

# Response of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ to perturbations on the $\text{CoO}_3$ sublattice

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**Abstract.** Emission and transmission Mössbauer studies of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  perovskites doped with  $\sim 0.02$  stoichiometric units of oxygen vacancy or 2.5% iron corroborate the occurrence of electronic phase separation in these systems. The effect of the small perturbation of the  $\text{CoO}_3$  sublattice with either iron ions or oxygen vacancies on the bulk magnetization as well as on the Mössbauer spectra is in good agreement with the double exchange based cluster model. The magnetoresistance does not show any peak near the Curie temperature, but reaches  $-84\%$  in a field of 7.5 T at  $T = 8$  K. Below  $T_C \approx 180$  K the Mössbauer spectra distinctly include the contribution from paramagnetic and ferromagnetic regions, providing direct evidence for phase separation. No contribution to the spectra from  $\text{Fe}^{4+}$  ions can be observed, which is an unambiguous evidence that at low concentration iron (either directly doped or formed from  $^{57}\text{Co}$  by nuclear decay) is accommodated in the cobaltate lattice as  $\text{Fe}^{3+}$  ion.

**PACS.** 75.47.Gk Colossal magnetoresistance – 75.30.Kz Magnetic phase boundaries – 75.10.Nr Spin-glass and other random models – 71.30.+h Metal-insulator transitions and other electronic transitions – 76.80.+y Mossbauer effect; other gamma-ray spectroscopy

## 1 Introduction

The ongoing interest in doped transition metal oxides is due to their complex electronic and magnetic structures which result in a series of intriguing phenomena such as high-temperature superconductivity and colossal magnetoresistance. One family of the promising magnetoresistive materials are  $\text{LaCoO}_3$  based perovskites doped with divalent ions (e.g. Ca, Sr) at the rare-earth site [1–6]. The partial replacement of trivalent lanthanum cations with divalent strontium introduces electron holes in the transition metal network (i.e. converting some  $\text{Co}^{3+}$  ions into  $\text{Co}^{4+}$ ) as well as oxygen vacancies [7, 8]. Consequently, the conductivity of Sr doped  $\text{LaCoO}_3$  increases with strontium concentration.  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  displays semiconducting characteristics for low Sr doping levels, but it becomes metallic if the strontium concentration is increased beyond  $x \approx 0.18$  [1–4, 7, 8]. The distinctions used in this classification are not rigorous: “semiconducting” and “metallic” means  $d\rho/dT < 0$  and  $d\rho/dT > 0$ , re-

spectively, where  $\rho$  is the resistivity and  $T$  is the temperature. The resistivity of some of the materials satisfying the latter criterion for metallicity exceeds the  $\rho \leq 10^{-3} \Omega \text{ m}$  limit set by Mott. The classification of the magnetic states of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  perovskites is even more problematic, because magnetic phase separation occurs from very low Sr concentrations onwards. Following the observation of the coexistence of ferromagnetic-like and spin glass properties in these perovskites [2, 9], it was suggested recently that the magnetic behavior of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  perovskites can be best described as “glassy ferromagnetism” [4]. That is, at low Sr doping levels only short range magnetic correlation is formed below the magnetic transition temperature, with a characteristic coherence length of a few nanometers [10]. According to some authors the resulting magnetic clusters may behave superparamagnetically [11], however recent experimental data did not support this picture [12]. At a lower temperature the magnetization freezes out to some locally preferred direction, and the material enters a glassy phase. The proportion of magnetic clusters as well as the

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magnetic coherence length increases with increasing Sr doping level [13], and at about  $x \approx 0.18$  the clusters coalesce, giving rise to a metallic and unconventional ferromagnetic state [4,13], which can be described as the coexistence of coalesced, long range ordered magnetic clusters and isolated magnetically disordered regions. The long range order can be characterized by several hundred nm long magnetic coherence [13]. The ferromagnetic and conductive nature of the clusters is related to the double exchange process between intermediate-spin trivalent and low-spin tetravalent cobalt ions. The magnetic phase separation in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $0.1 \leq x \leq 0.5$ ) perovskites was confirmed by  $^{59}\text{Co}$  NMR spectroscopy [14]: it was shown that three distinct spontaneously separated magnetic phases (ferromagnetic, spin glass and paramagnetic) exist simultaneously in these compounds [12,14,15].

