

Magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.15$ and 0.3)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 7313

(<http://iopscience.iop.org/0953-8984/16/41/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 18:16

Please note that [terms and conditions apply](#).

Magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.15$ and 0.3)

V V Sikolenko^{1,2,6}, A P Sazonov³, I O Troyanchuk³, D Többens¹,
U Zimmermann⁴, E V Pomjakushina^{2,4} and H Szymczak⁵

¹ Hahn-Metner-Institut, Glienickestraße 100, D-14109 Berlin, Germany

² Joint Institute for Nuclear Research, 141980 Dubna, Russia

³ Institute of Solid State and Semiconductor Physics, 220072 Minsk, Belarus

⁴ ETH Zürich & Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

⁵ Institute of Physics, 02-668 Warsaw, Poland

E-mail: Sikolenko@hmi.de

Received 1 June 2004, in final form 29 July 2004

Published 1 October 2004

Online at stacks.iop.org/JPhysCM/16/7313

doi:10.1088/0953-8984/16/41/012

Abstract

Neutron diffraction, transversal field μSR and magnetization studies of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with $x = 0.15$ and 0.3 has been performed. Long-range ferromagnetic ordering has been found only in the $x = 0.3$ sample. Magnetization measurements indicate the inhomogeneous magnetic state of this system. Magnetization data confirm well defined long-range ordering for the $x = 0.3$ sample with $T_C \approx 220$ K, whereas for the $x = 0.15$ compound this temperature marks the onset of magnetic order within ferromagnetic clusters. μSR data confirm that the transition in the ferromagnetic phase takes place in the large fraction of the $x = 0.3$ sample, but not in all of the volume. This data also provide evidence for the absence of long-range magnetic ordering for the $x = 0.15$ sample and show that even short-range ordering takes place only in part of the sample volume. Thus, all these data are in agreement with the phase separation scenario of the concentration phase transition in cobaltites.

1. Introduction

The members of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ solid solution have received much attention in recent years due to their unique magnetic and transport properties and possible technical applications.

End-member SrCoO_3 crystallizes in the cubic structure and exhibits ferromagnetic ordering. Replacement of Sr^{2+} by La^{3+} leads to two consequences: a ‘chemical’ pressure effect in lattice parameters (interatomic distances and bond angles) and substitution of tetravalent Co^{4+} ions by trivalent Co^{3+} ones. These effects modify the crystal and magnetic structure.

⁶ Address for correspondence: Hahn Meitner Institute, Glienickestraße 100, D-14109 Berlin, Germany.

Thus, pure LaCoO_3 has a rhombohedrally distorted perovskite structure. The ground state of LaCoO_3 is a non-magnetic insulator, the Co^{3+} ions are in the low-spin (LS) state ($t_{2g}^6 e_g^0$; $S = 0$). Spin-state transition to a paramagnetic state occurs with increasing temperature around $T = 100$ K [1]. The latest studies have suggested that the intermediate-spin (IS) state ($t_{2g}^5 e_g^1$; $S = 1$) of Co^{3+} ions is lower in energy than the high-spin (HS) state ($t_{2g}^4 e_g^2$; $S = 2$) [2] that makes the transition to the IS state more possible. The spin state configuration of Co^{4+} ions is also undecided.

