

Anomalous spin dynamics in the charge-ordered two-electron doped manganite $\text{Ca}_{0.9}\text{Ce}_{0.1}\text{MnO}_3$: Possibility of a spin-liquid phase

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The “two-electron” doped rare earth manganites $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0.1, 0.2$) are probed using resistivity, ac susceptibility, and electron paramagnetic resonance (EPR) measurements across their respective charge ordering (CO) temperatures $T_{\text{CO}}=180$ and 250 K. The EPR resonance field and intensity as well as the transport and magnetic behaviors of the two compositions are qualitatively similar and are as expected for CO systems. However, the EPR linewidth, reflective of the spin dynamics, for $x=0.1$, shows a strongly anomalous temperature dependence, decreasing with decreasing temperature below T_{CO} in contrast with the sample with $x=0.2$ and other CO systems. Keeping in view the evidence for magnetic frustration in the system, we propose that the anomalous temperature dependence of the linewidth is the signature of the occurrence of a disorder driven spin liquid phase, present along with charge ordering.

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I. INTRODUCTION

The complex phase diagrams and the fragile phase boundaries of the hole and electron doped rare earth manganites,^{1,2} $A_{1-y}R_y\text{MnO}_3$, where A is a divalent alkaline earth ion ($\text{Ca}^{2+}, \text{Sr}^{2+}, \dots$) and R is a trivalent rare earth ion ($\text{La}^{3+}, \text{Nd}^{3+}, \text{Pr}^{3+}, \dots$), continue to attract intense theoretical³ and experimental⁴ attention. [For $y < 0.5$, the Mn^{4+} ions (electronic configuration $3d^3$) of the parent compound AMnO_3 are replaced by y number of Mn^{3+} ions ($3d^4$) with one extra electron leading to “electron” doping and for $y > 0.5$, the material is considered to be doped with “holes.”] One of the activities at the center stage of this effort is the study of the fascinating phenomenon of charge ordering.^{5,6} Charge ordering (CO), refers to the real space ordering of the Mn^{4+} and the Mn^{3+} ions which occurs on cooling the paramagnetic insulating material below a certain sample-specific temperature T_{CO} , the charge ordering temperature. The CO insulating state dominated by Jahn-Teller polarons and the superexchange interaction between Mn^{3+} and Mn^{4+} ions and the colossal magnetoresistive (CMR) ferromagnetic metallic state dominated by the Zener double exchange (DE) interaction are understood to be two competing ground states in the phase diagram of doped manganites. The CO transition is usually accompanied by certain tell tale signatures like superlattice reflections in x-ray and neutron diffraction patterns, an increase in the resistivity and often, especially when the CO state terminates in an antiferromagnetic (AFM) phase on further cooling, a peak in the susceptibility. In recent years a large number of investigations have addressed the many interesting properties of the CO phenomenon such as the “melting” of the CO when subjected to perturbations such as magnetic field, irradiation, and the application of a current and the influence of the size, i.e., bulk versus nano,⁷ on the stability of the CO phase and so on.

Relatively less studied in this respect are the cerium doped manganites of the form $A_{1-x}\text{Ce}_x\text{MnO}_3$. It is found⁸ that Ce enters into these compounds in the 4+ valence state and therefore one expects these to have certain unique prop-

erties since the “ x ” amount of cerium doping at the A site inducts $x=2y$ number of Mn^{3+} ions, twice of what are induced by Ln^{3+} . Thus the cerium-doped oxides are expected to show a rapid change in their magnetic and electronic properties as a function of x compared to the Ln^{3+} doped oxides.⁸

Maignan *et al.* prepared electron doped $\text{Ce}_x\text{Ca}_{1-x}\text{MnO}_3$ (CCMO) by traditional solid state route.⁹ Zeng *et al.*⁸ studied the magnetic and electronic properties of CCMO and compared it with the conventional electron doped $\text{La}_y\text{Ca}_{1-y}\text{MnO}_3$ (LCMO). They gave a tentative magnetic T - x phase diagram for CCMO which was qualitatively similar to that of LCMO. Recently Caspi *et al.*¹⁰ in a comprehensive structural and magnetic study provided a detailed understanding of the structural and magnetic phase diagram of CCMO in the region $0 \leq x \leq 0.167$. One of the noteworthy features of their finding is that for a substantial composition range ($0.1 \leq x \leq 0.167$) the material exhibits a CO phase. However, for the $x=0.1$ composition, though they observed CO signatures in their x-ray diffraction and ac susceptibility measurements, neutron diffraction failed to give any evidence in that the CO peaks were absent in the diffraction pattern.