The magnetoresistance (MR) of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  depends strongly on the Sr doping level. While for  $x \geq 0.2$  a dominant MR peak was observed around the Curie temperature, for  $x \leq 0.18$  the MR was found to increase with decreasing temperature [1,4,15]. This low-temperature MR upturn is possibly due to weak localization effects. For intermediate doping rates ( $0.18 \leq x \leq 0.2$ ) the combination of the two types of magnetoresistance was found [1,4,15].

The effect of doping  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  perovskites at the transition metal site (i.e. replacement of some cobalt ions with iron ions resulting in  $\text{La}_{1-x}\text{Sr}_x\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$  perovskites) on the magnetoresistance has already been examined for  $x = 0.2$  and  $x = 0.33$  with  $y \geq 0.05$  [16–19]. It was suggested that the alteration of the MR properties of the investigated iron doped cobalt perovskites can be interpreted either by the modification of the magnetic field induced low-spin to high-spin transition of  $\text{Co}^{3+}$  ions [18], or by the changes in size distribution of the ferromagnetic clusters [19]. However, the electronic and magnetic properties and thus the physical roots of the magnetoresistance of cobalt-based perovskites are not clarified unambiguously yet.

Apart from the  $x$  and  $y$  concentrations of doping ions, the magnetic and electronic properties of  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  are also expected to depend sensitively on the  $\delta$  oxygen deficiency. As the procedure of preparation as well as the type(s) and concentration(s) of applied dopant ions may well have an influence on the value of  $\delta$ , the elucidation of the effect of oxygen deficiency on the electronic and magnetic structure of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  perovskites is also highly desirable.

In this paper we present magnetic, transport and Mössbauer measurements on 0.02 stoichiometric oxygen vacancy and 2.5% iron doped  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  samples. The phase diagram [4,20] of the parent compound described above motivated the choice of Sr concentration, 20%. This composition is in the cluster-glass region, very close to the dividing line to the spin-glass phase at 18% Sr doping level. In this intermediate region, according to our earlier study [21], below the Curie temperature (220 K) a pure paramagnetic phase converts to the coexistence of ferromagnetic and paramagnetic phases. The weight of

the ferromagnetic phase increases with decreasing temperature, however a part of the paramagnetic phase remains even at the lowest temperature studied (78 K). Distinct difference was observed in the electron localization in paramagnetic and ferromagnetic phases: independently of temperature, the ferromagnetic phase showed characteristically lower isomer shift values than the paramagnetic phase (corresponding to lower  $3d$  electron density on nucleogenic Fe in the former phase).

The consequences of iron substitution on the Co sublattice or oxygen removal have been studied before and the outcome was invariably that both effects are detrimental to ferromagnetism and, consequently, to the formation of ferromagnetic clusters [16–19]. A variety of mechanisms has been put forward as being responsible for this effect, but no consensus has emerged yet. Our purpose was to study this effect close to the transition to the spin-glass phase, where the clusters can be expected to be unstable. This expectation dictated the choice of a low concentration of iron and oxygen removal. In addition, the amount of doping iron ions (2.5%) was chosen with regard to the effect of 5% iron doping on the same parent perovskite. The latter material showed substantial change in the local magnetic structure as an emerging relaxation of the nanosize magnetic clusters [19]. The purpose of investigating the present 2.5% iron doped sample was to unveil whether an even smaller iron concentration can cause the same effect.

The local electronic and magnetic properties of the resulting compounds were examined with  $^{57}\text{Co}$  emission and  $^{57}\text{Fe}$  transmission Mössbauer spectroscopy, while the bulk properties of the 2.5% iron doped  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  sample was studied by AC magnetic susceptibility and magnetoresistance measurements. The interpreted results are compared to those of the parent  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  perovskite [21] and its doped  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.05}\text{Co}_{0.95}\text{O}_{3-\delta}$  derivative [19].

