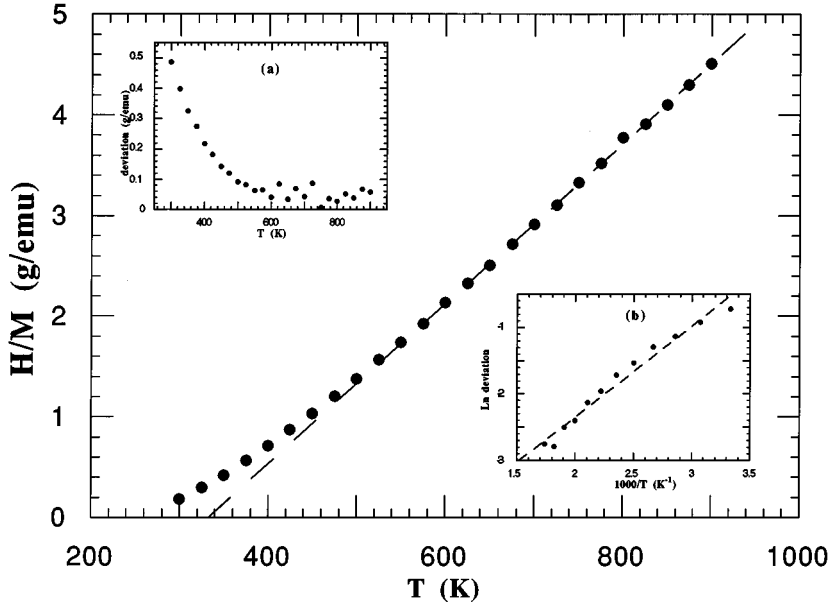


FIG. 4. Inverse dc magnetization H/M of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ as a function of temperature measured at $H=10$ kOe. Inset (a) shows the deviation of H/M from a Curie-Weiss law as a function of T . Inset (b) shows the \ln of the deviation of H/M from a Curie-Weiss law as a function of $1/T$. The dotted line represents the best fit to Eq. (1).

>290 K, and for all values of magnetic field used, up to 10 kOe, we find that the magnetization, is linear with applied field. In Fig. 4 we present H/M as a function of temperature for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ with $H=10$ kOe. The deviations from a Curie-Weiss law that are apparent below 600 K are presented in the insets as both a linear and log dependence. Similar deviations were reported before for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$.¹¹ The relationship to the EPR data will be discussed below.

DATA ANALYSIS

In this, as in the usual EPR experiment, we measure $d\chi''/dH$. Thus for samples such as ours, where M is linear with H , the double field integrated intensity of the resonance line is proportional to the magnetization. The temperature dependence of the intensity of the resonance line for these systems shows different behavior than the one predicted, at first glance, from Fig. 4. The intensity of the EPR line decreases exponentially as T increases. In Fig. 5, the normalized double integrated intensity as a function of T is given for different values of x , for samples annealed in air.

For T above the ordering temperature, we find that the intensity of the resonance line can be well fit by the expression

$$I = I_0 \exp(\Delta E/k_B T), \quad (1)$$

where I is the intensity extracted from the resonance line, I_0 is a fitting parameter, and ΔE is an activation energy. In Fig. 6 we show the intensity for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, as a function of $1/T$. The solid line represents the best fit to Eq. (1) down to 290 K, ~ 20 K above T_c . In Fig. 7 the activation energy ΔE is plotted as a function of x for samples corresponding to different annealing conditions (i.e., varying δ). Notice that for samples annealed in air, the maximum value of ΔE is near $x=0.33$. The size of ΔE at any value of x can also be modified, by varying the oxygen concentration, as can be seen by the open symbols in Fig. 7. A somewhat

similar temperature dependence of the EPR line intensity was reported for the ferromagnetic compound CdCr_2Se_4 and other parent compounds.¹²

It is interesting to note that one can drastically vary the intensity of the resonance signal and its T dependence either by Ca doping or by changing its oxygen content. We found that the intensity of the resonance lines and the resistivity for the argon-annealed samples, $\text{LaMnO}_{3.02}$ and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{2.85}$, are similar. The resistivity in both cases is of the order of $500 \Omega \text{ cm}$ at 300 K and has a maximum at about 70 K. These data support the valence interpretation that each oxygen removed results in the creation of two Mn^{3+} in place of two Mn^{4+} . In general, we found that the larger the intensity of the resonance line, the smaller is its electrical resistivity. For $x=0$ at 300 K, we measured the values of about $5 \cdot 10^{-2} \Omega \text{ cm}$, $2 \Omega \text{ cm}$, and $300 \Omega \text{ cm}$ for $\text{LaMnO}_{3+\delta}$ samples annealed in oxygen, air, and argon, with $\delta \sim 0.2$, 0.12 , and 0.02 , respectively. The maximum of the

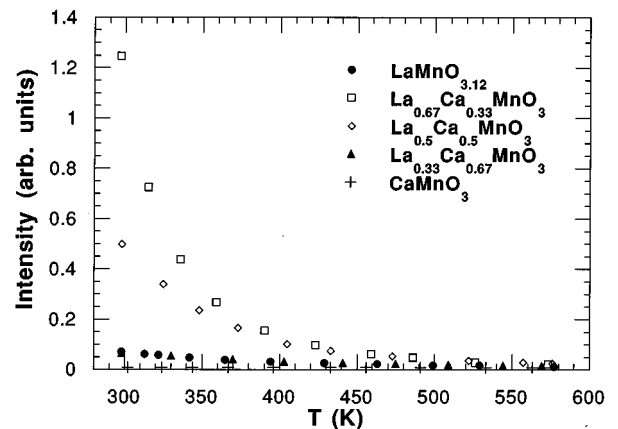


FIG. 5. Normalized integrated intensity for samples annealed in air as a function of T for different values of x as a function of T measured at 9.2 GHz.

