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Formation of magnetic polarons in lightly Ca doped LaCoO$_3$

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Abstract. We performed high field electron spin resonance, nuclear magnetic resonance and static magnetization measurements on a powder sample of lightly hole-doped La$_{1-x}$Ca$_x$CoO$_3$, $x \sim 0.002$ in order to study the influence of the size of the substitution ion on the formation of the hole induced spin-state polaron. Previous works [1, 2] showed that doping of LaCoO$_3$ with Sr in very small concentrations ($x \sim 0.002$) yields the formation of a magnetic polaron with a big spin value and large spin orbital coupling. The Ca^{2+} ion, in contrast to the Sr^{2+} ion, has almost the same ionic radius as the La^{3+} ion. Therefore, the substitution of Ca for La provides mainly a hole to the system without creation of a sizeable crystal field distortion around the substituted Ca ion. The data obtained on La$_{0.998}$Ca$_{0.002}$CoO$_3$ provide experimental evidence that the introduced hole indeed plays the main role in the formation of the spin-state polaron. Accompanying crystal field distortions seem to play a minor role, e.g. influencing the fine splitting of the spin polaron energy levels and the contribution of the spin orbital coupling.

1. Introduction

Hole-doped cobaltite La$_{1-x}$Sr$_x$CoO$_3$ with a pseudocubic perovskite structure attracts a permanent attention due to its rich phase diagram and unusual magnetic properties [3]. Undoped LaCoO$_3$ is a nonmagnetic insulator at low temperatures since Co^{3+}($3d^6$) occurs in the low-spin ($S = 0$) (LS) state. With increasing the temperature it becomes magnetic and conducting due to a thermally driven transition of Co^{3+} to a higher spin state. The substitution of a Sr^{2+} ion for La^{3+} provides hole doping which yields the formation of ferromagnetic clusters that show superparamagnetic and spin glass properties in the doping range $0.05 < x < 0.2$. Yamaguchi et al. [4] found that already very small doping levels ($x \sim 0.002$) give rise to an unexpectedly large magnetic susceptibility at low temperatures. Later, it was established that the reason of the strong magnetic response is a magnetic polaron with a large moment, induced by the Sr substitution [1, 2]: The hole localized at low temperatures near the Sr dopant transforms the six nearest neighboring Co^{3+} ions to the magnetic state forming octahedrally shaped spin-state polarons. The Sr^{2+} ion has a bigger ionic radius than the La^{3+} ion, therefore, the substitution leads not only to the introduction of a hole, but also to a crystal structure distortion occurring around the doped Sr ion. In order to understand the role of this distortion in the formation of the

magnetic polaron we performed Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR) and static magnetization experiments on a $La_{1-x}Ca_xCoO_3$ powder sample, where Ca^{2+} has almost the same ionic radius as the La^{3+} ion. Thus a much smaller structural distortion can be expected.
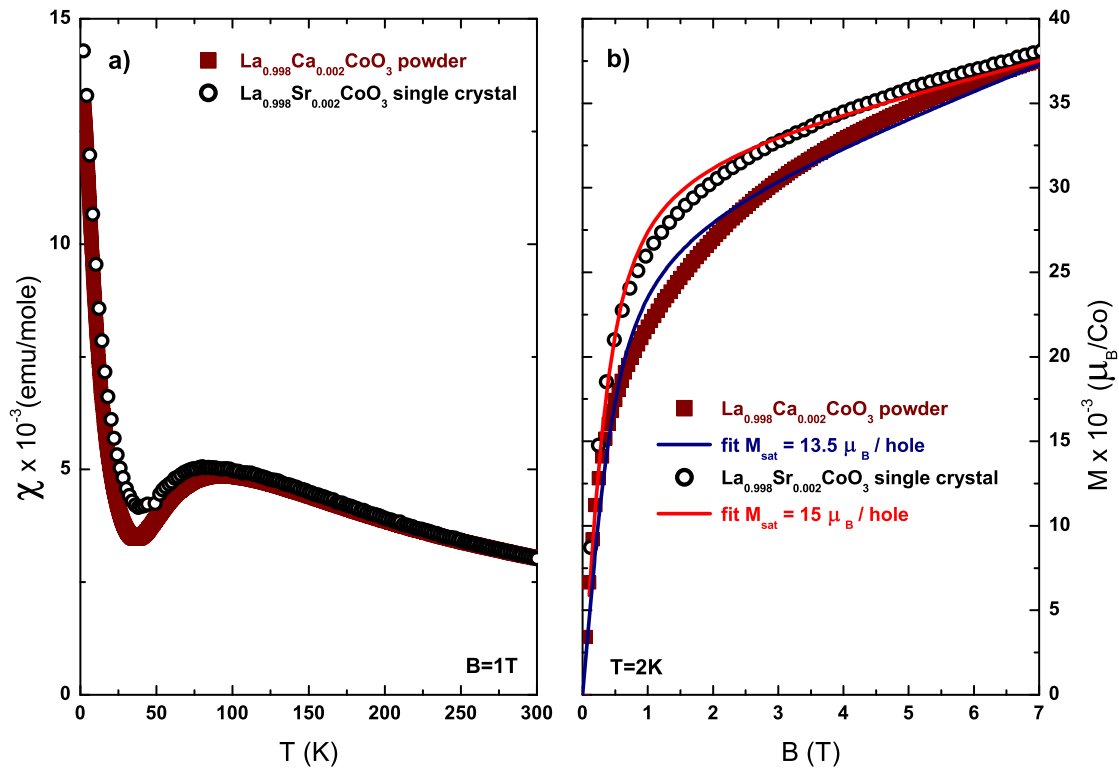