## 2 Experimental

The parent  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  sample (prepared by sol-gel method) was the same as that characterized in [21]. While the parent sample contained also oxygen vacancies (hence its oxygen stoichiometry is defined as  $3 - \delta$ ), the oxygen content was further reduced after the first series of  $^{57}\text{Co}$  emission Mössbauer measurements [21] by treating the sample in continuous  $\text{N}_2$  flow for 3 h at 650 °C. The change of oxygen concentration upon the heating was determined by the decrease of the mass of the sample: a change of  $\sim 0.02$  stoichiometric units was found.

The  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  sample was prepared as described in [16]. For the purpose of  $^{57}\text{Fe}$  Mössbauer measurements, a sample enriched in  $^{57}\text{Fe}$  was also prepared as follows. First, the precursors were vacuum evaporated (70 °C, 6 h), and the mixed solutions of  $\text{SrCO}_3$ ,  $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5 \text{H}_2\text{O}$ ,  $\text{CoCl}_3$ , and  $^{57}\text{Fe}$  dissolved in 1 M  $\text{HCl} + 0.1 \text{M HNO}_3$  were dried at 120 °C for 4 h. The mixture was pre-heated at 400 °C for 2 h in air, and then a pellet was made at 1000 kg/cm<sup>2</sup> pressure by CIP (Cold

Isostatic Pressing). Pyrolysis (800 °C, 1 day) and annealing (1000 °C for 4 days and 1200 °C for 2 days) of the sample was carried out to obtain the final composition. During the annealing treatments repetitive grinding and pressing to a pellet shape was carried out. The structures of the prepared perovskites were checked by X-ray diffractometry.

The  $^{57}\text{Fe}$  transmission Mössbauer measurements of the  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  sample were carried out on a powder sample using transmission geometry. Between 78 K and 300 K the temperature of the sample was controlled by a continuous flow liquid nitrogen cryostat (Leybold). An additional spectrum at 4.2 K was also recorded in a liquid helium cryostat. The  $\gamma$ -rays were provided by a  $^{57}\text{Co}(\text{Rh})$  source with  $10^9$  Bq activity. Isomer shift values are given relative to  $\alpha$ -Fe at room temperature.

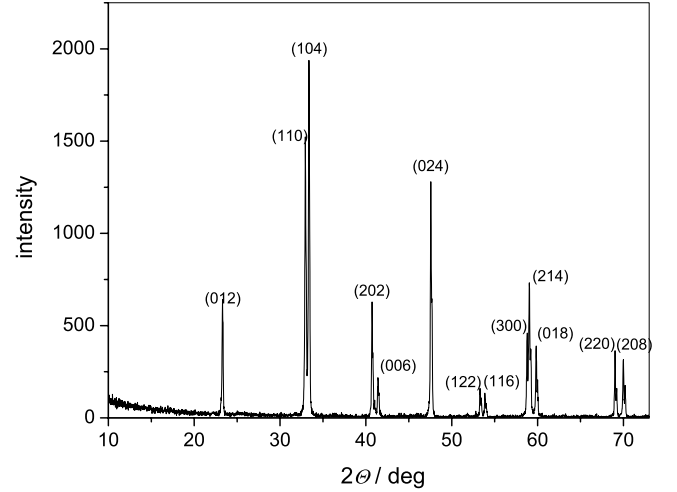
The  $^{57}\text{Co}$  emission Mössbauer measurements on the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  sample before the oxygen removal process were carried out using  $^{57}\text{Co}$  doping as described in [21]. Emission Mössbauer spectra were recorded between 78 K and 300 K in the above mentioned continuous flow liquid nitrogen cryostat using the conventional emission geometry. A standard potassium-hexacyanoferrate(II) (PFC) absorber of  $0.5 \text{ mg/cm}^2$   $^{57}\text{Fe}$  was moved relative to the sample. Calibration was done using a combined PFC +  $\alpha$ -Fe absorber: isomer shifts in emission Mössbauer spectra are given relative to  $\alpha$ -Fe with sign convention used in transmission measurements. All Mössbauer spectra were analyzed with the MossWinn 3.0 program [22].

AC magnetic susceptibility measurements of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_3$  were performed in the temperature range of 7–225 K using a 365 A/m AC magnetic field with 133 Hz, 1 kHz, and 10 kHz frequencies. Magnetoresistance of the iron doped sample was recorded using the standard four point contact method between 8 K and 290 K in a magnetic field of 7.5 T.

