Magnetic properties and crystal-field excitations in $R_x\text{Sr}_{1-x}\text{CoO}_3$

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Abstract. The perovskite-type oxides $R_x\text{Sr}_{1-x}\text{CoO}_3$ ($R = \text{La, Pr, Ho}$) have been studied by means of neutron-diffraction and magnetic susceptibility measurements. A ferromagnetic transition occurs in $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$ and $\text{Pr}_{0.2}\text{Sr}_{0.8}\text{CoO}_3$ at $T_c \sim 260$ K ($M = 1.84\mu_B$) and 175 K ($M = 1.29\mu_B$), respectively. No magnetic transition was observed in the Ho-doped compound. Inelastic neutron scattering has been employed to study the crystalline-electric-field (CEF) interaction in these compounds. We have succeeded in reproducing the observed energy spectra using CEF parameters required for cubic symmetry.

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The members of the $R_x\text{Sr}_{1-x}\text{CoO}_3$ solid solution have received much attention in recent years due to their unique magnetic and transport properties and possible applications as oxidation catalysts, electrode materials and oxygen-permeable membranes [1].

The undoped compound SrCoO_3 crystallizes in a simple cubic structure under high oxygen pressure. In this case it turns out to be ferromagnetic and metallic [2]. Partial replacement of Sr^{2+} by R^{3+} leads to: (i) a pressure effect in the lattice, which changes interatomic distances and bond angles; (ii) a high-spin Co^{4+} to low-spin Co^{3+} transition. Both effects modify the structural and magnetic properties of the parent system. The nature of the observed phenomena is presently not well understood and controversial (see for example [3, 4]). So far very little information has been published concerning neutron-scattering data in magnetic rare-earth-doped cobaltites, especially in the Sr-rich region of $R_x\text{Sr}_{1-x}\text{CoO}_3$, $x < 0.5$.

High-resolution neutron-diffraction experiments are indispensable for the crystal and magnetic structure determination. The crystalline-electric-field (CEF) interaction at the

rare-earth site reveals important information about the peculiarities of the electronic structure and plays a key role in determining the magnetic ground state. Very detailed information about the CEF interaction results from inelastic neutron scattering (INS). To our knowledge no INS data are available for the $R_x\text{Sr}_{1-x}\text{CoO}_3$ compounds.

In this paper we focus on the determination of the CEF splitting within the ground-state J -multiplets of the rare-earth ions R^{3+} . In particular, we studied the $R_x\text{Sr}_{1-x}\text{CoO}_3$ compounds in the cubic phase, i.e. $x \leq 0.4$ for La-, $x \leq 0.2$ for Pr- and $x \leq 0.1$ for Ho-doped compounds [5].

1 Experiment

The $R_x\text{Sr}_{1-x}\text{CoO}_3$ samples were obtained via a standard solid-state-reaction method. The final specimens were of single phase within the limit of experimental uncertainties of powder X-ray diffraction. The oxygen content in the as-synthesized oxides was found to be 3 ± 0.005 by reduction in the flow of $5 \text{ H}_2 + 95 \text{ He}$ with the help of a Setaram TG-DTA-92 thermoanalyzer, i.e. the oxygen content turned out to be very close to the stoichiometric one.

The neutron powder diffraction experiments were performed with use of the DMC diffractometer at the spallation source SINQ, Switzerland. The data were collected at a wavelength of $\lambda = 2.559 \text{ \AA}$ in a temperature range from 10 K to room temperature. The INS experiments with high energy transfer (up to 100 meV) have been performed on the TOF spectrometer KDSOG in inverted geometry at the pulsed reactor IBR-2 of JINR, Dubna, Russia. High-resolution measurements of the INS with energy transfer $\Delta E < 12 \text{ meV}$ have been performed using the triple-axis spectrometer TASP at SINQ. The use of two INS spectrometers enabled us to obtain complementary data in a wide energy window. $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$ was used to establish the phonon contributions to the energy spectra. The magnetic properties were measured using a Quantum Design SQUID magnetometer in the temperature range from 2 to 300 K.

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2 Results and discussion

The FullProf refinement [6] of the room-temperature neutron-diffraction patterns confirmed that all samples appeared to be single-phase materials with simple cubic structure (space group $Pm\bar{3}m$) with lattice parameter $a = 3.840(1)$ Å, $3.839(1)$ Å and $3.848(1)$ Å for La-, Pr- and Ho-doped compounds, respectively.

The magnetic data displayed in Fig. 1 showed that rare-earth doping modifies the magnetic properties of the $SrCoO_3$ parent compound in quite different ways. While the replacement of Sr by non-magnetic La (up to $x \sim 0.7$ [7] or even $x \sim 0.85$ [8]) does not significantly change $T_c \sim 260$ K, doping with magnetic rare-earth ions strongly suppresses long-range ordering of the Co sublattice.

