Nano-magnetic droplets and implications to orbital ordering in

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$

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Abstract

Inelastic cold neutron scattering on LaCoO$_3$ provided evidence for a distinct low energy excitation at 0.6 meV coincident with the thermally induced magnetic transition. Coexisting strong ferromagnetic (FM) and weaker antiferromagnetic (AFM) correlations that are dynamic follow the activation to the excited state, identified as the intermediate $S=1$ spin triplet. This is indicative of dynamical orbital ordering favoring the observed magnetic interactions. With hole doping as in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, the FM correlations between Co spins become static and isotropically distributed due to the formation of FM droplets. The correlation length and condensation temperature of these droplets increase rapidly with metallicity due to the double exchange mechanism.

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Transition metal oxides display rich phase diagrams due to strong correlation effects resulting from competing crystal field, spin-spin and spin-orbit interactions. The rhombohedral perovskite LaCoO$_3$ with $R\bar{3}c$ symmetry is a prime example where by manipulating the magnetic exchange and electron-phonon couplings either thermally or with doping [1, 2, 3], unconventional transport and magnetic characteristics emerge [4]. The ground state of the octahedrally coordinated Co$^{3+}$ ion is the nonmagnetic $S = 0$ that corresponds to the low spin (LS), $t_2^6 e_g^0$ configuration. As the gap ($\Delta$) between the $t_{2g}$ and $e_g$ orbital states becomes small in the presence of a large trigonal distortion [1, 5] aided by strong Co-O hybridization [6], the system can be thermally excited to a magnetic state. Evidence for this is provided by a broad peak in the bulk susceptibility, $\chi$, $\sim 100$ K that marks the onset to a paramagnetic state. The excited state can either be the so-called $S = 1$ intermediate spin (IS) state with a $t_{2g}^5 e_g^1$ configuration or the $S = 2$ high spin (HS) state with a $t_{2g}^4 e_g^2$ configuration. The two states are fundamentally distinct and should lead to very different interactions, considering that the $S = 1$ state is accompanied by orbital degeneracy and is Jahn-Teller active while the $S = 2$ state is not. The low temperature dependence of $\chi$ has been fit equally well with models that consider either spin state [8, 10] making this a controversial issue for several decades [7, 8, 9, 11]. Identifying the excited state that leads to the magnetic transition is important as it provides insights to the nature of the Co$^{3+}$ ion interactions. Early thermal neutron scattering measurements showed the existence of dynamic FM correlations [11] but the absence of studies on the low energy excitations has hindered the critical understanding of the transition mechanism and is the focus of the present work.

The interactions become even more complex with the introduction of charge carriers and the mixing of Co$^{3+}$ with Co$^{4+}$ ions [8]. When holes are doped by replacing the trivalent La$^{3+}$ ions with divalent Sr$^{2+}$ ions in La$_{1-x}$Sr$_x$CoO$_3$, a spin glass ($x > 5\%$) and a FM-metallic (FMM) state ($x > 18\%$) emerge in the phase diagram but without a structural transition as in the isostructural colossal magnetoresistive (CMR) manganites. Reports on the characteristic dynamics and spatial extent of the magnetic correlations provided limited information. Using the nuclear magnetic resonance (NMR) technique that probes local slow dynamics it was shown that the magnetic correlations develop to an FM cluster glass with doping [12]. A more recent NMR study suggested coexistence of FM and non-FM components [13] proposed to be driven by tendencies for phase separation, resulting in an
inhomogeneous metallic state. In this paper, we focus on the spatial distribution of the FM correlations and probe both their dynamic and static characteristics. Our results suggest that the intimate relation of the magnetic exchange energy to the orbital ordering tendency and electronic configuration is key to understanding the physical nature of the undoped LaCoO\(_3\) as well as of the La\(_{1-x}\)Sr\(_x\)CoO\(_3\).