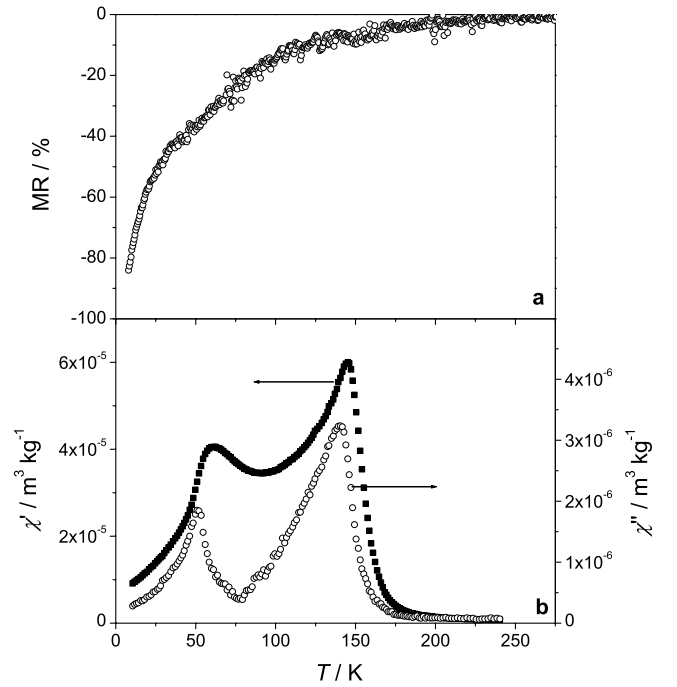
### 3 Results and discussions

The X-ray diffractogram of  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  (Fig. 1) reflects single phase perovskite system in very good accordance with the X-ray diffraction patterns of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$  perovskites with  $0 \leq y \leq 0.3$  [4, 16, 19].

The lower panel of Figure 2 shows AC magnetic susceptibility data of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$ . The Curie temperature of magnetic clusters, as signaled by the onset of magnetic losses with decreasing temperature, is estimated at about  $T_C = 180$  K. This temperature is roughly 40 K lower than that of the undoped compound [21]. The broad high-temperature peak in the susceptibility indicates glassy behavior and wide cluster size distribution. The former can be concluded from the frequency dependent nature of the peak, while the latter leads to its widening. At  $\sim 60$  K another structure can be observed in the susceptibility, which corresponds to the transition to a spin-glass or cluster-glass state.

