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Spin dynamics in $La_{1-x}Sr_xCoO_3$

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The spin dynamics of Sr-doped cobaltite $La_{1-x}Sr_xCoO_3$ ($x=0.14$ and $x=0.4$) has been investigated in both zero magnetic field and high field by NMR. The results are consistent with microscopically phase-separated regions of ferromagnetic and nonferromagnetic materials. Nuclear spin-lattice and spin-spin relaxation in the ferromagnetic regions is attributed to fluctuating hyperfine fields produced by double exchange between Co ions. The linear temperature dependence of the correlation time, obtained from the data analysis, suggests that lattice excitations modify the double-exchange process as the temperature is raised. In the nonferromagnetic regions, a distribution of nuclear spin-lattice relaxation times is found. It is likely that low-frequency fluctuating localized moments, such as small spin clusters, in spin-glass regions provide the relaxation mechanism for both the spin-glass and low-spin ($S=0$) regions. A simple model involving these ideas can account for the stretched exponential nuclear magnetization recovery in the nonferromagnetic regions, and permits an estimate to be made of the mean size of low-spin regions.

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I. INTRODUCTION

Recent experimental[1,2] and theoretical[3,4] work on doped cobaltite systems have revealed a rich variety of properties, many of which are not well understood. Certain of these properties are similar to those of doped manganites, but there are important differences, some of which are revealed in a comparison of the phase diagrams. Inhomogeneous effects appear to be significant in both systems, giving rise to phase separation, which is important in determining the magnetic and transport behavior in these and other doped perovskite systems.[5,6] For undoped $LaCoO_3$, it has been shown that transitions to Co^{3+} intermediate-spin (IS) and high-spin states occur as the temperature is raised.[7] Various microscopic properties, and the nature of the magnetic phases in doped material,[8] are the subjects of continuing interest. A recent comprehensive review[9] of the metal-insulator transition in various systems, with emphasis on transition-metal oxides, describes properties found in these materials and the theoretical descriptions which have been put forward to explain them. In both the cobaltites and the manganites, double exchange can provide the mechanism for ferromagnetism. In $La_{1-x}Sr_xCoO_3$ (LSCO) the small spin-gap energy separating spin states means that below 250 K the Co ions can exist in low-spin (LS) ($S=0$) or IS states, depending on temperature and dopant concentration.[1,3] Double exchange involving Co ions gives rise to intermediate valence and ferromagnetic coupling in the magnetic clusters. Unpaired t_{2g} and $\sigma^*(e_g)$ electrons are strongly ferromagnetically coupled. Ravindran *et al.*[3] have used full-potential linearized-augmented plane-wave methods to determine the electronic structure for undoped and doped $LaCoO_3$. Their results show itinerant band ferromagnetism in hole-doped material.

For doped material with $x>0.05$, spin-glass (SG) or cluster-glass (CG) behavior is found on cooling to low temperatures,[1,2,8] with history-dependent magnetization effects.[10] The metal-insulator transition at $x=0.18$ is accompanied by changes in the magnetic properties—from a state dominated by ferromagnetism (FM) to a predominantly CG phase as x decreases.[8,11] Phase diagrams for the system have been proposed.[2,8,11] Neutron diffraction[1] has shown that long-range FM spin correlations (coherence length ≈ 700 Å) exist at low temperatures for $x>0.1$. The neutron-diffraction results, together with small-angle neutron scattering (SANS), suggest that for $x=0.3$ the doped system makes a transition from itinerant to polaronic conduction at the Curie point $T_C=240$ K.[1,12] This was interpreted in terms of a narrowing of the σ^* bandwidth that leads to the formation of superparamagnetic clusters in a paramagnetic matrix at sufficiently high temperatures.[12] ac susceptibility measurements made as a function of Sr concentration have, for $x<0.20$, been interpreted in terms of intercluster interactions mediated by a hole-poor matrix.[13]

Our recent low-temperature zero-field ^{59}Co NMR experiments[14] in the ferromagnetic phase of doped cobaltite have shown that there is a distribution of hyperfine couplings which gives rise to a broad resonance spectrum, with a single maximum at 173 MHz, consistent with an intermediate ($Co^{3.5+}$) valence state. Rapid exchange effects average the hyperfine couplings for the different charge states of the Co ions. The shape of the spectrum depends only weakly on dopant concentration, indicating that the ferromagnetic clusters have similar distributions of hyperfine couplings independent of whether they are above or below the percolation limit. As the temperature is raised, the spin-echo signals become smaller and above 25 K are no longer observable. NMR signals at frequencies close to the unshifted Larmor frequency of 100 MHz in a field of 9.98 T give clear indication of LS and SG regions in LSCO samples for all x values in the range $x=0.1$–0.5.[14]