Jonker and van Santen [3] first described the magnetic properties of the Sr doped LaCoO_3 system and these properties were interpreted by the double-exchange mechanism of exchange interactions between Co^{3+} and Co^{4+} ions. However, Goodenough *et al* have shown [4] that ferromagnetic Co^{3+} – Co^{4+} interactions follow from modified superexchange considerations, and there is no need to have recourse to the double-exchange mechanism to account for the ferromagnetic coupling. Afterwards, ferromagnetic properties of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system were explained by Goodenough [5] in a model of itinerant-electron ferromagnetism. Thus, according to Itoh *et al* [6, 7] the Co sites without nearest Sr neighbours remain in the LS state, whereas the ground state of the Co sites with nearest Sr neighbours is considered to be converted to the tetravalent HS state Co^{4+} ($t_{2g}^3 e_g^2$; $S = 5/2$) or the trivalent HS state Co^{3+} . Then, the superexchange interactions Co^{3+} – Co^{3+} and Co^{4+} – Co^{4+} between alike spins are antiferromagnetic, whereas the double-exchange interaction between trivalent and tetravalent Co ions is ferromagnetic. Thus, the competition between competing exchange interactions leads to the spin-glass (SG) behaviour observed below $x = 0.18$. When the ferromagnetic interactions overcome the antiferromagnetic ones, the cluster-glass (CG) phase seems to appear. Sathe *et al* [8] have assumed that the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system is divided into a La rich region with Co^{3+} ions in the LS state and Sr rich regions with Co^{3+} ions in the HS state and Co^{4+} ions in the LS ($t_{2g}^5 e_g^0$; $S = 1/2$) state. They have suggested that the antiferromagnetic contribution, if present at all, is very weak compared to the double-exchange Co^{4+} – O – Co^{3+} mechanism responsible for the ferromagnetic ordering in this system. Señaris-Rodríguez and Goodenough [9] have shown that Co ions of the ferromagnetic Sr-enriched phase are in IS configuration; the hole-poor matrix experiences a thermally induced LS to HS transition. For low Sr doping ($x < 0.2$), the hole-rich regions are isolated from one another and show superparamagnetic behaviour below $T_C \approx 240$ K; long-range magnetic order via frustrated intercluster interactions occurs below a superparamagnetic freezing temperature that increases with x . At $x = 0.20$, the coupling between the IS, ferromagnetic clusters within an interpenetrating matrix reaches a magnetic percolation threshold that orders the clusters ferromagnetically below T_C . Caciuffo *et al* [10] have assumed that the delocalized e_g electrons provide strong ferromagnetic coupling of the localized t_{2g} configurations at the cobalt ions of hole-rich clusters. The superparamagnetic clusters become coupled ferromagnetically to one another via superexchange through the hole-poor matrix, and by $x = 0.1$ the long-range ferromagnetic order of a small volume fraction of the sample was found. In the range $0.15 \leq x \leq 0.25$ a cluster formation sets in and the volume of the hole-rich clusters approaches percolation. True long-range ferromagnetic order evolves for $x \geq 0.3$ only. It was shown that Sr doping leads to a phase separation into hole-rich ferromagnetic clusters and hole-poor LaCoO_3 -like matrix [6–10]. Anil Kumar *et al* [11] have invoked compositional inhomogeneity to explain the unusual magnetic behaviour. On the other hand, Mira *et al* [12] have proposed the existence of an electronic phase separation taking place in the material instead of in the presence of chemical inhomogeneities, etc.

Recent magnetic studies, both ac and dc and magnetotransport measurements [13] on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ have indicated a strong tendency towards magnetic phase separation in

this material. Magnetic phase separation has also been observed by ^{59}Co NMR data [14] in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ as well as in a similar $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ [15] system up to $x = 0.5$. However, at the present time the nature of observed phenomena in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system is still not well understood.

In our previous work [16] we studied the crystal and magnetic structure of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ by low resolution neutron diffraction. Here we present more detail and precise data obtained by high resolution neutron powder diffraction, zero-field and transverse-field μSR and magnetization measurements.

2. Experiment

The polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ samples were prepared by the ceramic method from a mixture of La_2O_3 , Co_3O_4 and SrCO_3 powders taken in stoichiometric ratios. The mixture was pressed into the pellet and heated at 1000°C for 6 h in air. Finally, the pellet was ground, re-pressed, sintered at 1200°C for 12 h in air and then cooled at a rate of 100°C h^{-1} to room temperature.

The oxygen content of the samples was determined using thermogravimetric analysis (TGA). All the samples were completely reduced to a mixture of La_2O_3 , MnO and Co metal in evacuated silica tubes at 800°C for a long time (24 h) and then cooled at a rate of 100°C h^{-1} to room temperature. Metallic tantalum was used as a reducing agent.

The identification of all the phases and determination of lattice parameters at room temperature were performed using a DRON-3M powder x-ray diffractometer with $\text{Co K}\alpha$ radiation with wavelengths $\lambda_1 = 1.78892 \text{ \AA}$ and $\lambda_2 = 1.79278 \text{ \AA}$.

Magnetization measurements were performed using a commercial vibrating sample magnetometer OI-3001. The temperature dependences of the magnetization were measured on warming from 4 to 250 K in a field of 100 Oe after cooling in zero magnetic field (ZFC) and in a field of 100 Oe (FC). Then, the field dependence of magnetization was measured at 7 K in fields up to 15 kOe.