Figure 1. a) Temperature dependence of the magnetization at $B = 1\,T$, $La_{0.998}Ca_{0.002}CoO_3$ - squares, $La_{0.998}Sr_{0.002}CoO_3$ - open circles; **b)** Magnetic field dependence of the magnetization at $T = 2\,K$, $La_{0.998}Ca_{0.002}CoO_3$ - squares, $La_{0.998}Sr_{0.002}CoO_3$ - open circles, Brillouin functions with $M_{sat} = 15\mu_B$/hole and $M_{sat} = 13.5\mu_B$/hole - solid lines

2. Experimental set-ups

High field/high frequency ESR (HF-ESR) measurements were performed with a home-made spectrometer (see Ref. [5]) at frequencies $\nu = 27 - 550\,GHz$ and magnetic fields $B = 0 - 15\,T$. The ^{139}La NMR was measured at a frequency of $94\,MHz$ and a magnetic field of $9.2\,T$ with a Tecmag pulse NMR spectrometer. The static magnetization measurements were done with a conventional QD VSM SQUID magnetometer. For investigations we used stoichiometric powder sample of $La_{1-x}Ca_xCoO_3$.

3. Results

The static magnetization $M(B, T)$ data (Fig. 1) of $La_{0.998}Ca_{0.002}CoO_3$ shows a behavior similar to $La_{0.998}Sr_{0.002}CoO_3$. The temperature dependence of the magnetization of the Ca doped sample (squares on Fig. 1,a) exhibits a very strong increase below $\sim 30\,K$ which is the first signature of the magnetic polaron [1]. In addition, there is a hump at $\sim 70\,K$ due to the thermal activation of the Co^{3+} high spin (HS) state ions. The $M(B)$-dependence (Fig. 1,b) at $T = 2\,K$ is also similar to the Sr doped sample. The estimation of the saturation moment M_{sat} in the Ca

doped sample yields a value of $\sim 13.5 \mu_B$ per doped hole, which is slightly lower than in the Sr doped sample ($\sim 15 \mu_B$/hole). Note that this value is much higher than the saturation moment of Co^{3+} or Co^{4+} ions in any spin state.
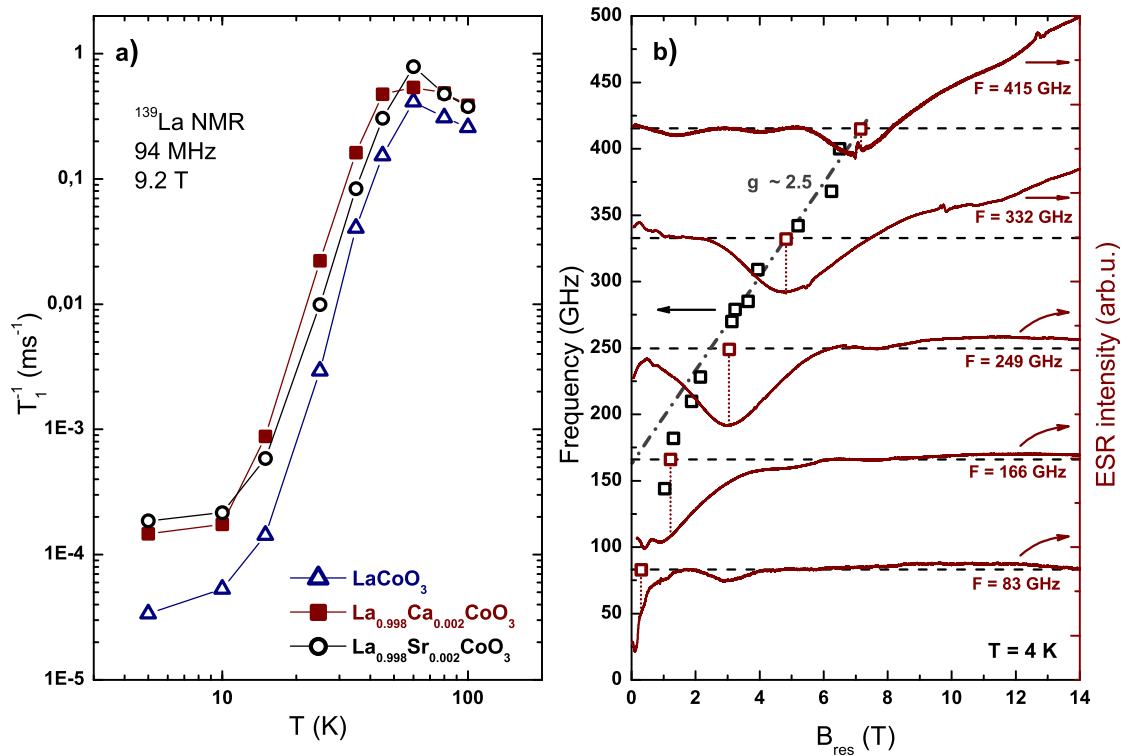

