Critical slowing down of longitudinal spin relaxation in $La_{1-x}Ca_xMnO_3$

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Using original modulation technique, the longitudinal electron spin-relaxation time T_1 has been measured directly in the paramagnetic state of three $La_{1-x}Ca_xMnO_3$ samples ($x=0.2$, 0.25, and 0.33). Well above the phase-transition temperature T_c, the longitudinal relaxation times are found to be equal to the transversal ones (T_2) as determined from the electron-paramagnetic-resonance (EPR) linewidth, whereas a steep slowing down of T_1 with a critical exponent $\alpha \simeq 0.5$ was observed as T_c was approached in all the materials. Various models are discussed, including extremely slow internal dynamics, formation of magnetic clusters, and inhomogeneous EPR broadening near T_c.

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Recently, there is a growing interest in properties of the $La_{1-x}Me_xMnO_3$ (where $Me=Ca,Sr,Ba,\ldots$) manganites with the perovskite structure. These compounds reveal very unusual magnetic and transport features, the most striking among them being the colossal magnetoresistance (CMR) effect found in the vicinity of the paramagnetic insulator to ferromagnetic metal transition temperature T_c. At present it is found that the CMR effect, as well as an extremely rich and peculiar magnetic phase diagram of these compounds, are due to specific interactions between the three- and four-charged Mn ions. The Mn ions interact with mobile carriers according to the ''double exchange'' mechanism with account made for the Jahn-Teller effect and related formation of magnetic polarons both above and below T_c (see, for example, the review articles[1,2]). The whole physical picture is still far from clear, thus promoting a large number of theoretical and experimental studies.

The magnetic-resonance methods [both NMR and electron-paramagnetic-resonance (EPR)] are powerful tools to study internal dynamics of the manganites (see, for example, Refs. 3–15). In the case of EPR (Refs. 8–15), a single intense line with $g \approx 2$ is commonly observed above T_c. The linewidth ΔB is temperature dependent: it has a minimum slightly above T_c and increases monotonically with heating in the paramagnetic region. While approaching T_c, a huge broadening is normally found (the broadening is absent in high-quality single crystals[12]), followed by transformation to ferromagnetic resonance below T_c.

Two different models describing the observed temperature dependence of ΔB have been discussed. In Refs. 8, 9, and 14 the EPR linewidth in the CMR manganites was supposed to be caused by spin-lattice relaxation of the entire exchange-coupled Mn^{3+}-Mn^{4+} spin system under the condition of a strong relaxation bottleneck. According to the last, more refined version,[14] the energy transfer at the most narrow section of the relaxation path is provided by thermoactivated hopping of small polarons related with jumps of e_g electrons from the Jahn-Teller Mn^{3+} ions to the Mn^{4+} ones. The main argument advanced in Ref. 14 is based on similarity of the temperature dependency of ΔB and that of the polaron hopping conductivity in $La_{0.8}Ca_{0.2}MnO_3$: in both cases, the $T^{-1}\exp(E_a/k_BT)$ law is apparently obeyed, with close values of the activation energy E_a (here k_B is the Boltzmann constant and T is the temperature).

Another mechanism is suggested in Refs. 10 and 13. According to this, the EPR linewidth in a wide variety of the perovskite manganites is determined by spin-spin (exchange) interactions between the Mn^{3+} (effective spin $S=2$) and Mn^{4+} ($S=\frac{3}{2}$) ions and so is unrelated to any spin-lattice processes. This model was used[13] to calculate the appropriate exchange integrals, with the Dzialoshinsky-Moriya terms taken into account. The main support for this interpretation is provided by a good agreement of the experimental data with the theoretical relation deduced in Ref. 13:

$$\Delta B \propto \frac{1}{T\chi(T)}, \tag{1}$$

where $\chi(T)$ is the temperature-dependent magnetic susceptibility. In any case, the nature of the EPR broadening is determined by the mechanism of the electron-spin relaxation that is closely related to the internal field dynamics in manganites and so is of substantial interest for CMR physics. It should be stressed that the measuring of the EPR linewidth allows determination of only transverse relaxation time T_2. For Lorentzian line shape, it is related to the peak-to-peak linewidth Δ_{pp} as follows:

$$T_2^{-1} = \left(\frac{\sqrt{3}}{2}\right)\gamma\Delta_{pp}, \tag{2}$$

where γ is the gyromagnetic ratio. As to the time T_1 of the longitudinal electron-spin relaxation, it was never measured directly in the CMR manganites. The obvious reason is that accounting for the expected relaxation rates ($10^9 - 10^{10}\ s^{-1}$), the standard pulse or cw saturation methods are inapplicable, since the requested values of the saturation factor $s \sim 1$ could be achieved at quite an unacceptable microwave power level (as high as 10^3 W). At the same time, the longitudinal relaxation rate T_1^{-1}, being proportional to

the spectral density of the fluctuating internal fields at the EPR frequency ($\omega_0 \sim 10^{11}$ s^{-1}), does not coincide necessarily with the T_2^{-1} value that is determined mostly by the static component of the random internal field. So measuring the temperature dependence of T_1 in manganites can yield information on internal dynamics, especially near T_c. This is just the aim of the present study, where we have employed an original version[16,17] of the modulation technique[18,19] enabling one to measure directly the T_1 values as short as $10^{-9}-10^{-10}$ s.

Ceramic samples of $La_{1-x}Ca_xMnO_3$ with $x=0.2$, 0.25, and 0.33 were prepared in the Laboratory for Neutron Scattering, ETH Zurich and PSI, by a solid-state reaction procedure using dried high-purity La_2O_3, $CaCO_3$, and MnO_2 starting materials. The well-ground mixture was heated in air at 1000 °C for 12 h, 1100 °C for 12 h, and 1200 °C for 20 h with intermediate grindings. The samples are clean single phase as checked by x-ray diffraction.

The EPR spectra were registered at 9.7 GHz (X band) with an ER-200 Bruker spectrometer from 170 to 300 K. Temperature was controlled by means of the Oxford system with an accuracy of 1 K. Powder samples of sufficiently small volume were used to avoid distortions caused by too-large resonance absorption near T_c.[10] No signs of the Dysonian line shape were observed in the whole temperature range, thus indicating that the powder grain dimensions are much less than the skin depth.

The measurements of the longitudinal electron-spin relaxation time T_1 were performed by means of the modulation technique described in Refs. 16 and 17. The microwave power ($\omega_0 = 2\pi \cdot 9.4$ GHz, 250 mW) was modulated at the frequency $\Omega = 2\pi \cdot 1.6$ MHz, providing the in-phase longitudinal magnetization response received with a special pickup coil. To determine T_1, the following relation was used:[16]

$$\Omega T_1 = A \frac{U}{P_{\mathrm{EPR}}}, \tag{3}$$

where U is the amplitude of the longitudinal magnetization response, P_{EPR} is the value of EPR absorption measured on the same sample and under the same conditions, and A is an instrumental coefficient to be determined by using a reference sample with a known T_1 value. We used diphenylpicrylhydrazyl (DPPH) as a standard reference; it has a narrow EPR line and temperature-independent value of $T_1 = 5 \cdot 10^{-8}$ s. The reference was placed as close as possible to the investigated sample and served for normalization of both the U and P_{EPR} signals. Note that the employed technique is in fact equivalent to the cw saturation one, with the difference being that the former enables one to work at saturation factors as small as 10^{-4}.

The EPR spectra taken at temperatures above and near T_c are shown in Fig. 1. They are consistent with the data known from the literature.[8–10,13–15] For all the samples, a single, nearly Lorentzian EPR line is observed with $g \approx 2$. A characteristic minima in the temperature dependences of the linewidths takes place at temperatures $T_{\min}$ slightly above the