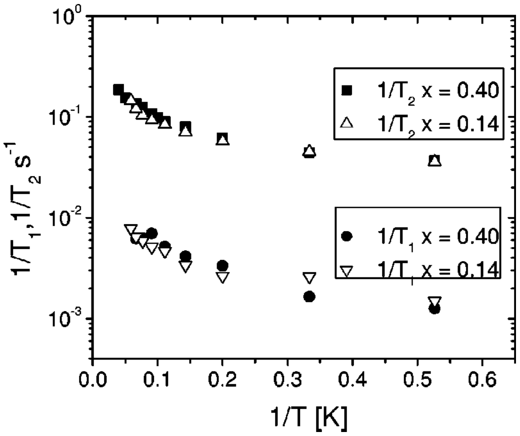

FIG. 1. Zero-field FM NMR ^{59}Co spin-lattice relaxation time T_1 (a) and spin-spin relaxation time T_2 (b) as a function of T (K) for $x=0.4$ and 0.14 samples. The relaxation behavior was not dependent on frequency within the broad spectrum observed.

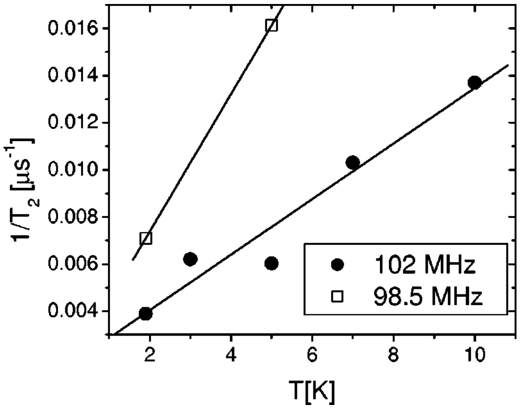

FIG. 2. ^{59}Co NMR spin-spin relaxation time T_2 as a function of T (K) at 9.97 T for LS (102 MHz) and IS (99.5 MHz) non-FM regions in the $x=0.14$ sample.

The spin dynamics in the doped cobaltite system have not previously been investigated in detail. In undoped LaCoO$_3$, NMR measurements suggest that the thermally activated LS to IS process provides the nuclear relaxation mechanism.[15] In the manganites, for comparison, ^{55}Mn and ^{139}La NMR spin-lattice relaxation-time measurements have recently been made as a function of temperature in the ferromagnetic phase of several (La,Na)MnO$_3$ perovskites.[16,17] The results provide interesting new information on double exchange dynamics in these systems. In the present investigation, ^{59}Co spin-lattice and spin-spin relaxation-time measurements have been made on FM LSCO as a function of Sr concentration, magnetic field, and temperature, with the objective of obtaining information on spin dynamics in this system.

II. EXPERIMENTAL DETAILS AND RESULTS

The samples were prepared by solid-state reaction and characterized by x-ray diffraction, scanning electron microscopy, energy dispersive analysis of x rays, and iodometric titration. Details of preparation and characterization have been given previously.[2,14]

Zero-field ^{59}Co spin-lattice (T_1) and spin-spin (T_2) relaxation-time measurements were made using a wide-bandwidth computer-controlled NMR spectrometer and spin-echo methods. The zero-field measurements are used to probe only the FM regions of the sample. Within experimental uncertainty, single exponential behavior was found for both T_1 and T_2. No dependence on Sr concentration x ($0.1<x<0.5$) or spectrometer frequency across the broad spectrum (100–200 MHz) was found. Application of magnetic fields of up to 3 T produced a change in the signal amplitude,[14] but no change in the relaxation times. Figure 1 shows a log plot of the relaxation rates $1/T_1$ and $1/T_2$ as a function of inverse temperature over the range 1.9–25 K. Above 25 K, T_2 became so short that measurements were no longer possible. The close correspondence of the T_1 values for $x=0.14$ and 0.4, with a similar correspondence for T_2, clearly demonstrates that the spin dynamics of FM clusters above and below the percolation (metal-insulator transition) limit (at $x=0.18$) are the same.