Electron paramagnetic resonance (EPR) is a powerful local probe for the study of static and dynamic magnetic correlations on a microscopic level and can help to clarify¹¹⁻¹⁴ the complex magnetic states exhibited by manganites. The technique has proven to be especially useful to understand the CO state through the characteristic behaviors of the resonance field, the intensity, and the linewidth across the CO transition.¹⁵⁻¹⁷ The resonance field, which is typically temperature-independent down to T_{CO} , varies strongly with temperature below the transition. The intensity of the signal is found to go through a peak close to T_{CO} . In particular, the EPR linewidth is observed¹⁵⁻¹⁸ to exhibit a continuous increase starting from T_{CO} down to the antiferromagnetic transition to which most of the CO manganites transform on further reduction in temperature. This linewidth behavior is explained in terms of a “motional narrowing”¹⁶ or a “variable range hopping”¹⁷ model.

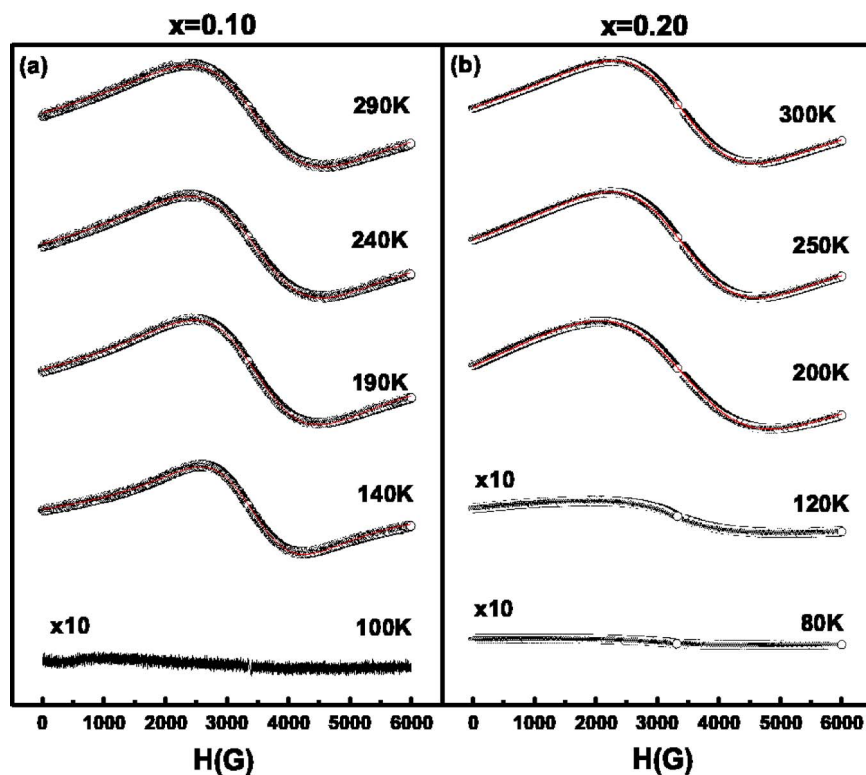


FIG. 1. (Color online) A few representative EPR signals plotted at different temperatures for the $x=0.1$ and $x=0.2$ compositions. The solid lines are the fits of the signals to the field derivative of the double Lorentzian line shape function (Ref. 16).

In this work, we present our results of magnetic, transport and EPR studies on $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ for $x=0.1$, and 0.2 especially focusing on the $x=0.1$ composition where neutron diffraction did not show CO peaks though x-ray diffraction did, with a view to clarifying the apparent inconsistency. The EPR signatures of CO are observed for $x=0.2$. However, for $x=0.1$, while the resonance field and the intensity behave as in $x=0.2$ and other CO systems, the linewidth shows a strongly anomalous decrease with decreasing temperature below T_{CO} . We attempt to understand this in terms of the presence of spin fluctuations that average out the linewidth broadening interactions. Such fluctuations, similar to those found in a spin liquid, could arise as a consequence of the magnetic frustration present in the CCMO sample.