Using cold neutron elastic and inelastic scattering with high instrumental resolution, we investigated the kind of spin correlations in La\(_{1-x}\)Sr\(_x\)CoO\(_3\) with \(x = 0.0, 0.10, 0.15, 0.20\), that prevail in the nonmagnetic insulating through the spin glass to the FMM state. In undoped LaCoO\(_3\), a distinct low energy excitation peaked at \(\sim 0.6\) meV was observed in support of the thermal activation of a zero-field split \(S = 1\) spin state. Concomitant with the population of this magnetic state are strong dynamic short-range FM and weaker AFM correlations observed for the first time that in turn provide evidence for dynamic orbital ordering conducive to the observed magnetic interactions. Upon doping, the short-range FM correlations become static while the dynamic AFM correlations disappear. Direct evidence for isotropic spread of the FM correlations indicating the formation of FM droplets is provided. The size of these FM droplets and their correlation length increase gradually at first in the spin glass phase and more rapidly in the FM metallic phase. Through the double exchange (DE) mechanism, the orbital states of Co\(^{4+}\) and Co\(^{3+}\) within the droplets allow for charges to propagate throughout the crystal structure.

Polycrystalline samples of LaCoO\(_3\) (30 grams) and single crystals of La\(_{1-x}\)Sr\(_x\)CoO\(_3\) with \(x = 0.0, 0.10, 0.15,\) and 0.20 (grown using the floating zone technique and \(\sim 6\) grams each) were used for the elastic and inelastic measurements. The powder samples were studied using the cold-neutron time-of-flight Disk Chopper Spectrometer (DCS) \[14\] at the NIST Center for Neutron Research (NCNR) with an incident wavelength of 5.0 Å (equivalent to an incident energy \(E_i\) of 3.27 meV). The single crystals were measured using the cold-neutron triple-axis spectrometer SPINS at the NCNR, with a fixed final energy of \(E_f = 3.7\) meV. The instrumental energy resolution was \(\Delta E = 0.22\) meV. The single crystals were mounted in the (h,h,l) scattering plane using the pseudocubic notation and a room temperature lattice constant \(a = 3.8377\) Å. A cooled BeO filter was placed in the scattered beam to eliminate higher order contaminations.

LaCoO\(_3\) was measured using the DCS spectrometer at temperatures ranging from 10 to 300 K. As this system is not magnetic at low temperatures, the 10 K data were used as the
background and subtracted from data at the other temperatures to obtain the dynamical structure factor, \( S(Q, \hbar\omega) \) where \( Q \) is the momentum transfer and \( \hbar\omega \) is the energy. The \( S(Q, \hbar\omega) \) was normalized in absolute units with an accuracy of 20% by comparison with the nuclear Bragg intensities [15]. The \( S(\hbar\omega) \) shown in Fig. 1 was obtained by integrating from \( Q = 0.5 \) to \( 2.0 \text{ Å}^{-1} \). Near \( \hbar\omega = 0 \), the data appear noisy because the low temperature elastic peak is subtracted from the higher temperature data. No observable signal is evident in the data beyond the elastic region at the first temperature shown, 25 K, indicating that the system is still non-magnetic at this temperature (Fig. 1a). With increasing temperature, the intensity increases at low energies and consists of two components: a broad inelastic continuum centered at \( \hbar\omega = 0 \) and distinct excitations at \( \pm 0.6 \text{ meV} \) [16]. The low energy inelastic scattering is commonly seen in paramagnetic phases of magnetic systems, and it continues to grow up to about 100 K. The peaks at \( \pm 0.6 \text{ meV} \) first increase in intensity and become well defined by 50 K (Fig. 1c) but then seem to fade away above 75 K (Figs. 1e and 1f). The fading is however a consequence of the powder average and is not seen in the single crystal data discussed below. The solid lines in the figure are the fits to 

\[
S(\hbar\omega) = \frac{\chi''(\hbar\omega)}{\pi(1-e^{-\beta\hbar\omega})}
\]

where the imaginary susceptibility \( \chi''(\hbar\omega) \) is given by two Lorentzian functions to account for the energy width of the two components 

\[
\chi''(\hbar\omega) = \frac{\chi_0 \Gamma_0 \omega}{\omega^2 + \Gamma_0^2} + \frac{\chi_1 \Gamma_1 |\omega \pm \omega_0|}{(\omega \pm \omega_0)^2 + \Gamma_1^2}.
\]  