As mentioned above, previous work[1,8,12,14] has established that phase separation is an important property of the cobaltites. We have also made high magnetic field (9.97 T) NMR measurements of the relaxation rates in the non-FM regions of LSCO for $x=0.14$. Analysis of the 9.97 T spectra, using two Gaussian-fitted peaks, showed[14] a narrow line centered at 102 MHz with the same Knight shift as in undoped samples[15] and a second very broad line centered at 100 MHz corresponding to the unshifted ^{59}Co magnetogyric ratio. The T_2 results are shown in Fig. 2 for NMR frequencies slightly higher and slightly lower than the unshifted NMR frequency of 100 MHz. The frequency of 102 MHz was chosen to coincide with the peak in the spectrum attributed to $S=0$ (LS) spins, while 98.5 MHz was chosen as a frequency close to the center of the broad 100 MHz peak in the IS regions. It can be seen that $1/T_2$ shows a linear dependence on T but the rates are considerably smaller than in the FM regions, with the LS non-FM regions having the lowest relaxation rate. Within experimental uncertainty, spin-spin relaxation followed single exponential behavior for both non-FM regions. The nuclear magnetization recovery due to spin-lattice relaxation following saturation for both frequencies, however, is found to follow a stretched exponential form,

$$M(t)=M_0[1-\exp(-(t/T_1)^{\alpha})], \tag{1}$$

as shown in Fig. 3. Values for α and T_1 are given in the figure caption for $T=1.9$ K and 5 K. In the case of the 102 MHz LS signal, T_1 decreases with T but α remains roughly constant at 0.5. The 98.5 MHz SG signal has a T_1 almost two orders of magnitude shorter than for the LS region and α decreases with increasing T, which implies an increased distribution of relaxation times at the higher temperatures.

III. DISCUSSION

The discussion is presented in two parts, corresponding to the results for the FM and non-FM phases.

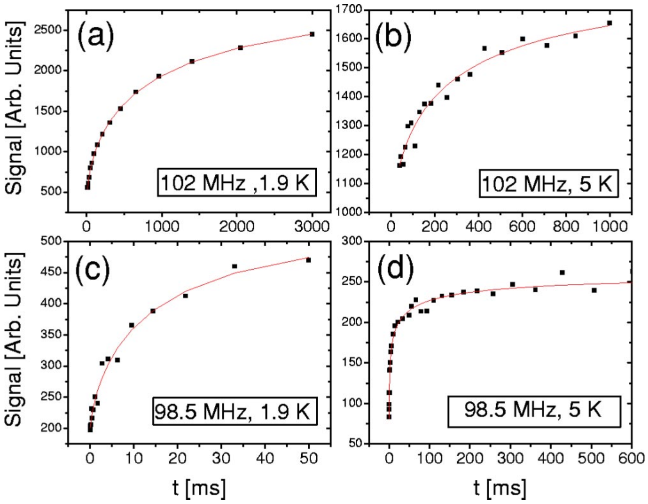

FIG. 3. Stretched exponential ^{59}Co nuclear magnetization recovery curves at 9.97 T for LS (102 MHz) and IS (98.5 MHz) non-FM regions in the $x=0.14$ sample. Data for $T=1.9$ K and 5 K are shown. The stretched exponential exponents α and T_1 values, defined in the text, are (a) $\alpha=0.54$, $T_1=950$ ms, (b) $\alpha=0.50$, $T_1=250$ ms, (c) $\alpha=0.64$, $T_1=16$ ms, (d) $\alpha=0.22$, $T_1=3.3$ ms.

A. Ferromagnetic phase

From Fig. 1, it can be seen that in the zero-field FM NMR, $1/T_1$ and $1/T_2$ have similar temperature dependences with a ratio that is roughly constant. This suggests a common relaxation mechanism. The ^{59}Co NMR data of Kobayashi *et al.*[18] on $LaCoO_3$ and $La_{0.95}Sr_{0.05}CoO_3$ show quite different relaxation-time behavior to that reported here, with a mechanism involving thermally activated LS to IS transitions. It is clear that, in the FM phase, a different relaxation mechanism is operating than in the undoped or lightly doped material. The metal-insulator transition at $x=0.18$ occurs when overlapping clusters reach a percolation threshold. It should be emphasized that the relaxation we observe is independent of x, with no change in behavior on crossing the metal-insulator transition. Relaxation in magnetic systems may be due to a number of possible mechanisms and these are briefly reviewed below. It is argued that conventional mechanisms do not provide the dominant contribution to the relaxation process in LSCO and that double-exchange effects are most important in this system.

