

Spin-State Polarons in Lightly-Hole-Doped LaCoO_3

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Inelastic neutron scattering (INS), electron spin resonance (ESR), and nuclear magnetic resonance (NMR) measurements were employed to establish the origin of the strong magnetic signal in lightly-hole-doped $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, $x \sim 0.002$. Both INS and ESR low temperature spectra show intense excitations with large effective g factors ~ 10 – 18 . NMR data indicate the creation of extended magnetic clusters. From the Q dependence of the INS magnetic intensity, we conclude that the observed anomalies are caused by the formation of octahedrally shaped spin-state polarons comprising seven Co ions. The present INS, ESR, and NMR data give evidence for two regimes in the lightly-hole-doped samples: (i) $T < 35$ K dominated by spin polarons; (ii) $T > 35$ K dominated by thermally activated magnetic Co^{3+} ions.

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Physical properties of nanostructured magnetic materials are extensively studied because of their fundamental interest and potential applications. A naturally occurring analog to the artificially fabricated heterostructures are doped perovskites with intrinsic inhomogeneities, i.e., with a spatial coexistence of magnetic clusters in a nonmagnetic matrix. Hole-doped cobaltites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ exhibit spin-glass and superparamagnetic behavior for $0.05 \leq x \leq 0.2$ [1–3]. Because of a progressive change with increasing temperature from low- (LS) to intermediate- (IS) or high-spin (HS) states of the cobalt ions, a reentrant metal-insulator (MI) transition was found for $0.2 \leq x \leq 0.3$ within $100 \leq T \leq 200$ K [1]. With the addition of charge carriers, the number and possibly the size of the clusters grow, leading to a percolation-type long-range ferromagnetic (FM) order and MI transition at $x \geq 0.2$ [1,3,4].

Most of the investigations up to now have been focused on a relatively high Sr concentration ($x > 0.1$). It is widely believed that the addition of each hole into pristine LaCoO_3 through the substitution of a divalent, e.g., Sr^{2+} , ion for the La^{3+} ion creates a Co^{4+} ion in the lattice which has a nonzero S in any spin-state configuration, thereby inducing a magnetic moment in the system. An amazing fact was found by Yamaguchi *et al.* in 1996 [5] and apparently forgotten later. Namely, already lightly doped material with $x \sim 0.002$ (i.e., with an estimated concentration of only two holes per thousand Co^{3+} ions) exhibits unusual paramagnetic properties at low temperatures: Few embedded spins in a nonmagnetic matrix give an order of magnitude larger magnetic susceptibility than expected. It was proposed that a doped hole in the spin-singlet ground state of LaCoO_3 behaves as a localized magnetic impurity

with unusually large spin value $S = 10$ – 16 [5] due to the formation of a magnetic polaron whose nature, however, remained unclear. Later, and for higher Sr doping $x > 0.05$, it was surmised that the addition of charge carriers forms Zener-type polarons or even many-site magnetopolarons [2,3]. However, experimental proof of the existence of such polarons is missing so far.

In this Letter, we elucidate the mechanism of how already the light hole doping $x \sim 0.002$ dramatically affects magnetic properties of LaCoO_3 . Combining inelastic neutron scattering (INS) data, obtained with and without an external magnetic field, with the single crystal electron spin resonance (ESR) and nuclear magnetic resonance (NMR) measurements on $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$, we find that the charges introduced by substitution of Sr^{2+} for La^{3+} do not remain localized at the Co^{4+} sites. Instead, each hole is extended over the neighboring Co^{3+} ions, transforming them to a higher spin state and thereby forming a magnetic seven-site (heptamer) polaron.