Figure 2. **a)** $1/T_1$ relaxation rate data of ^{139}La in LaCoO$_3$ - triangles, La$_{0.998}$Ca$_{0.002}$CoO$_3$ - squares and La$_{0.998}$Sr$_{0.002}$CoO$_3$ - open circles; **b)** HF-ESR spectra of a powder La$_{0.998}$Ca$_{0.002}$CoO$_3$ sample measured at different frequencies at temperature of 4 K; the frequency dependence of the resonance field B_{res} of the main line - squares

The signatures of the magnetic polaron are also seen in the ^{139}La NMR measurements (Fig. 2,a). There is a substantial difference between the $1/T_1$ nuclear relaxation rate of the undoped sample and both doped samples at low temperatures. In case of doped samples the relaxation rate is much faster, about 5 times, than in the undoped case indicating strong magnetic fluctuations at low temperatures seen by all La nuclei. The relaxation rate values of the Sr and Ca doped samples are almost equal, suggesting a similar nature of the fluctuations. At $T > 30$ K the rate $1/T_1$ becomes however very similar to that of the undoped LaCoO$_3$ indicating the activation of the Co^{3+} HS state ions in all samples.

Despite of the powder averaging, the ESR response of the La$_{0.998}$Ca$_{0.002}$CoO$_3$ sample shows similarities to that of the Sr doped single crystal data [1]. The spectra comprise several broad lines (Fig. 2,b), at low fields there is a set of ESR lines showing weak frequency dependence of the resonance magnetic field which indicates high g-factor values, similar as in the Sr doped case (see Ref. [1]). The main resonance line, which comprises $\sim 90 \%$ of the total intensity, is very broad, with the linewidth of about ~ 2 T. Increasing the measurement frequency yields the significant shift of this main line to higher magnetic fields which is similar to the main line of the Sr doped sample [1]. The slope of the frequency dependence on the resonance magnetic field gives the effective g-factor value of 2.6, which is somewhat lower than the g-factor of the

Sr doped sample ($g \sim 3.5$). Similar to the Sr case, at higher temperatures the Ca doped sample exhibits spectra typical for the Co^{3+} ions in the thermally activated HS state [6].

4. Discussion

The experimental data on the lightly doped $LaCoO_3$ obtained from different techniques enable an unambiguous conclusion that Ca as well as Sr substitution yields in this small doping regime a strong low temperature magnetic response which cannot be explained by the magnetism of a small amount (~ 0.002) of individual Co^{4+} ions created by the introduced hole. The similarities in the behavior of the magnetization, in the development of the $1/T_1$ relaxation rate of ^{139}La NMR and in the ESR frequency dependencies for Ca and Sr doping give evidence that the model of the spin state polaron [1] can also be applied in case of the Ca doped sample. Since the Ca ion has the same ionic radius as the La ion, the main role in the formation of the spin polaron should be played by the introduced hole. The crystal field distortion, which is stronger in the Sr doping case, seems to play a minor role, possibly changing the details of the fine splitting of the energy levels of the spin polaron and the influence of the spin orbital coupling.

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