In order to allow for double exchange, it is necessary to generalize available theoretical expressions. This is done following the review of various possible relaxation mechanisms in FM metals. The Hamiltonian for the spin system is

$$H=H_e+H_{hf}, \tag{2}$$

where H_e is the electron-spin Hamiltonian including exchange, dipolar, and magneto crystalline interactions, while H_{hf} is the nuclear hyperfine Hamiltonian. For cases where the hyperfine interaction is not isotropic and the nuclear spin I and electron spin S are quantized along different directions z' and z, respectively, we can write

$$\begin{aligned} H_{hf}=&A_1 I_{x'}(S_x\cos\theta+S_z\sin\theta)+A_2 I_{y'}S_y\\ &+A_3 I_{z'}(S_z\cos\theta-S_x\sin\theta), \end{aligned} \tag{3}$$

where θ is the angle between z and z', with y and y' chosen to coincide. The A_i are the principal values of the hyperfine coupling tensor, while S_z and S_y are the electron-spin components in the principal axis system. Fluctuations in either A_i or S_j lead to nuclear relaxation. Moriya[19] and others[20,21] have treated the case of fluctuations in electronic spin orientation due to spin waves and have obtained expressions for the relaxation rate in terms of a temperature-dependent correlation time, which is calculated for various magnon processes using time-dependent perturbation theory. The results are of particular importance in antiferromagnets.

In order to explain the observed linear T dependence of the relaxation rates in LSCO a single magnon process may be considered. The magnon dispersion relation for a FM in a field B has the form[21]

$$E_k=g\beta B+2JSk^2a^2, \tag{4}$$

where J is the exchange coupling, β the Bohr magneton, g the spectroscopic splitting factor, k the wave vector, and a the lattice spacing. In single-magnon nuclear relaxation processes, small-k excitations are important. An applied field produces a gap at $k=0$, which renders this process ineffective. In the present work, the relaxation rates were field independent. This indicates that the spin-wave mechanism does not dominate the relaxation in the temperature range of interest.

Moriya[22] has shown that orbital contributions due to scattering of d-band electrons are responsible for relaxation in FM transition metals. The fairly crude theory predicts a Korringa-like T dependence of the relaxation rate. An estimate of the contribution made by this process may be obtained from values found for FM cobalt in which d-band electrons are responsible for nuclear relaxation.[22] For Co at 4.2 K, the product T_1T is 244 ms K in applied magnetic fields sufficiently large to have swept out domain walls.[23] (In zero field, a distribution of relaxation times is found with a mean value approximately an order of magnitude shorter than in the nonzero field case.) In the present experiments on LSCO no field dependence of T_1 is apparent between 2 K and 10 K, with $T_1T=1.7$ ms K, roughly two orders of magnitude shorter than the product for metallic Co. Furthermore, the plot of $1/T_1$ vs T does not extrapolate to zero. The close correspondence in the form of behavior with temperature of T_1 and T_2 must also be taken into account. It appears unlikely that Moriya scattering provides the primary relaxation mechanism in LSCO and it is necessary to identify an alternative mechanism which is present in the FM phase of this material, independent of x in the range 0.14–0.40. The most likely candidate is the double-exchange process.

We have generalized the relaxation expressions, taking Eq. (3) as a starting point, to allow for fluctuations in the hyperfine coupling due to double exchange. Let the amplitudes of fluctuations in the A_i be given by $\Delta A_i=A_i-\langle A_i\rangle$. In the short correlation time limit, using the x and z components of I gives

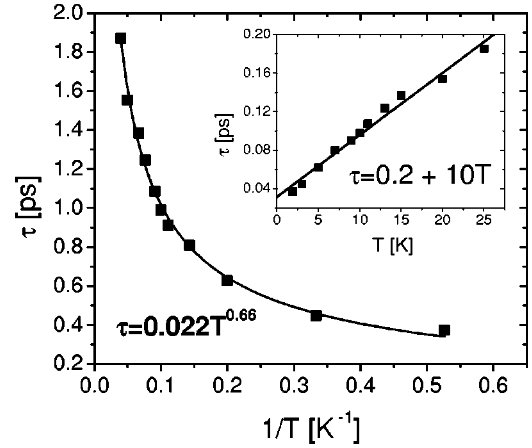

FIG. 4. The estimated double-exchange correlation time τ obtained from the data of Fig. 1(b) as a function of $1/T$ (K). The inset shows the approximately linear dependence of τ on T.