Highly stoichiometric powder and single crystal samples of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, $x = 0, 0.002$, were synthesized and characterized according to procedures described elsewhere [6]. The INS measurements were performed on the high-resolution time-of-flight spectrometers NEAT (Hahn-Meitner-Institut, Berlin, Germany) and FOCUS (Paul Scherrer Institut, Villigen, Switzerland). The data were collected using incoming neutron energies 3.26–3.5 meV, giving an energy resolution at the elastic position of ~ 0.09 – 0.15 meV. Raw data were corrected for sample self-shielding and detector efficiency according to standard procedures. The DAVE software package was used for elements of the data reduction and analysis [7]. High

field ESR measurements were performed with a home-made spectrometer based on a millimeter wave vector network analyzer from AB Millimètre at frequencies 27–550 GHz for the magnetic field B parallel to the [001] pseudocubic axis of the single crystal (see technical details in Ref. [8]). In the same field geometry ^{59}Co ($I = 7/2$) NMR was measured at a frequency of 47.65 MHz with a Tecmag pulse NMR spectrometer.

The susceptibility data (not shown) are similar to those of Ref. [5]. In order to estimate an effective magnetic moment of doped holes, we fitted measured magnetization $M(H)$ with a combination of the conventional Brillouin function $B_S(y)$ and a field-linear term $M(H) = N\mu_B g S B_S(y) + \chi_0 H$, $y = (g\mu_B S H)/(k_B T)$. Assuming a hole concentration $N = 0.002$, we found $gS \sim 15\mu_B/\text{hole}$, which is much larger than we can expect from Co^{3+} or Co^{4+} in any spin state and which agrees with [5].

Zero-field inelastic neutron spectra of $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ are shown in Fig. 1(a). In contrast to the parent compound LaCoO_3 , where no excitations have been found for $T < 30$ K [9], an inelastic peak at 0.75 meV was observed down to $T = 1.5$ K. One more inelastic peak at 0.6 meV was found at intermediate temperatures starting from $T \sim 30$ K similar to that found in pristine LaCoO_3 [9]. Clearly, the peak at 0.6 meV corresponds to the signal from the undisturbed matrix. We can thus interpret the peak observed at 0.75 meV as a signal which is due to Sr doping [6]. Already a weak magnetic field splits the transition into two lines whose widths widen considerably with increasing field strength [Fig. 1(b)]. The Zeeman splitting is enormous and can be explained with a g factor of the order of 10 in agreement with the aforementioned macroscopic measurements.

Similarly to INS, the undoped LaCoO_3 exhibits no bulk ESR signal for $T \leq 30$ K [10]. However, in $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ we observe a very intense ESR spectrum consisting of 7 absorption lines [Figs. 2(a) and 2(b)]. The dependence of their resonance fields B_{res}^i on the fre-

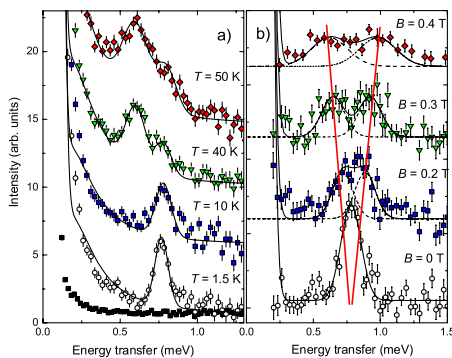


FIG. 1 (color online). Temperature ($B = 0$) and magnetic field ($T = 1.5$ K) evolutions of the INS spectra of $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ measured on FOCUS (data from Ref. [6]) and NEAT, respectively. Solid black squares correspond to data taken from non-magnetic LaAlO_3 at $T = 50$ K, black lines refer to least-squares fits of Gaussian functions, and red lines are guides to the eye.

quency ν (resonance branches) reveals that excitations 1, 2, 3, and 6 which comprise a significant part of the total spectral weight are gapped with a gap value $f_0 \approx 170$ GHz ≈ 0.7 meV [Figs. 2(a) and 2(b)], in nice agreement with the energy of the low- T INS peak. The effective g factors of the most intense branches $g_i = (h/\mu_B) \times (\partial\nu/\partial B)_i$ are significantly larger than a spin-only value of 2 and vary from ~ 2.1 to ~ 18.3 . With increasing T the intensity of these lines strongly decreases, whereas above ~ 35 K two new lines [marked A and B in Figs. 2(a) and 2(b)] emerge. Their branches (not shown) yield a gap $f_1 \approx 150$ GHz ≈ 0.6 meV and a g factor ≈ 3.43 . The behavior of A and B is very similar to the ESR data in Ref. [10] for undoped LaCoO_3 which allows one to unambiguously identify these lines with the thermally activated Co^{3+} HS state ions and thus with the thermally activated INS peak [9].