\( \omega_0 \) was fixed at 0.625 meV, \( \Gamma_0 \) and \( \Gamma_1 \) (with \( \Gamma_1 \) fixed at 0.197 meV) are the relaxation rates and \( \chi_1 \) is the amplitude of the 0.6 meV excitations. The first term corresponding to the inelastic continuum intensity contains \( \chi_0 \), the static staggered susceptibility, is compared to the bulk susceptibility, \( \chi \) (Fig. 2). The almost identical temperature dependence of \( \chi_0 \) to \( \chi \) clearly indicates the magnetic origin of the two. Shown in the inset is \( \Gamma_0 \) that behaves linearly with temperature, \( \Gamma_0 = 0.0143k_BT \).

The single crystal results on LaCoO\(_3\) as a function of \( \hbar\omega \) and \( \vec{Q} \) carried out at SPINS are summarized in Fig. 3. The constant-\( \vec{Q} \) scans in Figs. 3a and 3b performed around the FM \( \vec{Q} = (001) \) and AFM \( \vec{Q} = (\frac{1}{2},\frac{1}{2},0) \) wavevectors show that the 0.6 meV mode is clearly present at temperatures higher than 75 K, in contrast to the powder data of Fig. 1. Also shown are constant \( \hbar\omega = 0.6 \text{ meV} \) scans around \( \vec{Q} = (001) \) and \( \vec{Q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2}) \) in Figs. 3c and 3d from which the magnetic scattering is separated to three distinct components: dynamic AFM and FM correlations as well as single ion contributions that provide the \( \vec{Q} \)-
independent constant term underneath the FM and AFM peaks. While the latter shows little or no temperature dependence, the AFM and FM correlations change considerably with temperature. At 55 K, a distinct peak is present at the FM point $\vec{Q} = (001)$ (Fig. 3c) whereas at the AFM point $\vec{Q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ only the single ion contributions are visible. At 100 K, the FM peak gains in intensity while a clear peak appears at the AFM point as well with about half of the intensity of the FM peak. We will argue below that the 0.6 meV peak arises from single-ion transitions within the $S = 1$ triplet manifold.

Upon doping with 10 % Sr, the 0.6 meV mode disappears as shown for data collected at 100 K for a scan performed around the FM $\vec{Q} = (001)$ point (Fig. 3b). Also at this temperature, FM dynamic fluctuations are still present but suppressed while the AFM ones are absent altogether (Figs. 3c and 3d). The PM fluctuations although suppressed are also present. With cooling, the $x = 0.10$ sample starts to exhibit static short-range FM ordering below 70 K, as shown in Figs. 4a and 4b. The elastic FM peak becomes sharp and strong whereas the PM fluctuations weaken as the Sr concentration increases corresponding to the enhancement of static FM correlations. The elastic neutron scattering mapped in the vicinity of the (001) point in the (hhl) scattering plane shows that the spatial extent of the FM correlations is isotropic for all values of $x$ shown. The enhancement of ferromagnetism with increasing $x$ is also reflected in the spin freezing temperature, $T_c$, defined as the inflection point of the static magnetic scattering that increases with $x$ (Fig. 4 (b) and (d)). The width of the peak at the FM position (Fig. 4a) determined by fitting a single Lorentzian (for the broad magnetic contribution) and a Gaussian (for the temperature independent weak nuclear contribution at (001)) gives a direct measure of the correlation length, $\xi$, obtained from the inverse of the Half-Width-Half-Maximum of the Lorentzian. As shown in Fig. 4(c), $\xi$ increases abruptly but remains finite as the system enters the metallic phase due to the close relation between ferromagnetism and metallicity in this system. This indicates that the phase transition is percolative in nature involving FM clusters accompanied by macroscopic metallicity due to the double exchange mechanism. At the same time, we observed that for each concentration studied, $\xi$ showed no temperature dependence in the ordered phase that contradicts recent small angle neutron scattering (SANS) data using powder samples [19]. This discrepancy might be due to the powder averaging artifact and/or the fact that SANS does not clearly discriminate elastic from inelastic contributions.