The neutron powder diffraction experiments were carried out on the fine resolution neutron diffractometer E9 at the BER-II reactor in Hahn Meitner Institute [17]. Data were collected from 2 to 290 K over the range $4^\circ < 2\theta < 156^\circ$ with the wavelength $\lambda = 1.3075 \text{ \AA}$.

The neutron powder diffraction data were analysed with the Rietveld method using the FullProf program [18].

μSR (muon spin rotation/relaxation/resonance) experiments were performed at the GPD spectrometer at the Paul Scherrer Institute at zero field and at transversal field 100 G.

3. Results

3.1. Structural studies

Preliminary study of crystal structure of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.15$ and 0.3) compounds were performed using x-ray diffraction data. All observed Bragg peaks were indexed in the rhombohedral $R\bar{3}c$ space group in hexagonal axes. There were no impurities according to these data. The result of refinement of the neutron diffraction pattern is in agreement with the x-ray analysis.

The magnetic contribution to Bragg peaks was found only for the sample with $x = 0.3$ in contrast with [10], where it was reported that ferromagnetic order occurs even in the $x = 0.1$ sample. The result of Rietveld refinement of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ at $T = 2 \text{ K}$ is presented in figure 1. The growth in the intensity of low-angle magnetic reflections is most evident at the (102) peak (inset of figure 1). No magnetic satellites corresponding to any antiferromagnetic

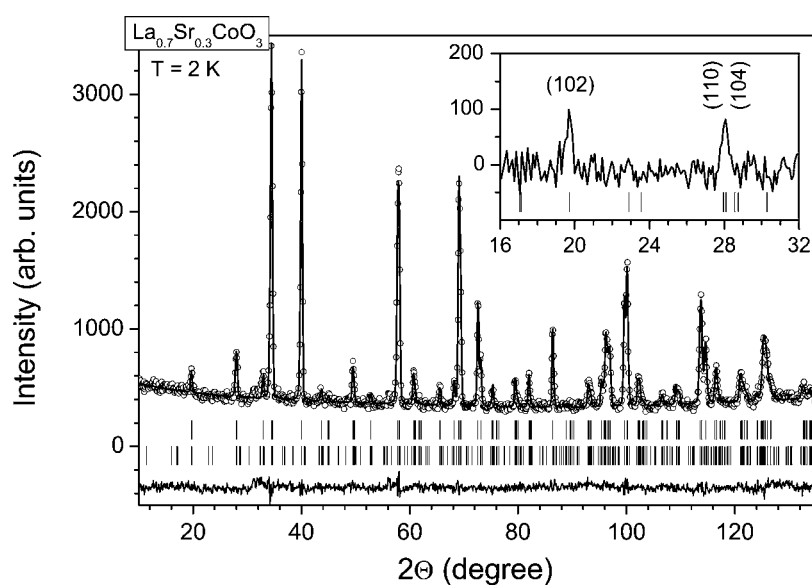


Figure 1. Diffraction pattern of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ at $T = 2\text{ K}$. Experimental points (open circles), refinement curve (continuous line) and their difference (continuous line below). The ticks show the predicted 2θ positions for the Bragg peaks of the crystal phase (upper row) and the magnetic phase (lower row). The plot in the inset shows some magnetic contributions into peaks revealed by subtracting the pattern measured at 2 K from that at 290 K.