The temperature-dependent neutron powder diffraction measurements of the La- and Pr-doped compounds confirm the ferromagnetic nature of the phase transition. No superlattice reflections and/or line splittings were observed, which implied the absence of rhombohedral or orthorhombic distortions down to $T = 10$ K. The Curie temperature T_c and the effective magnetic moment M obtained from the neutron-diffraction and magnetization measurements turn out to be $T_c = 260(3)$ K, $M = 1.84(5) \mu_B$ and $T_c = 180(3)$ K, $M = 1.29(5) \mu_B$ for $La_{0.4}Sr_{0.6}CoO_3$ and $Pr_{0.2}Sr_{0.8}CoO_3$, respectively. The observed magnetic moments μ_{Co} for the La- and Pr-doped cobaltites have close values. This suggests that there is no magnetic ordering in the rare-earth sublattices of these compounds. The $Ho_{0.1}Sr_{0.9}CoO_3$ sample is paramagnetic down to $T = 2$ K (inset in Fig. 1). On cooling below $T \sim 200$ K it shows evidence for the formation of a superstructure corresponding to a doubling of the unit cell. The deviation of the $\chi^{-1}(T)$ data from a straight line is mostly due to the CEF interaction. A detailed analysis of the crystal and magnetic structure study of these compounds will be published elsewhere [5].

Fig. 2 shows the energy spectrum of $Pr_{0.2}Sr_{0.8}CoO_3$ measured on the TOF spectrometer at $T = 10$ K. Two clear peaks are observed around 8 and 13 meV. The low-

Fig. 1. Temperature dependence of the magnetization of $La_{0.4}Sr_{0.6}CoO_3$ (○) and $Pr_{0.2}Sr_{0.8}CoO_3$ (□) in an applied field of 100 Oe. The inset shows the inverse magnetization as a function of temperature for $Ho_{0.1}Sr_{0.9}CoO_3$ (●)

Fig. 2. Energy spectra of $Pr_{0.2}Sr_{0.8}CoO_3$ (○) and $La_{0.4}Sr_{0.6}CoO_3$ (●) measured on the TOF spectrometer at $T = 10$ K. The lines are the result of a fit to a three-component spectral function assuming resolution-limited Gaussian line shapes

temperature INS spectrum of $Ho_{0.1}Sr_{0.9}CoO_3$ exhibits four inelastic lines at 1.2, 3.5, 13 and 20 meV, whose line widths are close to the instrumental resolution (Fig. 3). We can interpret these inelastic peaks in terms of CEF transitions, since the phonon density-of-states of the non-magnetic reference compound $La_{0.4}Sr_{0.6}CoO_3$ was found to exhibit little inelastic intensity in the considered energy-transfer range. The spectra taken for the Pr- and Ho-doped compounds above an energy transfer of ~ 35 meV coincide with the INS spectra of the La-based compound; thus there is no evidence for other CEF excitations of higher energies.

We now proceed to analyze the observed energy spectra on the basis of a CEF Hamiltonian in cubic symmetry:

$$\hat{H} = B_4(\hat{O}_4^0 + 5\hat{O}_4^4) + B_6(\hat{O}_6^0 - 21\hat{O}_6^4), \quad (1)$$

where B_n and $\hat{O}_n^m$ denote the CEF parameters and the Stevens' operator equivalents, respectively. Due to the fact

Fig. 3. (a) Low-energy INS spectrum of $Ho_{0.1}Sr_{0.9}CoO_3$ obtained from the triple-axis spectrometer at $T = 4$ K. The line is the result of a fit to a three-component spectral function. (b) High-energy spectra of $Ho_{0.1}Sr_{0.9}CoO_3$ (○) and $La_{0.4}Sr_{0.6}CoO_3$ (●) measured on the TOF spectrometer at $T = 12$ K

Fig. 4. Calculated energy-level scheme of Ho^{3+} and Pr^{3+} ions based on the cubic CEF parameters found. The arrows denote the allowed CEF transitions with the respective transition-matrix elements

that the observed CEF transitions are resolution-limited, i.e. they do not exhibit line broadening, we can neglect possible CEF level splittings due to a lowering of the symmetry and Zeeman splittings of the CEF states due to the molecular field associated with the Co sublattice for the Ho- and Pr-doped compounds, respectively. Since there is no a priori information available for the CEF parameters, we adopted the CEF parameterization scheme developed by Lea et al. [9] to search for all possible values of B_4 and B_6 . From a least-squares fit to the observed energy spectra, which is applied to both CEF energies and intensities of CEF transitions, we found the following CEF parameters:

– $\text{Pr}_{0.2}\text{Sr}_{0.8}\text{CoO}_3$:

$$B_4 = -0.63 \times 10^{-3} \text{ meV}, B_6 = -0.11 \times 10^{-3} \text{ meV};$$

– $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_3$:

$$B_4 = 0.45 \times 10^{-3} \text{ meV}, B_6 = -0.57 \times 10^{-6} \text{ meV}.$$

Figure 4 shows the calculated CEF level schemes, which are in good agreement with the observations.

3 Summary

The results can be summarized as follows:

- i) The substitution of Sr^{2+} by magnetic rare-earth ions in the SrCoO_3 parent compounds suppresses the long-range magnetic ordering of the Co sublattice, as distinguished from La substitution.
- ii) No magnetic ordering was observed in the rare-earth sublattice of these compounds.
- iii) We have been able to determine a set of CEF parameters based on cubic symmetry at the R^{3+} site.

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