$$1/T_2 = S(S+1)[|\Delta A_1|^2 \sin^2\theta + |\Delta A_3|^2 \cos^2\theta]\tau \qquad (5)$$

and

$$1/T_1 = 2S(S+1)[|\Delta A_1|^2 \sin^2\theta]\tau, \qquad (6)$$

with τ the correlation time for the hyperfine fluctuations. It is assumed that the correlation functions decay rapidly with time. From Eqs. (5) and (6), it follows that the ratio T_1/T_2 is temperature independent since we assume a temperature independent hyperfine coupling and only τ is temperature dependent. The constant ratio depends on the fluctuating hyperfine components and the anisotropy angle θ. These quantities are not known with precision, but it is expected that the fluctuating component along the hyperfine principal axis, $|\Delta A_3|^2$, is much larger than $|\Delta A_1|^2$, and that θ is small. This is consistent with T_1 being more than an order of magnitude longer than T_2. The correlation time τ at a given temperature may be estimated from the measured relaxation rate $1/T_2$ by choosing values for the fluctuating hyperfine component $|\Delta A_3|$ and the angle θ. We take $|\Delta A_3| \approx 50$ MHz, with a large uncertainty, θ small ($5°$–$10°$), and assume that any temperature dependence in these quantities is negligible over the range considered. The estimate for $|\Delta A_3|$ is based on the measured ^{59}Co zero-field NMR spectrum,[14] with peak frequency 173 MHz and half-width 50 MHz, together with typical values of 120–220 MHz for Co^{3+} frequencies in other systems. Co^{4+} frequencies are expected to be somewhat lower than this. Values for τ obtained from the T_2 data, which are reliable to at least an order of magnitude, are shown in Fig. 4 as a function of $1/T$. It can be seen that τ, which is in picoseconds, increases with increasing temperature, in contrast to the decreasing behavior expected for a thermally activated process with a temperature-independent energy gap. The fitted curve has the empirical form $\tau = 0.022T^{0.66}$ over the range shown. From a linear plot of τ vs T, it appears possible that τ is tending to a low-temperature limit which suggests the alternative form $\tau = \tau_0 + AT$ (see inset in Fig. 4), with $\tau_0 = 0.2$ ps and $A = 10$ ps K^{-1}. It is not possible to make a choice of which form is more appropriate over the limited range of these data.

In double exchange, electron transfer gives rise to intermediate valence and a FM exchange coupling J. The characteristic time is $\tau_0 \approx h/J$. τ_0 is expected to change somewhat with temperature since the transfer integral $t_{ij} = t\cos(\theta_{ij}/2)$ depends on the bond length and on the angle θ_{ij} between the spins at sites i and j.[24,25] While at the temperatures of interest changes in θ_{ij} are likely to be small, lattice vibrations lead to dynamical changes in bond lengths and angles, resulting in changes in τ_0 with T. Single-phonon scattering processes can, in this picture, have an effect on the exchange process, leading to changes in the correlation function and hence the spectral density at the Larmor frequency. Further work is needed to establish the details of a mechanism of this kind. For the present purposes, the correlation time is treated as a phenomenological parameter.

While it is recognized that comparisons must be made with care, it is worth noting that investigations of NMR relaxation in doped FM manganites have provided evidence of a coupling of spin dynamics and lattice distortions. Fluctuating hyperfine fields induced by e_g hole hopping provide the relaxation mechanism in a thermally activated process, with a temperature-dependent activation energy $E \propto T^2$. The correlation time is found to increase with temperature. This unusual behavior has been associated with magnetic polarons or nanoclusters which become increasingly important as T approaches T_C.[17,26] Theoretical considerations, based on earlier work, suggest that, in addition to double exchange, a strong electron-phonon interaction is necessary to account for the transport properties close to T_C.[27]

The spin polarons, or extended spin clusters, are thought to play a role in ^{55}Mn relaxation in $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ for $x = 0.3$. Savosta and Novak[28] have obtained NMR evidence for two different FM phases in FM manganite. The phase with lower hyperfine coupling has a temperature-dependent characteristic dimension of a few nanometer.