Our neutron scattering results provide important information on key issues of the physics
of La$_{1-x}$Sr$_x$CoO$_3$. In pure LaCoO$_3$, correlations between the thermally excited magnetic Co$^{3+}$ ions have both FM and AFM characteristics. This can be explained by the Co ions in the intermediate $t_{2g}^1e_g^1$, $S = 1$ state and with an orbital ordering that favors this state. The IS state is Jahn-Teller active as in the isostructural LaMnO$_3$ with $S = 2$, $t_{2g}^1e_g^1$. In the latter, the degeneracy is broken through static Jahn-Teller orbital ordering leading to A-type AFM ordering consisting of FM interactions in the $ab$-plane and AFM coupling between the planes coupled with a change in symmetry to orthorhombic \[20\]. The coexistence of dynamic FM and AFM correlations in LaCoO$_3$ suggests that orbital ordering analogous to the A-type ordering most likely occurs. We emphasize that the magnetic correlations are dynamic and short range with $\xi \approx 3.6$ Å that is close to the nearest neighbor Co-Co distance of $\sim 3.8$ Å. This implies that the orbital correlations are also dynamic and because of their short-range nature, they occur randomly in every direction. As a result, this generates dynamic FM and AFM correlations in every direction instead of the static and long-range A-type ordering of LaMnO$_3$. This can explain why magnetic scattering is observed at every integer and half-integer points. At the same time, the HS $S = 2$ state of the Co$^{3+}$ ion is unlikely because only AFM correlations are expected between the $S = 2$ states \[21\]. The 0.6 meV mode is most likely due to transitions within the manifold of the thermally induced magnetic state \[17\], split in zero field due to the trigonal lattice distortion \[22\]. This is in good agreement with recent electron spin resonance (ESR) studies that extracted from the field splitting of the resonance lines that LaCoO$_3$ has a spin triplet split by a uniaxial single ion anisotropy, $D \approx 0.6$ meV \[23\].

With hole doping, short-range static FM correlations emerge at low temperatures. The FM correlations rapidly enhance as the system enters the metallic phase indicating that spins couple with charge via the DE mechanism \[24\]. Upon doping, magnetic Co$^{4+}$ ($t_{2g}^5$, $S=1/2$) ions form and induce the IS spin states of neighboring Co$^{3+}$ ($t_{2g}^5e_g^1$) ions \[2\], forming FM droplets. Within a droplet, charge hopping requires the $e_g$ level for Co$^{4+}$ to be empty and for Co$^{3+}$ to be in the IS state and the two ions to be coupled ferromagnetically. Outside the droplet, spins couple dynamically and paramagnetically. When the droplet concentration gets large enough that connectivity is established between them, charge can then propagate over the lattice transforming the system to a metallic ferromagnet. In conclusion, our results provide indirect evidence in support of the thermally excited $S = 1$ IS state and dynamic orbital ordering in pure LaCoO$_3$. The addition of charges enhances the formation
of nanoscale ferromagnetic droplets due to local DE interactions between the Co$^{4+}$ and the IS spin state Co$^{3+}$ ions.