II. EXPERIMENT

The polycrystalline $\text{Ce}_x\text{Ca}_{1-x}\text{MnO}_3$ ($x=0.10, 0.20$) samples were prepared by solid state synthesis.⁹ Stoichiometric amounts of CaCO_3 , CeO_2 , and MnO_2 were mixed and heated at different temperatures (1100, 1200, and 1350 °C) with intermediate grindings. Single phasic materials were obtained only at 1350 °C. The pellets were finally sintered at 1400 °C. The powder x-ray patterns were recorded using a Philips diffractometer with $\text{Cu } K\alpha$ radiation and scanning (0.01 step in 2θ) over the angular range 10° – 110° . The diffractograms for the two compositions show single phases with no impurity peaks present. Both the powder patterns could be indexed in the orthorhombic system with space group Pbnm with $a \sim b \sim c/\sqrt{2}$. No impurity is detected by energy dispersive x-ray analysis (EDAX) either, and it gives expected cationic compositions. The oxygen stoichiometry

and the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio were confirmed by iodometric titration. The ac susceptibility measurements were done using a homemade apparatus in the temperature range of 80–300 K at a frequency of 100 Hz. The EPR measurements were carried out on powder samples using a commercial X-band spectrometer. The spectrometer was modified by connecting the X and Y inputs of the chart recorder to a 16-bit analog-to-digital (A/D) card, which in turn is connected to a personal computer (PC) enabling digital data acquisition. With this accessory, for the scan width typically used for our experiments, i.e., 6000 G, one could determine the magnetic field to a precision of ~ 3 G. The temperature was varied from 10 to 300 K (accuracy ± 1 K) using a continuous helium flow cryostat and the EPR spectra were recorded while warming the sample. A speck of DPPH was used as a field marker to find the center field of the signal accurately.

III. RESULTS AND DISCUSSION

Figure 1 shows the EPR spectra $[(dP/dH) \text{ vs } H]$, where P is the microwave power absorbed and H is the magnetic field for the two compositions from room temperature down close to their antiferromagnetic transition temperature T_N , where the signals disappear. The signals are seen to be quite broad, similar to those observed in other CO manganites. For the $x=0.2$ sample, as the sample is cooled, the signal further broadens, again a behavior found in other CO manganites. However, signal from the $x=0.1$ sample shows an anomalous temperature dependence in that it is found to narrow down with the decrease in temperature. The signals of both the samples are fitted to the Lorentzian line shape function.¹⁶ The sharp signals due to DPPH, used as a field marker, have

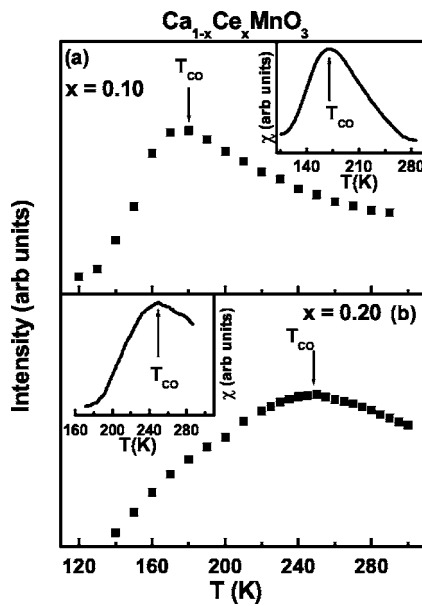


FIG. 2. EPR intensity plotted as a function of temperature for the two compositions. The insets show the ac susceptibility. Arrows indicate the charge ordering transition temperatures.