The present experiments on LSCO have been carried out at low temperatures and the dynamics are different to those found in the manganites. Caciuffo *et al.*,[1] using neutron-diffraction methods, have shown that the Co-O-Co bond angle is temperature dependent below T_C in LSCO ($x = 0.3$), changing from 168.2° to 167° as T is increased from 2 K to 250 K. The equilibrium Co-O bond length increases with T above 200 K. In SANS experiments on the same specimen, it has been shown[1] that a magnetic signal associated with spin-disorder scattering becomes increasingly important as T_C is approached from below. This is interpreted in a manner similar to that suggested for Ca-doped LaMnO_3, where short-range ordered regions become important as T_C is traversed.[29] These magnetic clusters are composite dynamical structures, with sizes $\approx$10–15 Å, induced by double-exchange processes.

Using pair density function analysis, Louca *et al.*[30] have shown that Jahn-Teller-like local distortions are important in LSCO for $x > 0.1$. In the metallic phase, the results are consistent with a Jahn-Teller (JT) glass component. At 20 K they obtain evidence of dynamic JT distortions for $x \geqslant 0.18$.

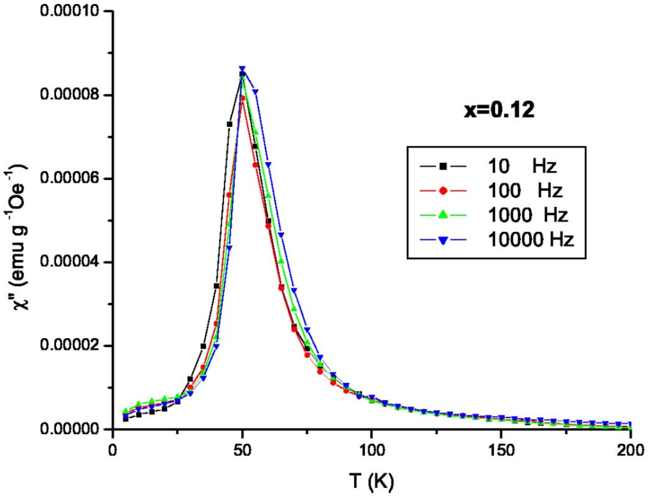

FIG. 5. Complex susceptibility χ'' vs T at several frequencies for a LSCO sample with $x=0.12$. Data from Ref. 2.

Due to the rapid decrease in the spin-echo signal with temperature, the present experiments were carried out at temperatures below 30 K. It is possible that precursor effects connected to the dynamical effects of the kind described above are responsible for the observed temperature dependence of the NMR relaxation times. The change in dynamics may be due to the structural changes and dynamic JT distortions,[1,30] some of which appear at low temperatures, as mentioned above, and which develop as the temperature is increased. In this model, the slowing of the correlation time will continue as the Curie temperature is approached. The rapid decrease in T_2 with increasing T prevented measurements at higher than 25 K.

B. Nonferromagnetic phases

As discussed in Sec. II spin-lattice relaxation in both the non-FM SG and LS phases in LSCO does not follow a single exponential form. The stretched-exponential form given in Eq. (1) gives a good fit to the recovery curves shown in Fig. 3 for the two frequencies shown. This shows that there is a distribution of spin-lattice relaxation rates, which suggests a distribution of environments. This type of relaxation behavior is characteristic of glassy systems and may, in some cases, be associated with nearby ''sinks,'' such as rapidly relaxing magnetic ions or spin clusters.[31] The relaxation results provide strong support for the inhomogeneous nature of LSCO. The value for the exponent α is found to decrease with temperature in the SG phase, which shows that the width of the distribution of relaxation times is increasing with T in this region. The LS phase does not show this change in α for the temperature range in which measurements could be made. ac susceptibility results on low-x samples show peaks in both χ' and χ'' at T near 40 K.[2] At this temperature, χ'' exhibits some frequency dependence in the range $10-10^4$ Hz, indicative of dynamical behavior of spin clusters. Figure 5 shows the χ'' vs T curve for $x=0.12$, where SG and CG regions are important.[2] A close inspection shows small frequency-dependent structure in the curves for $T<40$ K. These features are consistent with dynamical behavior of some regions, or clusters, in the SG phase persisting at low T, which is in agreement with the present interpretation of the NMR data.