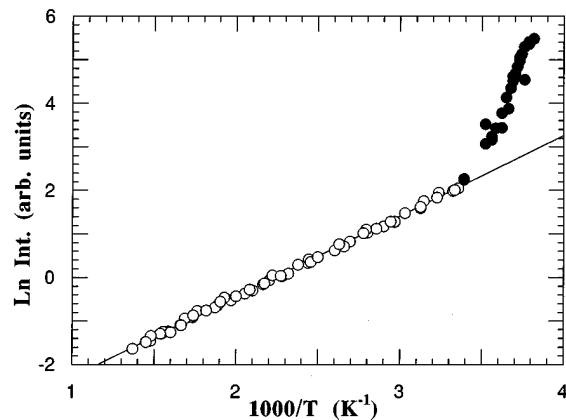


FIG. 6. Intensity of the EPR line for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ annealed in air as a function of $1/T$ measured at 9.2 GHz. The solid line represents the best fit to Eq. (1) for $T \geq 290$ K, (O). Also, data are presented for $T \geq 260$ K (●).

resistivity for these cases occurs at ~ 270 , 240, and 70 K, with $\delta=0.2$, 0.12, and 0.02, respectively.

DISCUSSION

As we discussed, since our data cannot be identified with the EPR of individual Mn ions, we may ask what is the origin of the resonance line? For T above 600 K the intensity of the EPR line is greatly reduced, to less than 5%, from that expected assuming all the individual paramagnetic Mn ions contributed to the resonance line. At temperatures ~ 20 K above T_c , where no shift of the resonance field has yet occurred, and the linewidth is close to a minimum, the intensity for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ is such that the cooperative precession corresponding to an effective spin ~ 30 would be required per formula unit. The entity associated with such a large magnetic moment, may be due to magnetic polarons, spin clusters, i.e., some form of short-range ordering among the spin-polarized carriers that dissociate with an activation energy ΔE . Whatever the nature of the cooperative spin entity we confirm that the g value remains at $g \sim 2$ for measurements made at both 9.2 and 35 GHz, and $T \geq 290$ K.

In contrast to the EPR data discussed above, the number of Bohr magnetons obtained from the dc magnetization data above 600 K agrees with that expected by a Curie-Weiss law, when using the ratio of Mn^{3+} and Mn^{4+} expected for the different dopings and oxygen content. Also, below this temperature we find deviations from a Curie-Weiss law, as can be seen in Fig. 4 and its insets. The discrepancy between the dc magnetization, and the EPR data in the two regimes may have separate explanations. In general, for the dc magnetization, one measures the contribution of all paramagnetic entities—singlets, pairs, triplets, etc.—whereas for EPR the resonance intensity may correspond only to those moments that have an appropriate relaxation rate, g value, etc. For T

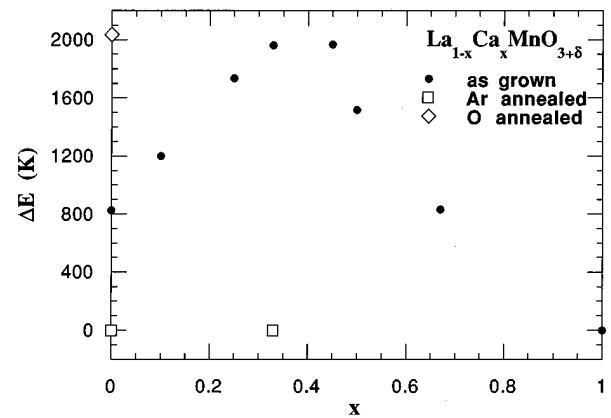


FIG. 7. Activation energy ΔE as a function of x for samples annealed in air (●), oxygen (◇), and argon (□).

>600 K the possible explanation is that it is very rare to observe isolated Mn^{3+} and Mn^{4+} via EPR, especially at such high temperatures. Below 600 K we find that there is a correlation between the temperature dependence of the intensity of the EPR data and these of the deviation of the magnetization from a Curie-Weiss law. When the linear part of the dc susceptibility is extrapolated from high temperature and subtracted, the remaining part also decays exponentially as is shown in the insets to 4(a) and 4(b). The EPR technique appears to be much more sensitive to the deviating component than the dc magnetization since, for the data shown, the sample mass was about 1000 times more than that used in the EPR.

In summary, we emphasize that the explanation of the EPR/FMR data are an important, but still unsolved problem in these compounds. The very nature of the ground-state spin configuration is not known. As shown, it cannot be attributed to isolated Mn ions. For $T > 600$ K the EPR signal may be due in part to “impurities,” but the predominant contribution comes from an “unknown” spin complex. The exponential increase of the \ln of the EPR intensity as we approach T_c , the fact that these spin entities interact with short-range order for an unusually long range of temperatures prior to when long magnetic order occurs, and the ability to reversibly change the nature of the spin complex coupling, as shown by the successive oxygen-argon-oxygen annealings in the same compound, that result in dramatic changes in ΔE , may prove to be a valuable tool in the formulation of the Hamiltonian for these materials.

ACKNOWLEDGMENTS

This research was sponsored at San Diego State University by NSF Grant No. DMR-91-17212 and at the University of California San Diego, by NSF Grants No. DMR-93-02913 and BIR-94-15294. We wish to thank S. Shtrikman, D. Rao, E. Trovatto, and P. Platzman for helpful discussions.

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