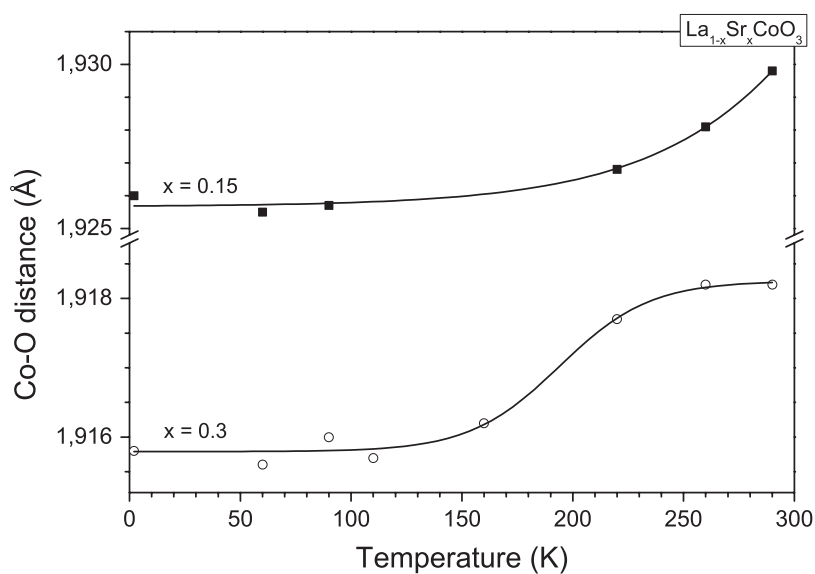


Figure 2. Temperature dependence of the Co-O bond length.

type of ordering have been detected in both samples at least down to 2 K. Some structural parameters calculated from the neutron diffraction pattern are reported in table 1.

Figures 2 and 3 present the temperature dependences of the Co-O distance and the Co-O-Co bond angle for both samples. LaCoO_3 has a rhombohedrally distorted crystal structure [10].

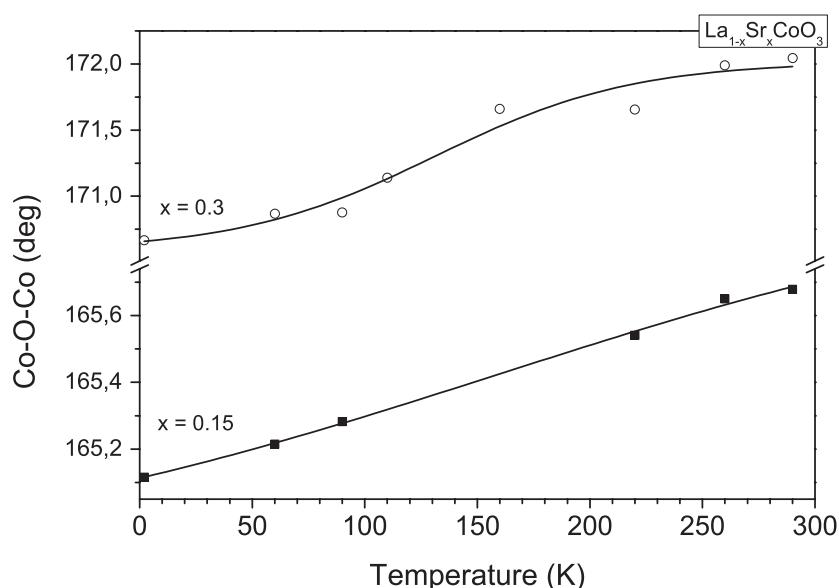


Figure 3. Temperature dependence of the Co–O–Co angle.

Table 1. Structural parameters for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ obtained at different temperatures with the E9 diffractometer. a , c —lattice parameters, y_{O} — y -coordinate of the oxygen.

x	$T = 2 \text{ K}$		$T = 90 \text{ K}$		$T = 290 \text{ K}$	
	0.15	0.3	0.15	0.3	0.15	0.3
a (Å)	5.4306(3)	5.4131(7)	5.4309(2)	5.4134(7)	5.4406(2)	5.4208(5)
c (Å)	13.0854(7)	13.1690(3)	13.0860(5)	13.1765(3)	13.1423(5)	13.2152(9)
y_{O}	0.4539(3)	0.4712(3)	0.4544(2)	0.4718(3)	0.4557(2)	0.4755(8)
μ (μ_{B})	—	2.1(3)	—	1.9(6)	—	—

The introduction of the Sr^{2+} cations, which has larger ionic radii (1.44 Å with a coordination number of 12) as compared with those (1.36 Å) of La^{3+} ions, reduces the rhombohedral distortion. For instance, the deviation of the Co–O–Co angle from the ideal rhomboidal, which is a measure of deviation from the perfect CoO_6 octahedron for the $\text{La}_{0.85}\text{Sr}_{0.15}\text{CoO}_3$ sample more than for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ one. For the $x = 0.3$ sample the Co–O bond length very slightly changes with the temperature increasing in the magnetic phase, but rapidly increases after crossing the Curie temperature, whereas for the $x = 0.15$ sample we observed only smooth increasing of the bond with the temperature increasing. This result is similar to that observed in [10].