The strong low- T ESR response of $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ cannot be explained by the occurrence of isolated Co^{4+} ions with an effective spin $\tilde{S} = 1/2$ in the LS state or isolated Co^{3+} in the HS or IS state with $\tilde{S} = 2$ or 1. A large number of lines implies the existence of resonating centers with larger spin multiplicity, since, e.g., for $\tilde{S} = 1$ not more than 3 lines can be expected. Therefore the ESR data strongly suggest that small Sr (i.e., hole) doping results in the formation of spin clusters with large effective g factors involving several interacting magnetic Co sites [11].

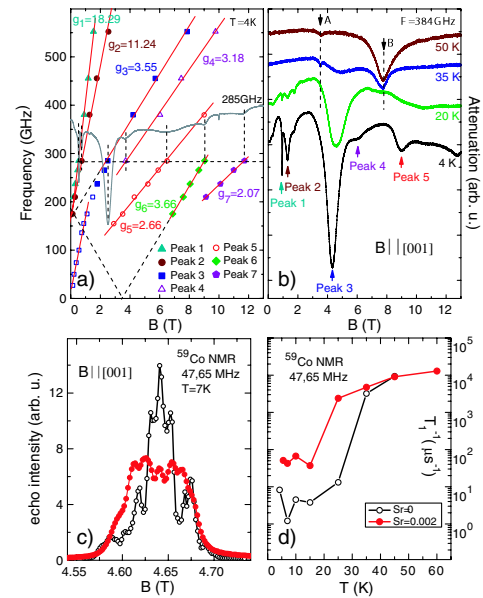


FIG. 2 (color online). (a) Frequency vs magnetic field dependence (branches) of the ESR modes of the low- T spectrum. Straight lines through data points are linear fits (see text). Open squares denote a small presumably impurity peak visible below ~ 200 GHz. (b) T dependence of the ESR spectrum at 384 GHz. A and B label ESR modes due to thermally activated Co^{3+} HS state ions. (c), (d) Low- T ^{59}Co NMR spectra and T dependences of the nuclear relaxation rate T_1^{-1} , respectively, for LaCoO_3 and $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ single crystals (open and closed circles). Lines connecting the data points are guides for the eye.

The ^{59}Co NMR data are summarized in Figs. 2(c) and 2(d). The spectral shape and the spin-lattice relaxation rates of the undoped LaCoO_3 agree very well with previous ^{59}Co NMR studies [12,13]. According to a simple estimate, doping with 0.2% Sr, which yields 0.2% of Co^{4+} sites, should change the electric field gradient for at most 5% of nuclei. It means that the doping-induced change of the low- T spectrum, which gets barely resolved [Fig. 2(c)], is not due to the quadrupole interaction and has probably a magnetic origin. It becomes even more apparent in the nuclear spin dynamics yielding at low T a more than 15 times enhanced relaxation rate T_1^{-1} [Fig. 2(d)]. The observed stretch-exponential shape of the nuclear magnetization recovery suggests a substantially nonuniform distribution of local magnetic environments at low T seen by the Co nuclei [14]. Thus ^{59}Co NMR data of $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ clearly indicate the formation of spatially extended magnetic clusters at low T . In contrast, above ~ 35 K, where a considerable part of Co ions is in the thermally activated HS state, the NMR spectra and relaxation for doped and undoped samples are very similar, and the shape of the nuclear magnetization recovery testifies to an almost homogeneous distribution of magnetic centers [15].