been digitally subtracted to aid the fitting of the line shapes. The line shape parameters *viz.* the intensity, the resonance field H_0 and the linewidth are extracted from the fits. Figure 2 shows the temperature dependence of the EPR intensity for the two compositions. For both the samples, the intensity initially increases with the decrease in temperature, shows a broad peak at T_{CO} and decreases with further decrease of temperature in the CO phase. This behavior is observed in other CO systems as well and also qualitatively mimics the behavior of the susceptibility of the CO materials, shown in the insets to Fig. 2 for $x=0.1$ and 0.2 . Neutron scattering studies on $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ have shown¹⁹ that for $T > T_{CO}$, close to T_{CO} , double-exchange induced ferromagnetic spin fluctuations are present which are progressively replaced by the superexchange mediated antiferromagnetic spin fluctuations as the system goes into the CO phase. This explains why a broad peak is seen in the susceptibility, magnetization as well as EPR intensity at T_{CO} . The AFM spin fluctuations increase in the CO phase and on further cooling an antiferromagnetically ordered phase appears. This is accompanied by a decrease in the intensity of the EPR signal in the CO phase before the complete disappearance of the signal at a temperature close to T_N . According to Caspi *et al.*, for $x \geq 0.1$, CCMO shows phase coexistence at low temperatures. The $x=0.10$ sample undergoes a CO transition at $T_{CO}=170$ K, and a transition to a C-type AFM phase at 152 K and a further transition to a “magnetically charge ordered” (MCO) phase at $T_{MCO}=107$ K. The EPR signal disappears at 100 K [Fig. 1(a)], close to the T_{MCO} . Similarly for $x=0.20$, $T_{CO}=250$ K, the EPR signal [Fig. 1(b)] becomes very weak below 140 K and disappears completely below 90 K. The temperature below which the signal becomes weak matches with the onset of C-type AFM phase. As there is still some ferromagnetic order present along one of the crystallographic axes, the signal is observed in the C-AFM

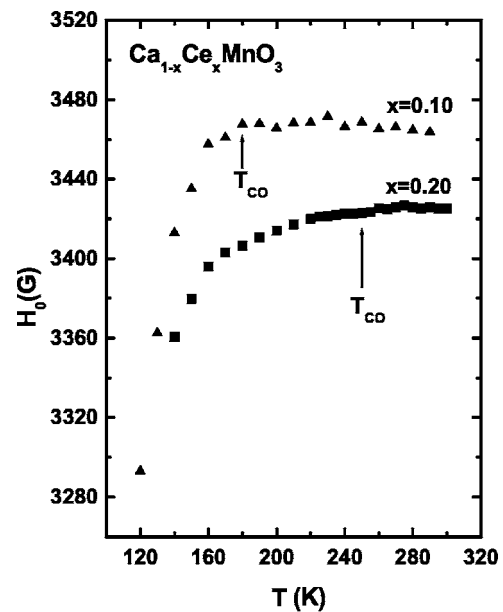


FIG. 3. The resonance field plotted as a function of temperature for the two compositions. The size of the symbols indicates the error in the field measurement.

phase. In the MCO phase the signal disappears completely. Thus EPR signals give an indication of the two magnetic phases.

The temperature dependence of the resonant field H_0 for the two samples is shown in Fig. 3. For both the samples, from room temperature down to T_{CO} , H_0 is essentially independent of temperature. However, for $T < T_{CO}$, both show strong decrease of H_0 with decreasing temperature. Figure 4 shows the temperature dependence of EPR linewidth $\Delta H(T)$, for the two compositions. In the paramagnetic phase the linewidth for the two samples is of the order of 2000 G. This

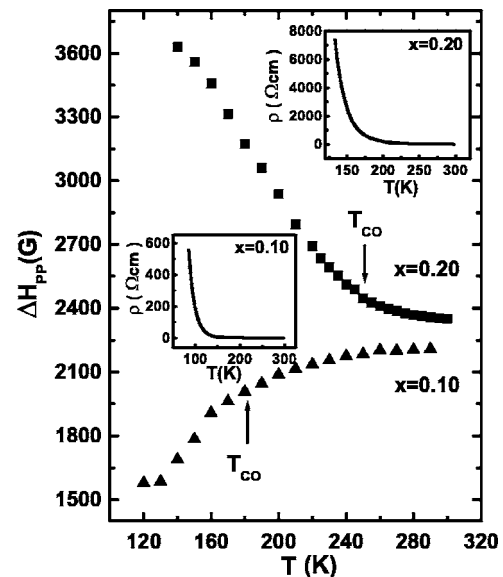


FIG. 4. The EPR linewidth plotted as a function of temperature for the two compositions. The insets show the temperature dependences of the corresponding resistivities.