3.2. Magnetic properties

According to magnetization measurements, the transition into the paramagnetic state of $\text{La}_{0.85}\text{Sr}_{0.15}\text{CoO}_3$ occurs in a wide temperature interval, indicating the inhomogeneous magnetic state of this system. An increase in $M(T)$ below $T \approx 220 \text{ K}$ marks the onset of magnetic order within ferromagnetic clusters. A maximum in the ZFC magnetization versus temperature (ZFC $M(T)$) curve at about 75 K indicates the ‘effective’ freezing temperature

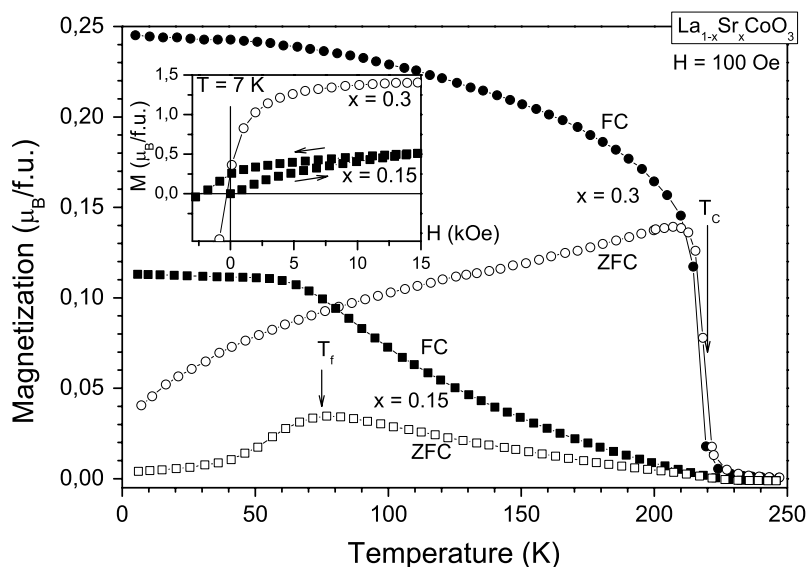


Figure 4. Temperature dependences of the magnetization of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ measured on warming from 4 to 250 K in a field of 100 Oe after the field cooling (closed symbols) or zero field cooling (open symbols) procedure. The plot in the inset shows the field dependence of magnetization measured at 7 K in fields up to 15 kOe.

T_f of ferromagnetic clusters (figure 4). The field dependence of magnetization $M(H)$ for this sample demonstrates that no saturation occurs up to 15 kOe and indicates a high coercivity H_C (inset of figure 4).

For the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ sample coercivity H_C drops, whereas FC $M(T)$ abruptly increases at $T_C \approx 220$ K, indicating well defined long range ordering. Below T_C the FC magnetization curve shows a monotonic increase with decreasing temperature. It is worth noting that the onset of the transition into the magnetically ordered state coincides with that for $\text{La}_{0.85}\text{Sr}_{0.15}\text{CoO}_3$ composition. For the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ sample ZFC $M(T)$ deviates from FC $M(T)$ below T_C and exhibits a gradual reduction with decreasing temperature. This large difference between FC $M(T)$ and ZFC $M(T)$ below T_C indicates the appreciable magnetic anisotropy of this compound. The hysteresis loop approaches a saturation of M at 15 kOe, where the magnetic moment per cobalt ion is $1.5 \mu_B$. However saturation is also not completely achieved, therefore we cannot define the magnetic moment from magnetic data. On the other hand, the refined magnetic moment from neutron data at 2 K is about $2 \mu_B$ per cobalt ion. The Curie temperature obtained from neutron data is in agreement with that from the magnetization measurement.

3.3. μSR studies

Figure 5 presents the temperature dependence of the asymmetry of muon precession in a weak transversal magnetic field for both samples. In the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ sample we observed a sharp drop of asymmetry at the Curie temperature to the value $\sim 2/3$ for paramagnetic value. This fact confirms that the transition in the ferromagnetic phase takes place in a large fraction of the sample, but not in all of the volume. In the $\text{La}_{0.85}\text{Sr}_{0.15}\text{CoO}_3$ sample we also observed a decrease of muon precession asymmetry with the temperature decrease, but very broad with temperature. Coherent muon precession in zero external field has not been observed. This fact could be explained by the inhomogeneous distribution of local magnetic moments in bulk samples.

