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Magnetic properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ single crystals

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Abstract

DC magnetization and optical measurements have been carried out for $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ single crystals ($x = 0.1, 0.15, 0.2$). The results indicate an inhomogeneous distribution of Ca^{2+} ions in a microscopic local scale, and existence of phase separation into a hole-rich ferromagnetic regions and a hole-poor host matrix. It was shown that with a temperature decrease the system evolves from a paramagnetic state of weakly interacting cobalt ions, through weakly interacting spin clusters, to the cluster glass state. The measured magnetic field dependences of magnetization have indicated that the volume of a hole-rich ferromagnetic cluster grows in magnetic field. These clusters can be considered as a precursor of the doping-induced ferromagnetic state. The analysis of the Curie–Weiss behavior at high temperature has shown that Ca doping stabilizes Co^{3+} ions in the intermediate spin state. Nevertheless, the small part of cobalt ions in the low spin state, up to about 10%, was suggested to exist for all levels of doping in paramagnetic phase up to room temperature. The long-time relaxation phenomena were found to follow a power law.

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1. Introduction

Primary attention is paid to cobalt perovskites of formula $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ (where $\text{A} = \text{Sr}, \text{Ca}$) because of the important spin-state transitions

phenomena [1] and large magnetoresistance [2–4] observed in this group of materials. Among the perovskite oxides other than manganites only cobaltites have been found so far to show magnetoresistance exceeding 30%. Recently, calcium-doped LaCoO_3 films were found to have the largest anomalous Hall effect of any ferromagnetic metal [5,6]. The substitution of A^{2+} for La^{3+} in $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ converts a selected number of Co^{3+}

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to Co^{4+} ions. Co^{3+} ions take nominally $3d^6$ configuration and can exist in low-spin (LS, $S = 0$, t_{2g}^6), intermediate-spin (IS, $S = 1$, $t_{2g}^5e_g^1$) or high-spin (HS, $S = 2$, $t_{2g}^4e_g^2$) states. Co^{4+} ions take $3d^5$ configuration and can exist also in low-spin (LS, $S = \frac{1}{2}$, t_{2g}^5), intermediate-spin (IS, $S = \frac{3}{2}$, $t_{2g}^4e_g^1$) or high-spin (HS, $S = \frac{5}{2}$, $t_{2g}^3e_g^2$) states. This variety of possible spin states is a consequence of the interplay between the intra-atomic exchange and the crystal-field interactions, which are of comparable magnitudes in cobaltites. The parent compound LaCoO_3 transforms with increasing temperature from a diamagnetic insulator (Co^{3+} in LS state) to a paramagnetic insulator above 100 K. The paramagnetic behavior above 100 K is attributed to the thermal population of the excited IS state [7–11].

The $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ crystals belong to a family of compounds that exhibit a mixed valence. In this system, depending on the spin states of considered ions, the $\text{Co}^{4+}\text{--Co}^{3+}$ pairs can interact ferromagnetically due to the double-exchange interaction, while the $\text{Co}^{3+}\text{--Co}^{3+}$ and $\text{Co}^{4+}\text{--Co}^{4+}$ pairs can be coupled antiferromagnetically due to the superexchange interaction. The coexistence and competition of antiferromagnetic and ferromagnetic interactions can lead to the frustration, which is responsible for spin-glass ordering observed in cobaltites [7–22]. In the case of low doping it is assumed that the system separates into hole-rich metallic ferromagnetic clusters (with $\text{Co}^{3+}\text{--Co}^{4+}$ pairs) and the hole-poor matrix similar to LaCoO_3 . Co ions of the ferromagnetic regions (clusters) should be in the IS state. This type of magnetic and electronic phase separation is characteristic of perovskites. The concept of phase separation has been successfully applied to explain many peculiar properties of magnetic and superconducting oxides (see review paper [23]). At sufficiently low doping the hole-rich regions can be isolated from one another showing a superparamagnetic behavior. With increase in doping, the interaction between the hole-rich regions begins and the cluster glass state can appear. Most of the papers considering a spin-glass behavior of cobaltites are devoted to $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ materials [7–22] but only few consider the spin-glass state of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ [6,13].

In several papers [11–14,24] it is suggested that the substitution of Sr or Ca for La is responsible for the fact that Co ions remain in the IS state down to the lowest temperature, even for very low doping level ($x = 0.05$). This suggestion is in contradiction to the results obtained by NMR [25]. The ^{59}Co NMR measurements on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ indicate the existence of low spin regions at all x values from 0.1 to 0.5. It is worth mentioning that one could expect a different behavior of cobaltites doped with Sr or Ca because of the difference in ionic radii of Sr^{2+} and Ca^{2+} ions. The transformation of all cobalt ions from LS to IS due to Sr-doping is suggested to be related to the lattice expansion induced by doping. If this concept is correct such an effect should not be expected to exist in Ca-doped LaCoO_3 because of distinctly smaller ionic radius (1.35 Å) of the Ca^{2+} ion as compared with the Sr^{2+} ion (1.44 Å). The ionic radius of Ca^{2+} is almost equal to that of La^{3+} (1.32 Å). Therefore Ca-doping should have very weak influence on lattice parameters of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ [13]. The reported data on Ca-doped LaCoO_3 cobaltites are not sufficient to determine the probable spin state of Co^{3+} ions and to clarify the nature of spin-glass-like behavior observed in these materials. In this paper, we present magnetic studies performed on $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ single crystals, in contrast to majority of previous studies, which have been carried out on ceramic samples.

2. Experimental details and results

The crystals were grown by the floating-zone method with radiation heating. The starting materials La_2O_3 , CaCO_3 and Co_3O_4 with their nominal composition were calcined at 900 °C, mixed, compacted into pellets and preliminarily sintered at 1250 °C. Next, the pellets were milled and the reground powder was pressed to form the feed rods with a diameter of 8 mm and a length of 90 mm. These rods were finally sintered at 1250 °C for 12 h in air. The growth rate was 1 mm/h. Crystallization was performed in oxygen atmosphere at the pressure of 1 atm. X-ray diffraction measurements were performed at room temperature

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