Thus, a contribution of several Co ions, i.e., the formation of magnetic clusters, is required to explain the results of our magnetic susceptibility, INS, ESR, and NMR measurements. The hole is not localized on one particular ion but dynamically distributed over the cluster. A reasonable mechanism for such a resonant state was proposed by Louca and Sarrao [2]. Neighboring LS- Co^{4+} and IS- Co^{3+} ions can share an e_g electron by swapping configuration. The t_{2g} electrons, in turn, couple ferromagnetically via double exchange interaction. Therefore, we propose that the holes introduced in the LS state of LaCoO_3 are extended over the neighboring Co sites forming spin-state polarons and transforming all involved Co^{3+} ions to the IS state. An important question remains: How many Co ions are involved in a single hole-doped cluster?

The wave-vector dependence of the intensity of the INS signal yields direct information about the geometrical configuration of the magnetic ions in the cluster. We studied in detail the Q dependence of the 0.75 meV peak for $0.4 \leq Q \leq 2.0 \text{ \AA}^{-1}$. The excitation is dispersionless, indicating that intercluster interactions can be neglected [Fig. 3(a)]. The intensity of the observed transition exhibits a clear oscillatory behavior reflecting the size as well as the shape of a spin-state polaron through the structure factor. For a cluster comprising n magnetic ions, the neutron cross section for polycrystalline materials is given by [16]

$$\frac{d^2\sigma}{d\Omega d\omega} \propto F^2(Q) \sum_{j < j'=1}^n \left(|\langle S \| T_j \| S' \rangle|^2 + 2 \frac{\sin(Q|R_j - R_{j'}|)}{Q|R_j - R_{j'}|} \langle S \| T_j \| S' \rangle \langle S' \| T_{j'} \| S \rangle \right), \quad (1)$$

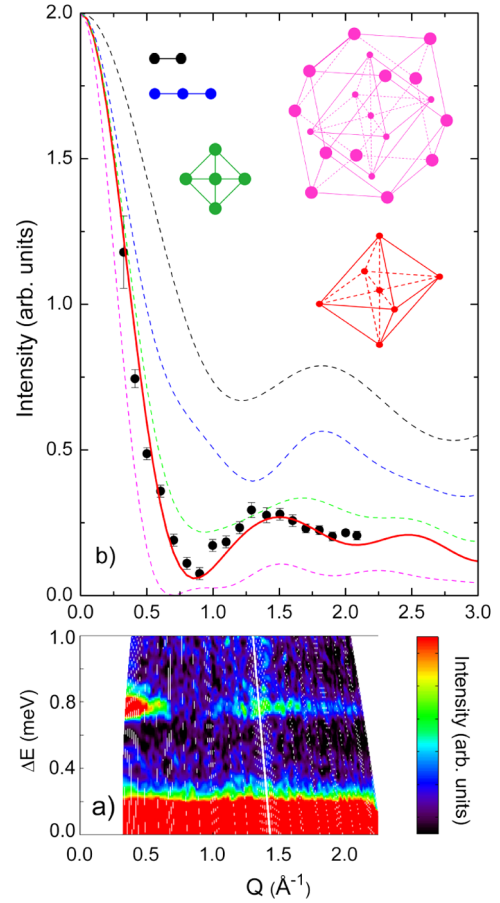


FIG. 3 (color online). (a) Excitation INS spectrum collected on FOCUS from $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ at $T = 1.5$ K. (b) Circles: Experimental Q dependence of the intensity of the peak observed at 0.75 meV. Lines: Calculated Q dependence of the neutron cross section [Eq. (1)] for different Co multimers (visualized in the figure) in the cubic perovskite lattice of LaCoO_3 and for $|S\rangle \Rightarrow |S\rangle$ transitions. The nearest-neighbor Co-Co distance was fixed at $R_{\text{Co-Co}} = 3.9 \text{ \AA}$ determined for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ from the Co-O pair density function [2].