relatively large linewidth, seen in other manganites as well, is understood to originate in the Dzialoshinsky-Moriya (DM) antisymmetric exchange interaction and the crystal field (CF) anisotropy. In the CO phase, for $x=0.20$, for $T < T_{CO}$, the linewidth increases with the decrease of temperature as seen in other CO manganites. This behavior *viz.*, the continuous decrease of the linewidth with the increase in the temperature from T_N to T_{CO} in the CO phase has been explained by invoking the model of motional narrowing or in terms of variable range hopping. In both of these cases, the decrease in the linewidth for increasing T from T_N to T_{CO} was accompanied by a decrease in the resistivity as well. In contrast, for $x=0.10$, the linewidth increases with an increase in temperature in the CO phase, (accompanied by a *decrease* in the resistivity), which is not observed in the CO phase of any other manganite.

Thus we have this quite surprising result in the case of $x=0.1$ compound that the resonance field and the intensity of the EPR signals as well as magnetic, transport, and structural studies give evidence of a CO phase while the linewidth behavior is exceptional. In the following we try to understand this result in terms of the present knowledge of the linewidth behavior in manganites and other materials undergoing magnetic transitions. We find that none of these models is applicable to the present example and a new explanation is needed.

A number of reports have addressed the behavior of EPR linewidth in manganites. In manganites undergoing a transition from a paramagnetic to a ferromagnetic state, the linewidth $\Delta H(T)$ in the paramagnetic state is found to increase quasilinearly with increasing T . Different models have been proposed to explain this result such as contribution from spin-phonon interaction,¹¹ a relaxation bottleneck behavior^{20,21} or in terms of a combined effect of DM and CF interactions.¹² The latter model seems to be able to explain most of the CMR EPR linewidth results and can be described in terms of the equation, $\Delta H(T) = [\chi_0(T)/\chi(T)]\Delta H(\infty)$ where $\chi_0(T) \propto T^{-1}$ is the free ion (Curie) susceptibility, $\chi(T)$ is the measured susceptibility, and $\Delta H(\infty)$ is a temperature independent constant attributable to the high temperature limit of the linewidth. It is found that a large number of CMR manganites follow a “universal” behavior^{14,22} when $\Delta H(T)/\Delta H(\infty)$ is plotted against T/T_C . We examine the applicability of this model to the present CO systems in Fig. 5. According to this model, $\Delta H(T)$ should be proportional to $\chi_0/\chi(T)$, i.e., to $1/[T \times \chi(T)]$. However, as clearly seen in the figure, the proportionality does not hold for either of the two CO compounds. This is really not surprising if we note that in these systems the narrowing is a consequence of the enhancement of the susceptibility as one approaches T_C . In the CCMO samples, as well as in other CO systems, for $T < T_{CO}$, the susceptibility actually decreases thus violating the basic premise of the model.

There has been a considerable number of EPR studies^{23–26} over the years on antiferromagnetic materials above their T_N . In these systems, typically, as one approaches T_N from above, the EPR linewidth is found to decrease either linearly or quasilinearly down to a temperature close to the transition, go through a minimum and then diverge as $T \sim T_N$. A relation

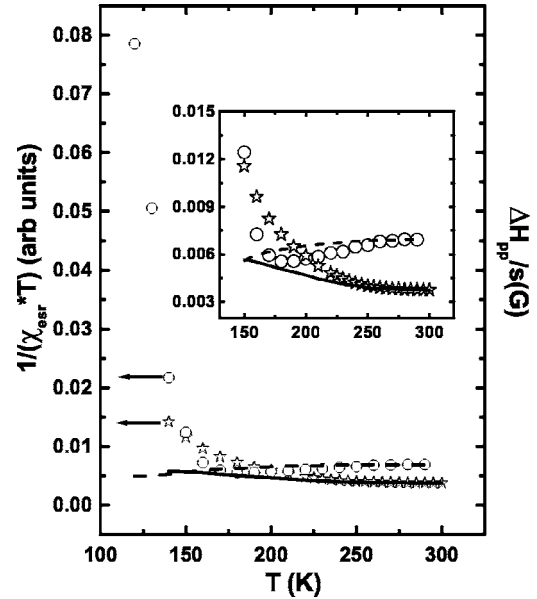


FIG. 5. Test for the applicability of the model used for fitting the EPR linewidths of CMR materials to the present data. Circles correspond to $x=0.1$ and stars to $x=0.2$. The dashed and the solid lines are linewidths divided by a scaling factor (right “y” axis), for the 0.1 and 0.2 sample, respectively. Inset shows the relevant region on an expanded scale. The inapplicability of the model in the CO region is clearly seen.