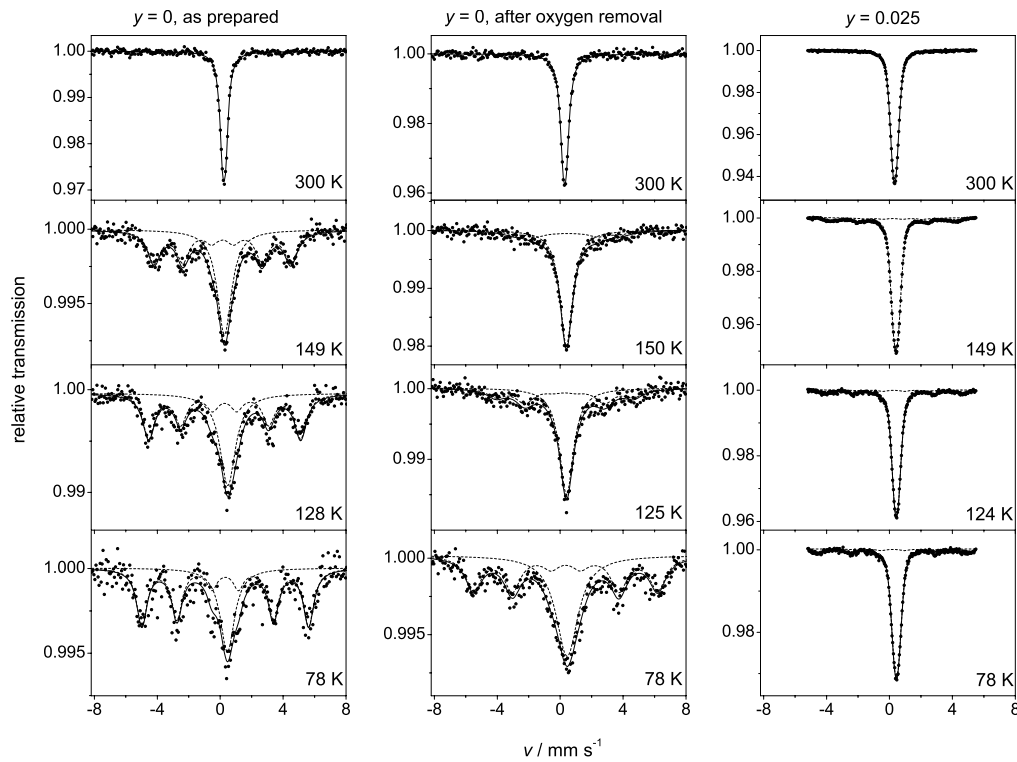


**Fig. 1.** X-ray diffraction pattern of  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  measured at room temperature. The  $hkl$  indexes are indicated above the peaks in brackets. Intensity is given in arbitrary units. The diffractogram was recorded using Nifiltered  $\text{Cu K}\alpha$  radiation.



**Fig. 2.** Plot of (a) magnetoresistance at  $B = 7.5$  T magnetic field and (b) AC magnetic susceptibility (real and imaginary part) of  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  as a function of temperature. AC magnetic susceptibility data were recorded at 133 Hz frequency and 365 A/m magnetic field.

The upper panel of Figure 2 shows the magnetoresistance (MR) data for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$ , defined as  $\text{MR} = (R_B - R_0)/R_0$ , where  $R_B$  and  $R_0$  are the electric resistances measured at  $B = 7.5$  T and 0 external magnetic field, respectively. The MR decreases monotonically down to  $-84\%$  at 8 K, which is the largest MR observed for iron doped cobalt perovskites up to now, according to



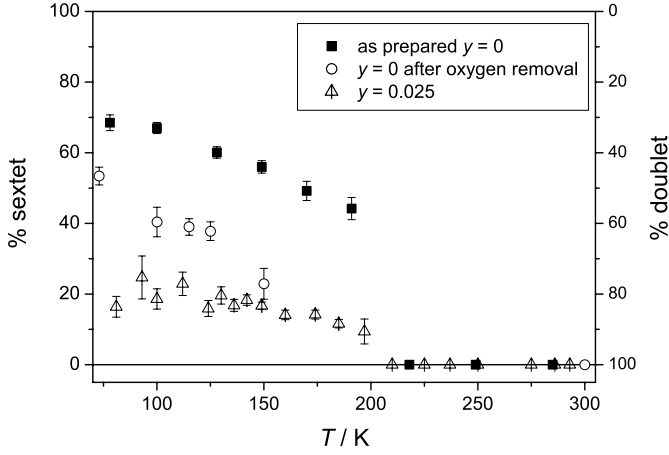
**Fig. 3.** Selected  $^{57}\text{Co}$  emission Mössbauer spectra of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\alpha}$  before (left column) and after (second column) the oxygen removal and  $^{57}\text{Fe}$  transmission Mössbauer spectra of  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  (right column) measured at the indicated temperatures (the data of the first column were taken from [21]).

our knowledge. The MR signal starts to exceed the error of measurement at around the same temperature as in the parent compound (Fig. 2a, [21]). In contrast to the iron-free compound no distinguishable MR peak was observed at any temperatures. It should be noted though that around the magnetic transition temperature (where the MR peak could be expected) the value of the monotonically growing MR is of the same order of magnitude as the MR peak in the parent material.

Before discussing the results of Mössbauer spectrometry, we would like to remark that, as described in [23], in the case of the  $^{57}\text{Co}$  emission Mössbauer measurements of cobaltate perovskites the resultant spectra reflect the electronic state of the nucleogenic iron ions, as the electronic relaxation processes after the  $^{57}\text{Co} \xrightarrow{\text{E.C.}} ^{57\text{m}}\text{Fe}$  transformation are completed well within the life time of the excited  $^{57\text{m}}\text{Fe}$  nucleus state ( $\tau \approx 141$  ns). However, this time is not enough to modify the number of the coordinating oxygen anions around the transition metal ion, thus the nucleogenic  $^{57}\text{Fe}$  ion possesses the oxygen environment of the parent Co. Furthermore, the detection of the ferromagnetic component in our case indicates the presence of exchange coupling between iron and cobalt. Therefore, whereas the hyperfine parameters obtained from the emission Mössbauer spectra reflect the electronic and magnetic properties of the nucleogenic iron ions, these parameters should be strongly influenced by the inherited environment of the parent cobalt ions (e.g. average density of electron holes, magnetic order, and presence of oxygen vacancies). On the other hand, assuming a homogeneous distribution of both the  $^{57}\text{Co}$  (in the case of the emission Mössbauer measurements) and  $^{57}\text{Fe}$  dopants (in the iron