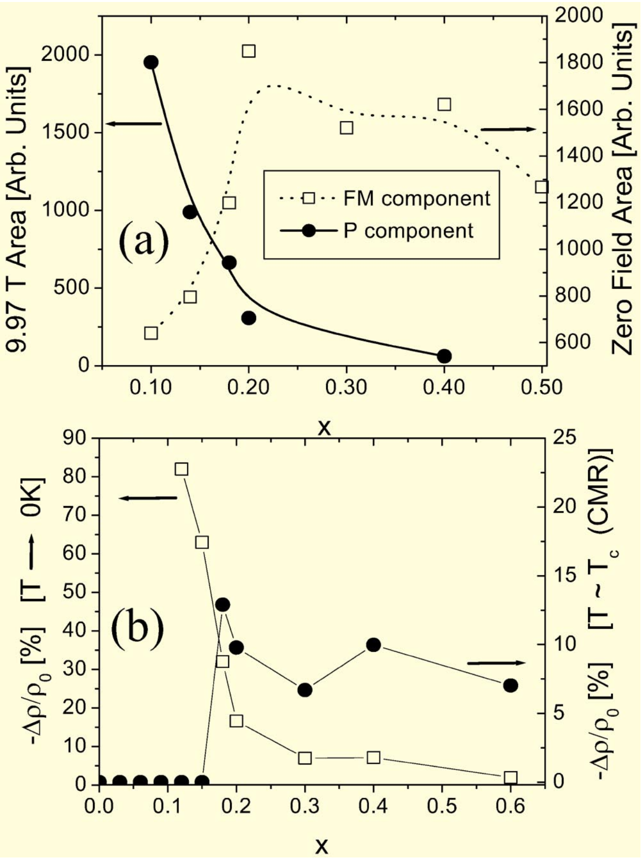

FIG. 6. (a) Plot of magnetoresistance as a function of x for LSCO at low T and for $T\approx T_C$. Data from Ref. 2. (b) Integrated ^{59}Co NMR signal amplitudes vs x for LS and FM phases at $T=1.9$ K. Data from Ref. 14.

It is instructive to compare the integrated signal amplitudes for the FM and non-FM LS phases[14] as a function of x with the magnetoresistance (MR) results for the same samples.[2] Plots of these data are shown in Fig. 6. Clearly, there is a close correspondence of the FM phase with the colossal-magneto resistance-type (CMR-type) behavior and of the non-FM phase with the low-T MR. At low temperatures, the MR is primarily determined by the spins in SG or CG regions, while close to T_C the CMR is due to the FM regions. The sizes of the LS and CG phases are likely to be similar (see below). It is apparent that, in magnetic fields of several tesla, there are fluctuating moments present at low T in the non-FM regions, consistent with the model used for the present NMR analysis.

The size of the IS cluster-glass and LS regions in LSCO has not been well determined. A possible model for these regions may be sought in work done on lightly doped material. Yamaguchi and co-workers have made magnetic[32] and infrared spectroscopy[33] measurements on an undoped sample and on samples with x values in the range 0.002–0.01. Hole doping is found to induce local IS structures, interpreted as spin polarons, with effective spins S in the range 10–16. The magnetic susceptibility at low T shows Curie-like behavior. For $x = 0.002$, the magnetization at a given T can be fit using a Brillouin function plus a linear field term, which allows for interactions between the clusters. At the maximum field used (5 T), the magnetization has not saturated, implying that the interactions are still important. It is plausible that low-frequency temperature-dependent dynamical effects of small localized magnetic clusters provide a spin-lattice coupling mechanism in the non-FM phase-separated regions of more highly doped material. These data can also be interpreted in terms of superparamagnetic clusters. However, it is uncertain that relatively large superparamagnetic clusters will exhibit fluctuations on a time scale sufficiently short to be important in nuclear relaxation at low temperatures but this possibility cannot be excluded.

In our model, local spin fluctuations give rise to fluctuating fields which induce nuclear relaxation according to the relation[34]

$$\frac{1}{T_1} = Cr^{-6}, \tag{7}$$

with

$$C = \frac{2}{5}\,\frac{\gamma_S^2 \gamma_I^2 \hbar^2 S(S+1)\tau}{(1+\omega^2\tau^2)}. \tag{8}$$

Here τ is the S spin-correlation time for the spin polaron fluctuations, and r is the separation between a nuclear spin and the effective fluctuating electronic moment. γ_S and γ_I are the electron and nuclear magnetogyric ratios, respectively. The other symbols have been defined previously. Note that S is the effective spin, which may be an order of magnitude larger than that of a single spin. The distribution of relaxation times follows naturally in this picture because of the distribution of distances r. It is furthermore likely that the fluctuating moments have a distribution of correlation times τ. Spin-diffusion effects can play a role by increasing the length scale over which relaxation operates. The fact that T_2 shows single exponential behavior suggests that spin diffusion may be effective, at least in the LS regions, since the distribution of nuclear quadrupolar couplings, which is observed in the doped material, may be smaller than in the FM regions.[15] The disordered nature of LSCO on a microscopic scale makes quantitative analysis of the relaxation-time results difficult.