of the type $\Delta H = A + BT + C(T - T_N)^{-p}$, which describes the observed quasilinear dependence far above T_N and the critical behavior close to the transition has been often used²³ to fit $\Delta H(T)$. However, we find that $\Delta H(T)$ in CCMO as well as in other CO systems shows neither divergence close to T_N , nor a quasilinear behavior far away from T_N . Therefore, it is unlikely that the models used to explain the $\Delta H(T)$ behavior in other AF materials are applicable to CO systems.

In most CO materials in the CO state, $\Delta H(T)$ decreases with increasing T and in as much as it is associated with a decrease in the resistivity, hopping of the spins along with the charge carriers (i.e., holes or electrons) was understood^{16,17} to cause averaging out of the broadening interactions such as DM and CF, leading to a narrowing of the linewidth. However, while the $\Delta H(T)$ for $x=0.2$ may be explained according to one of these models, the $\Delta H(T)$ for $x=0.1$ obviously cannot be explained in terms of either of these models because for this compound the results on $\Delta H(T)$ and $\rho(T)$, where ρ is the resistivity, show that with decreasing temperature below T_{CO} , while charge dynamics slows down, spin dynamics becomes faster.

According to the comprehensive study of CCMO by Caspi *et al.*,¹⁰ for $x \sim 0.1$, with decreasing T , the sample undergoes a transition from a monoclinic, paramagnetic phase to a monoclinic orbitally ordered C-type phase. As mentioned before, their resistivity, x-ray structure and ac susceptibility measurements indicate that this phase is also charge ordered. This conclusion is further supported by our resistivity, ac susceptibility, EPR resonance field, and intensity behaviors. For $x \geq 0.125$, all indicators mentioned above, both in the studies of Ref. 10 and ours provide the evidence for a

transition from room temperature paramagnetic phase to a low temperature charge ordered phase. Indeed Caspi *et al.*,¹⁰ conclude that the CO phase is of Wigner crystalline type as well. However, quite interestingly, they are not able to see CO peaks in their neutron diffraction study though they observe CO signatures in their x-ray experiments. More importantly, they provide evidence for frustration in part of the Mn-O bonds in the CO structure. The concentration of the frustrated bonds is found to increase with decreasing x . Thus with the presence of both disorder and frustration, it is quite likely that the spin system acquires the possibility of entering into either a spin glass or a spin liquid state.²⁷ Considering the relatively high temperature range of the experiment, the latter appears to be the more likely scenario. This proposed spin liquid state is also qualitatively consistent with the recent work of Huber²⁸ who finds that for a geometrically frustrated Heisenberg antiferromagnetic system, for T approaching T_N from above, below the susceptibility peak there is a rapid increase in the spin diffusion constant with decreasing temperature as well as a decrease in the spin-spin correlation time. Both these effects would go towards decreasing the EPR linewidth. We note, however, that in the present case one is concerned with the peak in the susceptibility at T_{CO} . Moreover, the system is also quite anisotropic, though the

spin system if it were in the liquid phase would acquire the isotropy inherent in Huber's treatment. Clearly more theoretical work is required along these lines as well as experimental investigations using other techniques such as inelastic neutron scattering, especially looking for the presence of any diffuse scattering.

Summarizing, we have studied the two-electron doped rare earth manganites $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0.1, 0.2$) using resistivity, ac susceptibility, and EPR measurements across their CO transition temperatures. While for $x=0.2$, all measurements are consistent with the CO phase, for $x=0.1$, the EPR linewidth alone, which is an indicator of spin dynamics, shows anomalous behavior. We examine this result in terms of the existing theories and models of EPR linewidth in manganites and other materials undergoing magnetic transitions and find that they are not able to explain this anomalous linewidth behavior. Further, the more recent qualitative models proposed for CO manganites also are found to be not applicable. Therefore, we put forward a proposal, which needs to be confirmed by other techniques, that the anomalous temperature dependence of EPR linewidth in $\text{Ca}_{0.9}\text{Ce}_{0.1}\text{MnO}_3$ could be due to the presence of a spin liquid state.

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