doped sample), the emission and transmission Mössbauer spectra can be compared after proper velocity calibration.

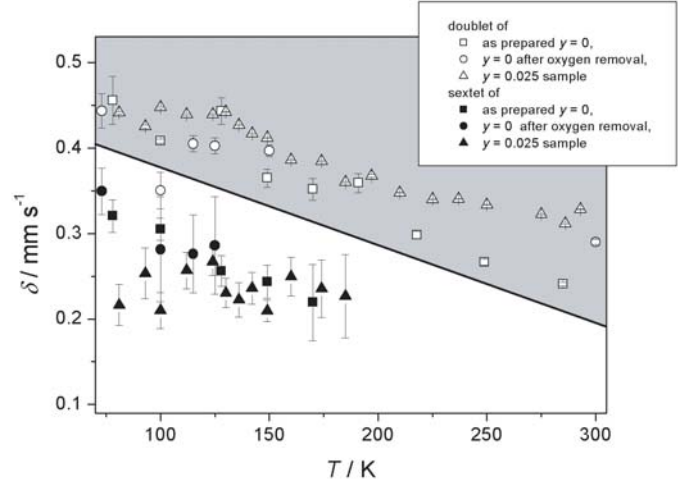
The  $^{57}\text{Co}$  emission Mössbauer spectra recorded after oxygen removal of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  and the  $^{57}\text{Fe}$  transmission Mössbauer spectra of  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  showed a coexistence of magnetic (FM) and paramagnetic (PM) subspectra below the magnetic transition temperature, similar to spectra observed in the unaltered parent compound (Fig. 3, [21]). In all cases the FM/PM ratios change quite abruptly at the transition temperature (Fig. 4). On the other hand, these spectra show marked difference to those found at higher doping levels [19]. At 5% Fe doping a transition from the pure paramagnetic state to the pure magnetic state takes place in a temperature window (from 120 K to 65 K) with slow relaxation process, which arise due to the small size (and thus the easiness of relaxing) of the magnetic clusters (or droplets) [19]. At  $y \leq 2.5\%$  the magnetic sextets show no relaxation effect (beside a small distribution of hyperfine magnetic field), i.e. well defined magnetic sextets appear at around  $T_C$  (that is, the temperature window of the transition is far below of our temperature resolution). The FM/PM ratio increases below  $T_C$  with decreasing temperature but still at 78 K a dominant fraction of the iron ions contribute to a paramagnetic Mössbauer subspectrum (Fig. 4). These imply that the magnetic structures of  $y \leq 0.025$  and  $y = 0.05$  iron doped perovskites differ. Up to  $y = 2.5\%$  iron doping traces of long range magnetic order still persist and the magnetic state of the investigated cobalt perovskites resembles the metallic FM side of the metal-to-insulator transition (MIT) of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  type perovskites. This means that



**Fig. 4.** Area ratio in percentage of the magnetic (and paramagnetic) subspectrum in the  $^{57}\text{Co}$  emission and  $^{57}\text{Fe}$  transmission Mössbauer spectra of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$  ( $y = 0$  and  $0.025$ , respectively) as a function of temperature (the data of the as prepared  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  were taken from [21]).

for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$  an MIT transition, similar to that found at about  $x = 0.18$  strontium doping in the iron free  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  perovskites, can be observed between  $y = 0.025$  and  $y = 0.05$  iron doping values.

