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Magnetic order in the lamellar compounds $La_{1-x}Sr_{1+x}CoO_4$ $(0 \leqslant x \leqslant 0.4)$

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Abstract

We have studied the AC and DC magnetic properties of the lamellar compounds $La_{1-x}Sr_{1+x}CoO_4$ $(0 \leqslant x \leqslant 0.4)$. These materials are found to evolve towards an anomalous "cluster-glass"-like behaviour as x increases. The onset of the ferromagnetic order in the bidimensional phases is seen to occur at around 150 K, followed by a blocking process around 125 K. Also, present in the magnetic behaviour of these materials is the signal coming from small intergrowths of a perovskite phase, also detected by TEM, although invisible for powder-X-ray diffraction.

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The influence of the dimensionality on the magnetic and transport properties of mixed-oxides is a hot topic in Physics and Chemistry of Solids, especially in the search for new superconductors, magnetoresistive materials, etc.

In the case of cobalt mixed-oxides with structures related to the perovskite—these latter being materials well-known for their interesting properties and for their complexity due to spin transitions at the cobalt ions [1]—this is a relatively unexplored and attracting area, and even more after the very recent discovery of superconductivity in lamellar cobalt oxides [2].

In this work we focus on the magnetic properties of one of these perovskite-derived systems with reduced dimensionality: the quasi-bidimensional $La_{1-x}Sr_{1+x}CoO_4$ compounds (formal oxidation state of cobalt $\geqslant 3+$) with K_2NiF_4 structure. The magnetic behaviour of the parent compound $LaSrCoO_4$ is already controversial: whilst some authors found a spin-glass behaviour [3], according to other groups the compound is ferromagnetic [4], or paramagnetic [5]. Also, it has been first proposed that both low spin ($t_{2g}^6e_g^0$) and high spin ($t_{2g}^4e_g^2$) Co^{3+} ions coexist in the material [5]. Nevertheless, more recent work gives evidence for an intermediate spin configuration ($t_{2g}^5 1_g$) [3,6].

More information on these lamellar systems is clearly needed. Here we give a brief account of the results obtained by a systematic investigation of the DC magnetic properties of $La_{1-x}Sr_{1+x}CoO_4$ $(0 \leqslant x \leqslant 0.4)$ compounds. The results of AC magnetic susceptibility measurements, especially useful to reveal magnetic transitions in complex systems, are also presented.

The compounds under study were obtained by decomposing a mixture of nitrates in the presence of KNO_3, as reported elsewhere [7]. According to Rietveld refinement of the X-ray powder diffraction data these samples were single-phase materials. Nevertheless, TEM studies revealed the presence, in some microcrystals, of small intergrowths of a perovskite phase [8].

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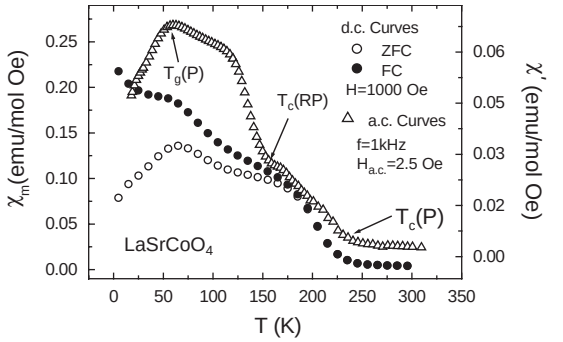

Fig. 1. DC (ZFC and FC) and AC molar magnetic susceptibility data for $LaSrCoO_4$.

Fig. 1 shows the temperature dependence of DC and AC magnetic susceptibility, $\chi_m(T)$, recorded for the as-prepared $x = 0$ compound, with nominal composition $LaSrCoO_4$.

Strong variations of the susceptibility behaviour are observed at the characteristic temperatures marked by arrows in Fig. 1. Particularly remarkable are the increases below $\sim$220 and $\sim$150 K. Some of these features show clear analogies with those typical of low-doped $La_{1-y}Sr_yCoO_3$ perovskite materials [9,10]. Indeed, comparison with previous results leads us to identify the features marked as $T_c(P)$ at $T \sim 250$ K and $T_g(P)$ at $T \sim 60$ K with the Curie temperature and the glass-freezing temperature of minority low-doped $La_{1-y}Sr_yCoO_3$ perovskite phases [9]. We therefore assume that the sample with nominal composition $LaSrCoO_4$ is a mixture of $La_{1-y}Sr_yCoO_3$ and $La_{1-x}Sr_{1+x}CoO_4$ lamellar phases with $x > 0$ (and therefore 3+ and 4+ mixed-valency in the cobalt ions). The increase at $\sim$150 K and the maximum at $\sim$125 K, which become more evident with increasing x, are assigned to the lamellar phases. Measurements of the Seebeck effect on the same sample corroborate these conclusions [8].

As the formal doping increases ($x > 0$), the samples develop a cluster-glass-like behaviour. As shown in Fig. 2, the sharp increase below $\sim$220–200 K in the real component χ' of the AC susceptibility is followed by a shoulder at $\sim$150 K that signals the onset of ferromagnetic ordering within the lamellar phase. The maximum at $\sim$125 K is attributed to a blocking process in the lamellar phase. As x increases the intensity of these features increases markedly, and their position shifts slightly towards higher temperatures.

The DC $\chi_m(T)$ data can be fitted to a Curie–Weiss (C–W) law in the temperature range $220 < T(K) < 300$. The estimated effective magnetic moment per cobalt ion and the C–W temperature are given in Table 1. The reported values suggest an intermediate spin state configuration of the Co^{3+} ions ($t_{2g}^5\, e_g^1$). Such a configuration could be stabilised by the tetragonal distortion of the octahedral site revealed by the X-ray diffraction

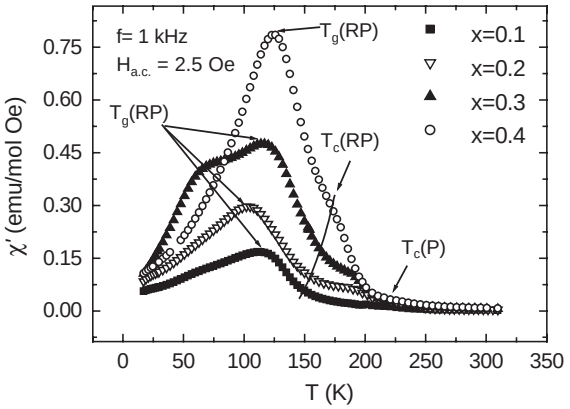

Fig. 2. AC magnetic susceptibility results of $La_{1-x}Sr_{1+x}CoO_4$ ($0.1 \leqslant x \leqslant 0.4$) compounds.

Table 1
Effective magnetic moment per Co ion (μ_{Coeff}) and C–W temperature (Θ) of the $La_{1-x}Sr_{1+x}CoO_4$ $0.1 \leqslant x \leqslant 0.4$ compounds

	$x = 0.0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$
$\mu_{eff\text{-}Co}$ (μ_B)	2.80	2.72	2.93	2.90	2.91
Θ (K)	−14	92	133	169	200

data. The C–W temperature is slightly negative in the $x = 0$ compound, but evolves to positive values as the ferromagnetic interactions get stronger with increasing x.

In summary, magnetic measurements on the lamellar phases $La_{1-x}Sr_{1+x}CoO_4$ reveal that ferromagnetic ordering sets in at $\sim$150 K, followed by a blocking process at $\sim$125 K. The possible presence of an intergrowth perovskite phase must be taken into account when analyzing the physical behaviour of these systems.

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