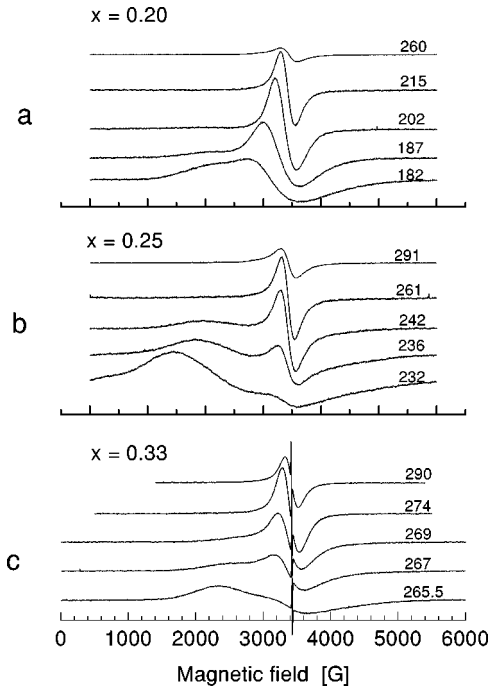

FIG. 1. EPR spectra (absorption derivatives) of $La_{1-x}Ca_xMnO_3$ with $x=0.2$ (a), 0.25 (b), and 0.33 (c) at various temperatures (indicated at the curves in degrees Kelvin) within paramagnetic regions. The narrow signal in the c panel is due to the reference (DPPH).

critical ones. The latter is clearly seen in Fig. 2, where the T_2 values as determined from Eq. (2) are plotted.

The T_1 data obtained by the above-described modulation method are also shown in Fig. 2. It can be seen that for all the samples ($x=0.2$, 0.25, and 0.33) at high-enough temperatures (well above T_c), the transverse and longitudinal relaxation times practically coincide. Approaching T_c from the high values leads to a steep rise in T_1 with simultaneous decreasing of T_2, so the T_1/T_2 ratio increases by more than 1 order of magnitude within a temperature range of a few degrees Kelvin.

It is well known that approaching T_c in the paramagnetic region results in a steep increase of susceptibility approximately obeying the Curie-Weiss law [see the inset in Fig. 2(c); more detailed data for various manganites are reported, for instance, in Refs. 9, 10, and 13). This can lead to systematic errors in measuring P_{EPR} due to overloading of the microwave cavity.[10] Besides, an increase in the sample susceptibility can result in redistribution of the radio-frequency field in the pickup coil that, in turn, could lead to an error in calibration by the reference probe. In order to determine these errors, the experiments were repeated with different volumes of the manganite samples and at various couplings of the microwave cavity with the waveguide. The error of the measurements was estimated to be 10–20 % (see the bars in Fig. 2).

Below T_c one deals with ferromagnetic resonance so, strictly speaking, Eq. (3) is no longer valid. Nevertheless, some T_1 values determined formally by the same method are also shown in Fig. 2(c) for comparison. Despite the large