The change of electron localization in the PM and FM phases can be well followed by the comparison of Mössbauer isomer shifts of the sextets ( $\delta_s$ ) and doublets ( $\delta_d$ ). These shifts differ explicitly in each measured spectrum (Fig. 5; for comparison, the data of the as prepared  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  are quoted from [21]): while  $\delta_d$  of  $\text{La}_{1-x}\text{Sr}_x^{57}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$  with  $y = 0$  and  $0.025$  varies between  $0.46 \text{ mm/s}$  and  $0.24 \text{ mm/s}$  for  $78 \text{ K} \leq T \leq 300 \text{ K}$  (see grey area in Fig. 5), the values of  $\delta_s$  are in the range of  $0.35 \text{ mm/s}$  and  $0.21 \text{ mm/s}$  between  $78 \text{ K}$  and  $190 \text{ K}$ . At a given temperature, one observes an average gap of about  $0.15 \text{ mm/s}$  between  $\delta_d$  and  $\delta_s$ . It should be noted that these isomer shifts are clearly outside the range where  $\text{Fe}^{4+}$  ions would contribute, which is expected near  $\delta \approx 0.1 \text{ mm/s}$  at room temperature [24], and they also exceed the value of  $\delta = 0.18 \text{ mm/s}$  determined for  $\text{La}_{0.5}\text{Sr}_{0.5}^{57}\text{Fe}_{0.022}\text{Co}_{0.978}\text{O}_3$  and assigned to  $\text{Fe}^{4+}$  with delocalized  $3d$  electrons [25]. It follows then that the observed room temperature isomer shifts refer to  $\text{Fe}^{3+}$  ions. Moreover, the fit of all the doublets result quadrupole splittings of about  $0.25 \text{ mm/s}$ . From the absence of a substantial quadrupole splitting we can also conclude that in all cases we are dealing with high-spin trivalent ions. The gap between  $\delta_d$  and  $\delta_s$  indicates the existence of an electronic phase separation in the investigated perovskites below the magnetic transition temperature, which is in good agreement with the cluster model. In the FM metallic cobalt clusters the  $e_g$  electrons of the intermediate-spin  $\text{Co}^{3+}$  ions are delocalized due to the double exchange interaction between the trivalent and tetravalent cobalt ions, while in the paramagnetic, presumably strontium-poor matrix they remain more localized, which can be



**Fig. 5.**  $^{57}\text{Fe}$  Mössbauer isomer shift ( $\delta$ ) of the fitted quadrupolar doublets (empty symbols) and sextets (full symbols) of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  (as prepared (taken from [21]) and after oxygen removal) and  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  at different temperatures. The separation of grey and white areas is arbitrary and serves only didactic reasons (see text).

well seen as the difference of the observed isomer shifts of the Mössbauer doublets and sextets. That is, the doublets with higher isomer shifts correspond to formally  $\text{Fe}^{3+}$  ions embedded in a nonmetallic matrix, while the lower  $\delta_s$  values to  $\text{Fe}^{3+}$  ions with  $3d$  electrons sufficiently delocalized to provide a metallic matrix. Evidently, the level of delocalization in iron-doped  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  [25] exceeds what we see here in the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ -based samples. As the temperature increases above  $T_C$ , the long-range ferromagnetic coherence is destroyed by thermal agitation, which leads to the localization of the  $e_g$  electrons (and so of the electron holes) within the clusters. Surprisingly the isomer shift of the quadrupolar doublet in the Mössbauer spectra above the Curie temperature is in good agreement with the values of  $\delta_d$  below  $T_C$ . This suggests that the electron localization in the clusters above  $T_C$  seems to prefer the (nucleogenic or doping) iron ions. Otherwise, an additional doublet with lower isomer shift (corresponding to  $\text{Fe}^{4+}$  valence state) should have appeared above  $T_C$ , as well.