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[1] P. M. Raccah and J. B. Goodenough, Phys. Rev. 155, 932 (1967).
[2] D. Louca and J. L. Sarrao, Phys. Rev. Lett. 91, 155501 (2003).
[3] A. Ishikawa, J. Nohara and S. Sugai, Phys. Rev. Lett. 93, 136401 (2004).
[4] Y. Tokura et al., Phys. Rev. B 58, R1699 (1998).
[5] G. Thornton, B.C. Tofield, A. W. Hewat, J. Solid State Chem. 61, 301 (1986).
[6] M. A. Korotin et al., Phys. Rev. B 54, 5309 (1996).
[7] V. G. Bhide et al., Phys. Rev. B 12, 2832 (1975); S. Yamaguchi, Y. Okimoto, and Y. Tokura, Phys. Rev. B 55, R8666 (1997).
[8] T. Saitoh et al., Phys. Rev. B 56, 1290 (1997).
[9] D. Louca et al., Phys. Rev. B 60, R10378 (1999).
[10] K. Asai et al., Phys. Rev. B 40, 10982 (1989).
[11] K. Asai et al., Phys. Rev. B 50, 3025 (1994).
[12] M. Itoh and I. Natori, J. Phys. Soc. Jpn. 64, 970 (1994).
[13] P. L. Kuhns et al., Phys. Rev. Lett. 91, 127202 (2003).
[14] J. R. D. Copley and J. C. Cook, Chem. Phys. 292, 477 (2003).
[15] S.-H. Lee et al., Phys. Rev. B 56, 8091 (1997).
[16] The 0.6 meV mode is of magnetic origin as the intensity does not follow the $Q^2$ dependence of phonon modes and a field effect has been reported in Ref. [17].
[17] The 0.6 meV excitation was also observed recently in a powder by A. Podlesnyak et al.
Figure captions:

Figure 1: The $\hbar \omega$-dependence of the neutron scattering cross section, $S(\hbar \omega)$, obtained from the DCS measurements on a powder sample of LaCoO$_3$ at various temperatures: (a) 25 K, (b) 50 K, (c) 75 K and (d) 100K.

Figure 2: The temperature dependence of the static staggered susceptibility, $\chi_0$, as determined from eqn. 1 (open squares) and the bulk magnetic susceptibility, $\chi$, (filled circles). The upturn below 35 K in $\chi$ might be from a surface ferromagnetic component as described in Ref. [25]. Beyond 75 K, the two peaks are not resolved and only one term is used for fitting $\chi''(\hbar \omega)$. The temperature dependence of $\Gamma_0$ is shown in the inset.

Figure 3: Inelastic neutron scattering data obtained from the single crystals of LaCoO$_3$ and La$_{0.9}$Sr$_{0.1}$CoO$_3$ at SPINS. Constant-$\vec{Q}$ scans at (a) AFM $Q = (\frac{1}{2}, \frac{1}{2}, 0)$ and (b) FM $Q = (001)$ wavevectors. Constant $\hbar \omega = 0.6$ meV scans centered at (c) AFM $Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and (d) FM $Q = (001)$ points.

Figure 4: (a) Elastic scan along (0,0,L) performed on single crystals of La$_{1-x}$Sr$_x$CoO$_3$ with $x = 0.1$, 0.15, and 0.2 at 8 K. The temperature dependence of (b) the elastic neutron scattering intensity, (c) of the ferromagnetic correlation length, $\xi$, and (d) of the spin freezing temperature, $T_c$. 

[18] L. P. Regnault et al., Phys. Rev. B 38, 4481 (1988).
[19] J. Wu et al., Phys. Rev. Lett. 94, 037201 (2005).
[20] T. Mizokawa and A. Fujimori, Phys. Rev. B 51, R12880 (1995).
[21] R. H. Potze, G. A. Sawatsky, and M. Abbate, Phys. Rev. B 51, 11501 (1995).
[22] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, (Clarendon, Oxford, 1970), p. 19.
[23] S. Noguchi et al., Phys. Rev. B 66, 094404 (2002).
[24] C. Zener, Phys. Rev. 81, 440 (1951).
[25] J.-Q. Yan, J.-S. Zhou and J. B. Goodenough, Phys. Rev. B 70, 014402 (2004).
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