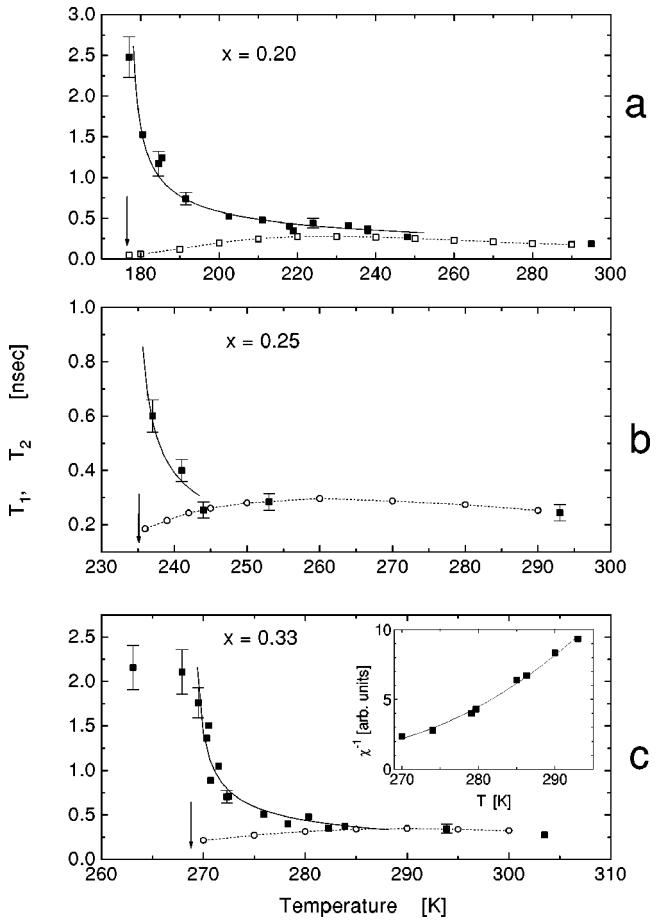

FIG. 2. Temperature dependencies of the longitudinal (T_1, filled squares) and transversal (T_2, open circles) relaxation times in $La_{1-x}Ca_xMnO_3$ with $x=0.2$ (a), 0.25 (b), and 0.33 (c) above and near Curie temperature (indicated by the arrows). Solid curves are the best fits of Eq. (6) with $\alpha=0.5$. Dotted curves are guides for the eyes. Inset: temperature dependence of the inverse spin susceptibility χ^{-1} measured as an area under the EPR absorption line for $x=0.33$.

error, one can see that these data are rather close to the longest relaxation times obtained near T_c.

Consider first the temperatures $T>(T-T_c)$ far enough from critical phenomena. Under these conditions, the equality

$$T_1=T_2 \tag{4}$$

is clearly obeyed for all the three compounds ($x=0.20$, 0.25, and 0.33) that is characteristic of paramagnetic relaxation caused by very fast fluctuations of internal fields. Just this situation is expected for both the above-mentioned mechanisms of the EPR broadening in the manganites. Whatever is the cause that determines the ΔB value far away from T_c, whether it be fast spin-lattice relaxation[8,9,14] or strong exchange narrowing,[10,13] the equality of the transverse and longitudinal relaxation times seems to be quite natural and, besides, serves as independent support for validity and accuracy of the modulation method used for measuring T_1.

It is much more difficult to suggest an unambiguous explanation of the steep increase in T_1 as the critical temperature is approached. Without question the nature of this phenomenon is a critical one, so it can be called the critical slowing down of the longitudinal relaxation of the Mn ions. At present, we cannot suggest an ultimate interpretation of this effect and so shall restrict ourselves to some plausible hypotheses.

According to general theory of magnetic relaxation,[20] the relaxation rate T_1^{-1} is proportional to spectral density of internal field fluctuations at the EPR frequency. For qualitative estimations, a simple equation can be used:

$$T_1^{-1}\approx(\gamma H_i)^2\frac{\tau}{1+\omega^2\tau^2}, \tag{5}$$

where H_i^2 is the mean-square amplitude of the fluctuating internal field, and τ is the correlation time. One can conclude from Eq. (5) that the observed steep slowing down of the longitudinal relaxation near T_c can be associated with a decrease in H_i^2 or (and) changing of τ. We will consider both opportunities more in detail.

Assume first that the EPR line is homogeneous with $T_2^{-1}\approx(\gamma H_i)^2\tau$. Then the equality $T_1=T_2$ evidences for the ''fast motion limit'' ($\omega_0\tau\ll1$) at high-enough temperatures, whereas the inequality $T_1\gg T_2$ suggests that the correlation time increases up to $\tau>\omega_o^{-1}\sim10^{-11}$ s as the Curie point is approached. Note that neither the characteristic frequency of the exchange interactions in the model of Refs. 10 and 13, nor the polaron hopping rate in the mechanism suggested by Ref. 14 is consistent with this constraint, both being much faster than ω_0. On the other hand, anomalous slow $\tau\sim10^{-8}$ s were deduced in Ref. 6 from the field dependence of the ^{139}La nuclear spin-lattice relaxation time in $La_{0.67}Ca_{0.33}MnO_3$ at 300 K. The authors[6] have attributed this extremely slow dynamic to magnetic clusters. Other data[3] obtained on $(LaMn)_{1-\delta}O_3$ with $T_c=237$ K should be also noted: in this case, some sort of ''antidivergence'' was found in the ^{139}La nuclear spin-lattice relaxation rate when passing through T_c, quite similar to our work.