where $F(Q)$ is the magnetic form factor, Q the scattering vector, R_j the position vector of the j th ion in the cluster, and T_j an irreducible tensor operator of rank 1 [17]. This cross section corresponds to a superposition of damped sine functions which reflect the geometry of the cluster. Each particular transition $|S\rangle \Rightarrow |S'\rangle$ has its specific Q dependence due to both the sign and the size of the reduced matrix elements. Lines in Fig. 3(b) correspond to calculated cross sections for different Co clusters in the cubic approximation of the perovskite lattice of LaCoO_3 and for the special case of a $|S\rangle \Rightarrow |S\rangle$ transition [18], which, as will be seen below, is relevant in the context of the present work. We clearly see that the Q dependence of the cross section is an unambiguous fingerprint of the geometry of the multimers; in particular, the data observed for the 0.75 meV transition in $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ are perfectly explained by the scattering from an octahedrally shaped Co heptamer [see Fig. 3(b), red heptamer and red solid

line]. The total moment of this heptamer [consisting formally of one LS Co^{4+} ($S = 1/2$) and six IS Co^{3+} ($S = 1$)] is $13\mu_B$, in good agreement with our magnetic measurements.

Considering only nearest-neighbor coupling J between a central Co^{4+} ion in the LS state and six Co^{3+} ions in the IS state, the Heisenberg exchange Hamiltonian is given by $H_{\text{ex}} = -2J\vec{S}_1 \cdot \vec{S}_A$, where $\vec{S}_A = \vec{S}_2 + \dots + \vec{S}_7$ and the total spin is $\vec{S} = \vec{S}_1 + \vec{S}_A$. The Co-Co coupling J is ferromagnetic via the double exchange mechanism [2]. The ground state of the cobalt heptamer is therefore the state with maximum spin quantum numbers, namely, $|S_1, S_A, S\rangle = |1/2, 6, 13/2\rangle$. The first excited state $|1/2, 5, 11/2\rangle$ lies higher up by J . The exchange coupling J of cobalt oxides is of the order of 10 meV [19]; thus, the first excited multiplet heptamer state lies far above the energy window covered by the present experiments. What is then the origin of the peak observed at 0.75 meV? As argued above, even light doping promotes neighboring Co^{3+} to an IS state already at $T = 0$. The ground state of the Co^{3+} ions in the IS state comprising the main part of the magnetic polarons is an orbitally degenerate triplet [see Ref. [9], Fig. 4 (right)] which is split by a small trigonal field into a singlet and a doublet. Transition between these levels is, in our opinion, the source of the 0.75 meV peak. Here this transition due to a magnetic (IS) Co^{3+} exists already at $T = 0$, whereas for the undoped system the similar transition at 0.6 meV is only due to a thermally activated magnetic (HS) state [9].

In summary, our work gives a clear microscopic explanation why hole doping of as little as 0.2% may dramatically affect the overall magnetic properties of the entire system. We have found that holes introduced in the LS state of LaCoO_3 by substitution of Sr^{2+} for La^{3+} transform the six nearest neighboring Co^{3+} ions to the IS state forming octahedrally shaped spin-state polarons. The formation of spin-state polarons may be a common mechanism present in other Co-based compounds. Spin-state polarons behave like magnetic nanoparticles embedded in an insulating nonmagnetic matrix. Additional charge carriers increase the number of such spin-state polarons, which form a percolative network resulting in a metallic state with long-range FM order at the critical concentration $x_c = 0.18$ [3]. It is difficult to draw a definite conclusion if the spin polarons survive in the “high” temperature regime. Plausibly, owing to the activation of magnetic state of Co in the bulk [1,3,9], the existence of spin polarons is not anymore energetically favorable, and therefore they continuously dissolve upon raising the temperature in the regular magnetic lattice of IS or HS Co ions.

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