The ^{59}Co spacing in the pseudocubic structure is 0.384 nm (Ref. 1) and the calculated second moment contribution due to Co-Co dipolar interactions is 1.1 g^2. This gives a contribution to $1/T_2$ of 6.103 s^{-1}. If ^{139}La contributions are included, the calculated second moment is increased by roughly 0.3 g^2 for $x = 0.14$, with a corresponding increase in the estimated $1/T_2$ contribution to 7.5×10^3 s^{-1}. This is comparable to the low-temperature asymptotic experimental value obtained by Kobayashi *et al.*[23] (3.0×10^3 s^{-1}) for one of the nuclear quadrupole resonance satellite peaks in undoped $LaCoO_3$. The measured values of T_2 at 2 K for the present samples were considerably shorter than this value, consistent with additional contributions from magnetic ions.

It is possible to obtain an upper limit on the size of the LS regions using the relaxation rate expression for the fluctuating spin cluster model. Ignoring any distribution of correlation times, assuming τ is 10^{-9} s, which is near the optimal value for relaxation ($\omega = 1/\tau$), and taking $S = 10$ gives a length scale of 6 nm. While spin diffusion is likely to be strongly inhibited in this noncubic system, if allowance is made for some spin diffusion with a diffusion constant $D \approx 2\times10^{-13}$ $cm^2\,s^{-1}$, as calculated from the ^{59}Co dipolar second moment, r could be increased by roughly a factor of 2, leading to an upper limit of 12 nm for the effective length scale of a low-spin region. The average size is likely to be somewhat less than this. Note that because of the inverse sixth power dependence of the relaxation rate on r, the choice of values for quantities used in determining C is not crucial in the above estimate. Assuming that the fluctuating moments are distributed in the IS regions, it is likely that these are of similar size to the LS regions. However, no direct estimate of the size of the IS regions can be given from the present results. In principle, the behavior of T_1 with T provides information on the spin cluster dynamics. The decrease of the relaxation rate with T in the above model can be explained if it is assumed that the correlation time τ for the fluctuating moment is decreasing with T and that $\omega\tau > 1$, with ω the NMR frequency. The poor signal-to-noise ratio prevented measurements at temperatures above 10 K and the model could not be tested properly. In a more complete treatment, allowance should be made for spin state transitions in the LS regions.

IV. CONCLUSIONS

The present work, involving ^{59}Co relaxation-time measurements, has confirmed the mixed phase properties of Sr-doped cobaltites and has established that double exchange is the likely source of nuclear relaxation in the FM regions of these materials. The correlation time for the double-exchange process is in the picosecond range and is found to increase with temperature between 2 and 25 K. Possible mechanisms for this behavior with temperature include the coupling of spins and dynamical lattice distortions. ^{55}Mn NMR results for $(La,Na)MnO_3$ perovskites, obtained by other workers, lead to similar conclusions, although the detailed behavior for the two systems is different. Electron-lattice interactions are clearly of great importance in understanding the interesting properties of these materials, and the NMR results provide information on these interactions.

High-field ^{59}Co relaxation-time measurements made in the non-FM phase confirm the presence of both LS and IS regions, which interpenetrate the FM regions. A clear correlation is observed between the CMR-type magnetoresistance, which occurs near T_C, and the extent of the FM regions as determined by NMR, whereas the low-temperature magnetoresistance response is correlated with the non-FM regions.

For the non-FM phases it is suggested that the relaxation behavior is due to spin fluctuations. The observed stretched exponential recovery of the nuclear magnetization points to a distribution of fluctuating moments,with a distribution of correlation times. Relaxation processes are significantly stronger in the IS regions than in the LS regions, indicating that the fluctuating clusters are distributed in the IS spin-glass phase. An estimate of the size of the LS regions, based on the present results, suggests an upper limit of 12 nm. This is consistent with the nanoscale texture found in other doped perovskite systems.

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