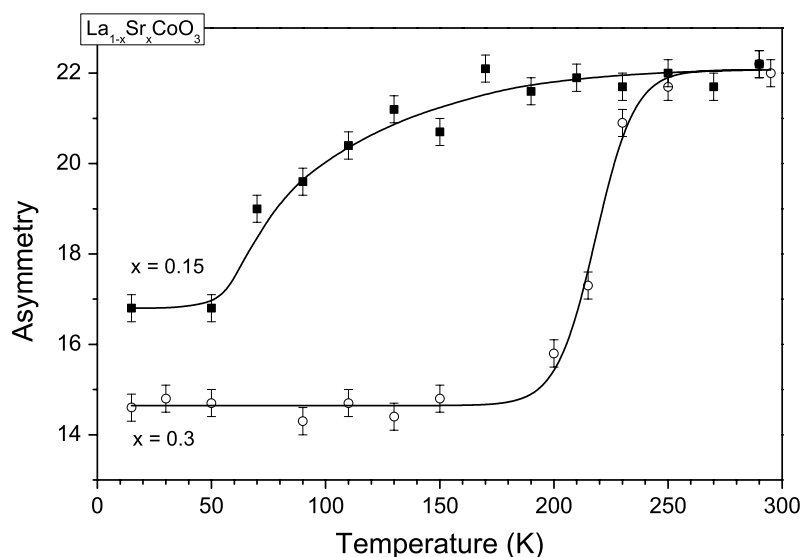


Figure 5. Temperature dependence of muon precession asymmetry.

4. Discussion and conclusions

As was noted in the introduction, a lot of experimental data for the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system have been interpreted by using such terms such as ferromagnet, paramagnet, superparamagnet, spin glass (SG) and cluster glass (CG). As a result, there are different models to explain the unusual magnetic properties of this system. These models differ from each other both in a spin state configuration of Co ions and in type of exchange interactions between them.

Strontium substitution of lanthanum drastically changes the magnetic properties of LaCoO_3 , which does not contain Co^{4+} and is non-magnetic. Magnetic moments appear with Sr^{2+} doping due to the conversion of Co^{3+} to Co^{4+} ions. Thus, neutron diffraction and the magnetization measurement indicate well defined long range ordering in the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ compound. However, in accordance with our neutron diffraction data there is no long-range order for $x = 0.15$ as compared with [10], apparently due to the difference in the preparation conditions. The μSR data also provide evidence of the absence of long-range magnetic ordering for the $x = 0.15$ sample. Our data agree with [19] who have considered that the fraction of ferromagnetically ordered material becomes smaller and smaller with increasing annealing temperature and the system behaves as a CG for $0.1 < x < 0.2$. Thus, Caciuffo *et al* [10] sintered at 1000°C , whereas our synthesis temperature was 1200°C .

A high-resolution electron microscopy (HREM) study of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ series has detected inhomogeneous distribution of La^{3+} and Sr^{2+} ions up to $x = 0.3$ composition [10]. The absence of zero-field muon precession also indicates a high inhomogeneity. According to [13], at lower Sr doping ($x < 0.18$) the system enters a mixed phase that displays the characteristics of both a SG and a ferromagnet. Moreover, ^{59}Co NMR measurements on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [14] establish unequivocally the coexistence of ferromagnetic regions, SG or CG-like regions, and hole-poor low spin regions at all x values from 0.1 to 0.5. The NMR data for $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ [18] are consistent with this phase separation scenario. Our magnetization data also indicate that there is no simple ferromagnetic ordering for $x = 0.3$ compound. As regards the $x = 0.15$ compound, our data confirm the existence of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ -like

ferromagnetic clusters for this sample, which is indicated by the onset of the transition into the magnetically ordered state at $T \approx 220$ K both for the $x = 0.3$ sample and the $x = 0.15$ one (figure 4). The decrease of the muon asymmetry of precession is broad with temperature for $x = 0.15$ sample. Low changes of asymmetry also show that even short-range ordering takes place only in part of sample volume. The x-ray absorption fine structure measurements of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ manganites [20] as well as other studies [21] are in agreement with the phase separation scenario. So, in accordance with [20], lightly doped manganites like $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ consist of strongly distorted LaMnO_3 -like regions and low distorted regions enriched by Sr ions.