Within the limit of experimental resolution and in contrast with the outcome of bulk magnetic susceptibility measurements, the paramagnetic-to-ferromagnetic transition temperature as shown by the Mössbauer spectra is not affected by the small iron doping. However, we find that the relative area of the magnetic subspectrum is smaller in the case of the 2.5% iron doped as well as the higher oxygen deficient samples than in the parent  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  (cf. Fig. 4). As the concentration of oxygen vacancies in  $\text{La}_{0.8}\text{Sr}_{0.2}^{57}\text{Fe}_{0.025}\text{Co}_{0.975}\text{O}_{3-\delta}$  is not known, this result cannot be unambiguously interpreted in the case of the iron doped sample, however, the authors believe that this does not alter qualitatively the influence of 2.5% iron doping. The effect of oxygen removal and iron doping shown in Figure 4 implies that the relative weight

of the FM component decreases, which in turn substantially affects bulk electronic and magnetic properties. In the case of oxygen removal this can be attributed mainly to the decreasing number of  $\text{Co}^{4+}$  ions, as the oxygen vacancies compensate the extra electrons from  $\text{Sr}^{2+}$ . Additionally, the shortening of the long-range magnetic coherence within the clusters can be explained by the partial removal of the double exchange process between  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions, which is caused either by the missing intermediate oxygen ion in the case of the oxygen vacancy doped  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  perovskite or by the change of exchange interaction due to the  $\text{Co}^{3+}/\text{Fe}^{3+}$  replacement in the case of the 2.5% iron containing descendant perovskite.

This change of the underlying magnetic cluster structure is reflected in the observed magnetoresistance, most conspicuously in the absence of the MR peak at the Curie temperature [Fig. 2a], which was present in the as-prepared  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  perovskite [21]. That is, in the latter case the MR peak around the Curie temperature is expected to arise due to the ordering effect of an external magnetic field. The efficiency of ordering depends on the size, number and interconnectivity of available clusters, which factor enhances most drastically at the percolation threshold. This is the reason, why a maximum of MR at  $T_C$  versus strontium doping level appears at this regime, as was presented by Aarbogh et al. in [26]. In this region introducing a small amount of oxygen vacancies or iron ions should reduce the effect of the applied magnetic field significantly. Consequently, the suppression of the CMR peak upon doping cobalt perovskites on the cobalt sites can be comprehended as the clusters becoming too separated to produce colossal magnetoresistance around  $T_C$ .

On the other hand, the low-temperature magnetoresistance is enhanced drastically with small iron doping [Fig. 2a]. This type of magnetoresistance of cobaltate perovskites is believed to origin from spin-dependent electron transfer between isolated ferromagnetic clusters, where the external magnetic field orientates the spins of clusters, thus increasing hopping probability [13]. The intensity of the resulting MR should depend on the size and distance of clusters, and increases with decreasing strontium content in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  perovskites [4, 13, 26]. In our case, the intense growth of MR at low temperatures as a result of 2.5% iron doping can also be explained by the breaking up of the clusters, which was discussed above. However, it should be noted that further increase of iron content decreases low- $T$  MR [18, 19]. As a first assumption, we can explain this effect with the iron ions blocking the electron transfer between FM cobalt clusters. On the other hand, field induced tunneling between polycrystalline grains, resulting grain size dependent MR, cannot be excluded as an additional factor to low- $T$  magnetoresistance, so further experimental work is needed to clarify this point.

## 4 Conclusions

Investigations by means of  $^{57}\text{Co}$  emission and  $^{57}\text{Fe}$  transmission Mössbauer spectrometry proved the coexistence of magnetic and paramagnetic regions in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$

doped with  $\sim 0.02$  stoichiometric oxygen units or 2.5% iron below the Curie temperature. The Mössbauer spectra confirmed the 3+ oxidation state of doping or nucleogenic iron ions, however in the magnetic phase the 3d electrons of Fe were found to be more delocalized. Slight increase of the oxygen vacancy concentration as well as small (2.5%) iron doping shrink the ferromagnetically ordered regions in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  perovskite, however the long range magnetic order seems to disappear between 2.5% and 5% iron doping. Our results can be well described by the electronic phase separation model introduced for doped perovskite systems. We conclude that the obstruction of the double exchange interaction between neighboring  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions either by removing the intermediate oxygen ion or by replacing the  $\text{Co}^{3+}$  with  $\text{Fe}^{3+}$  derogates the magnetic clusters. As a result, the MR peak around the Curie temperature diminishes, because the external magnetic field applied slightly above  $T_C$  can not achieve the coalescence of the magnetic clusters to counterbalance the disordering effect of the temperature. On the other hand, the separation of the clusters by iron doping or oxygen removal forms smaller scale magnetic areas, the presence of which induces strong low temperature MR effect.

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