At the same time, under the condition of $(\gamma H_i)^2=$const, the temperature dependence of T_1^{-1} predicted by Eq. (5) should pass through a maximum at $\tau_{\max}=\omega_o^{-1}\sim10^{-11}$ s. Such a maximum (minimum in T_1) is not yet observed, see Fig. 2. This implies that H_i^2 changes (decreases) on cooling. The fall in the amplitude of the fluctuating component of the internal field related to the Mn-Mn spin-spin interactions can be due to a progressive alignment of the spin magnetic moments as ferromagnetic order is approached. This resembles the ''freezing off'' of the nuclear spin-lattice relaxation due to interaction with highly polarized paramagnetic centers; in this case, a factor $1-P^2$ arises in the relaxation rate, where P is the electron-spin polarization.[21] In our samples, a substantial freezing off of the fluctuating field could be caused by formation of magnetic clusters similar to those reported[11] in the quasi-two-dimensional manganite $La_{1.35}Sr_{1.65}Mn_2O_7$. An extra EPR line attributed to the magnetic clusters was observed in Ref. 11 in a temperature range above T_c. Addi-

tional lines arise in our samples as well (see Fig. 1), close to the points where the $T_1=T_2$ relation breaks down (Fig. 2). These lines can be considered as precursors of the ferromagnetic resonance, thus evidencing for short-range magnetic order.

Finally, we shall discuss one more idea allowing interpretation with minimum suppositions. One can suggest that Eq. (4) is indeed valid until the transition point, the true T_2 value being correspondent to the width ΔB_{hom} of a homogeneous spin packet rather than to the observed (inhomogeneous) linewidth ΔB. As T_c is approached, the spin packets continue to narrow in a critical manner. Such interpretation is consistent with Ref. 12, where the inhomogeneous nature of the EPR line at $T<T_{\min}$ was shown to be caused by the demagnetization fields of the pores between crystallites. From this viewpoint, a minimum homogeneous width of the spin packet in our samples is as low as 30 G, which is about 1 order of magnitude less than the EPR linewidth observed in the most perfect single crystals of the CMR manganites.[9,10,12,15]

In these terms, it is instructive to compare the temperature dependence of ΔB_{hom} with that predicted by the ''spin-spin'' theoretical model,[10,13] see Eq. (1). According to this, in close vicinity of the critical point, the T_1 value should be practically proportional to χ, so the divergence of χ at the Curie point should lead to a critical slowing down of the relaxation time with the same critical exponent. The best fit of our data by the expression

$$T_1 \propto \left(\frac{T}{T_c}-1\right)^{-\alpha} \tag{6}$$

(see Fig. 2) allows for the critical exponent $\alpha=0.5$. At the same time, the Curie-Weiss law corresponds to $\alpha=1$, and allowance made for the short-range order leads to $\alpha>1$ for the $\chi(T)$ dependence[10] [see also the inset in Fig. 2(c), where a positive curvature is seen in the $\chi^{-1}(T)$ dependence, also evidencing for $\alpha>1$]. So the model of Eq. (1) provides no more than qualitative agreement with our experimental data. This looks natural because the theory developed in Refs. 10 and 13 makes use of the high-temperature approximation and hence cannot describe quantitatively the critical phenomena near the Curie point. On the other hand, it is unlikely that the polaron model[14] can be applied to the reported T_1 behavior. According to Ref. 14, the spin relaxation rate is proportional to the polaron hopping probability. It is known, however, that the latter strongly increases at T_c due to formation of the conduction band.[1,2] Thus, according to Ref. 14, an increase in T_1^{-1} should be expected that contradicts our finding.

In conclusion, the longitudinal electron-spin relaxation time T_1 has been directly measured in the CMR manganites. A critical slowing down of T_1 is discovered in $La_{1-x}Ca_xMnO_3$ with $x=0.2$, 0.25, and 0.33 near the temperatures of the ferromagnetic phase transitions. Several alternative mechanisms of the observed phenomena are discussed, the most plausible explanations being the extremely slow internal spin dynamics and inhomogeneous EPR broadening near T_c.

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