We interpret all these data by assuming the magnetic phase separation into regions with different magnetic states both for $x = 0.15$ and 0.30 compounds, and magnetic properties depend on fraction one or other regions. Thus in $\text{La}_{0.85}\text{Sr}_{0.15}\text{CoO}_3$ the ferromagnetic clusters exist in the paramagnetic matrix. However, in $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ the ferromagnetic clusters have already reached the percolation threshold and there are long-range ferromagnetic regions together with paramagnetic ones.

Apparently, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ solid solutions are non-homogeneous objects and consist of several magnetic phases. We believe that the local clustering leads to intrinsic chemical inhomogeneities providing a magnetic phase separation. As was noticed, substitution of Sr^{2+} for La^{3+} creates Co^{4+} . The chemical inhomogeneities separating strontium-free regions, where localized 3d electrons occur at LS Co^{3+} ions, from strontium-rich regions, where the 3d electrons are collective and give ferromagnetism at low temperatures. Strontium-rich regions contain Co^{3+} ions which are surrounded by few Co^{4+} ions among its LS/IS Co^{3+} neighbours. Thus the mixture enriched by Sr ion magnetic regions and LaCoO_3 -like non-magnetic ones give rise to peculiar ferromagnetic properties.

References

- [1] Imada M, Fujimori A and Tokura Y 1998 *Rev. Mod. Phys.* **70** 1039
- [2] Korotin M A, Ezhov S Yu, Solov'yev I V, Anisimov V I, Komski D I and Sawatsky G A 1996 *Phys. Rev. B* **54** 5309
- [3] Jonker G H and van Santen J H 1953 *Physica* **19** 120
- [4] Goodenough J B 1958 *J. Phys. Chem. Solids* **6** 287
- [5] Goodenough J B 1968 *J. Appl. Phys.* **39** 1209
- [6] Itoh M, Natori I, Kubota S and Motoya K 1994 *J. Phys. Soc. Japan* **63** 1486
- [7] Itoh M, Natori I, Kubota S and Motoya K 1995 *J. Magn. Magn. Mater.* **140–144** 1811
- [8] Sathe V G, Pimpale A V, Siruguri V and Paranjpe S K 1996 *J. Phys.: Condens. Matter* **8** 3889
- [9] Se  ar  s-Rodr  guez M A and Goodenough J B 1995 *J. Solid State Chem.* **118** 323
- [10] Caciuffo R, Rinaldi D, Barucca G, Mira J, Rivas J, Se  ar  s-Rodr  guez M A, Radaelli P G, Fiorani D and Goodenough J B 1999 *Phys. Rev. B* **59** 1068
- [11] Anil Kumar P S, Joy P A and Date S K 1998 *J. Appl. Phys.* **83** 7375
- [12] Mira J, Rivas J, Baio G, Barucca G, Caciuffo R, Rinaldi D and Se  ar  s-Rodr  guez M A 2001 *J. Appl. Phys.* **89** 5606
- [13] Wu J and Leighton C 2003 *Phys. Rev. B* **67** 174408
- [14] Kuhns P L, Hoch M J R, Moulton W G, Reyes A P, Wu J and Leighton C 2003 *Phys. Rev. Lett.* **91** 127202
- [15] Ghoshray A, Bandyopadhyay B, Ghoshray K, Morchshakov V, B  rner K, Troyanchuk I O, Nakamura H, Kohara T, Liu G Y and Rao G H 2004 *Phys. Rev. B* **69** 064424
- [16] Sikolenko V V, Pomjakushina E V and Istomin S Ya 2003 *J. Magn. Magn. Mater.* **258/259** 300
- [17] T  bbens D, St   ber N, Knorr K, Mayer H M and Lampert G 2001 *Mater. Sci. Forum* **378–381** 288
- [18] Rodr  guez-Carvajal J L 1992 *Physica B* **55** 192
- [19] Baio G, Barucca G, Caciuffo R, Rinaldi D, Mira J, Rivas J, Se  ar  s-Rodr  guez M A and Fiorani D 2000 *J. Phys.: Condens. Matter* **12** 9761
- [20] Shibata T, Bunker B, Mitchell J F and Schiffer P 2002 *Phys. Rev. Lett.* **88** 207205
- [21] Loudon J C, Mathur N D and Midgley P A 2002 *Nature* **420** 797