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Neutron diffraction studies of perovskite-type compounds $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$)

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Abstract. Neutron diffraction measurements on the title compounds have been carried out over a range of temperature from 10 to 300 K. The compounds have a rhombohedrally distorted perovskite structure. A paramagnetic to ferromagnetic transition is observed for samples with $x \geq 0.2$. The ordered magnetic moments obtained for $x = 0.2$ and 0.3 are found to be 1.5 and 1.89 μ_B respectively at 10 K and are in agreement with those reported from other macroscopic measurements. A possible magnetic structure is discussed.

1. Introduction

LaCoO_3 crystallizes in a rhombohedrally distorted perovskite structure. This compound and the La substituted by Sr systems have been of great recent interest because of the metal–insulator and magnetic transitions [1]. The parent compound displays a low-spin (LS) to high-spin (HS) transition as a function of temperature [2–9]. In LaCoO_3 the temperature dependence of magnetic susceptibility can be divided into three regions. (i) In the low-temperature range it increases with temperature and peaks around 90 K. In the range $90 \text{ K} < T < 400 \text{ K}$ it obeys the Curie–Weiss law. (ii) It is temperature independent between 400 and 650 K and (iii) beyond 650 K it starts decreasing again [6]. At 1210 K there is a localized electron \rightarrow collective electron transition [5]. Recently an anomalous thermal expansion has also been seen near 100 K [11]. Neutron diffraction measurements do not show any indications of long-range magnetic order down to 4 K. The HS–LS transition in LaCoO_3 has a controversial explanation based on different measurements. The transition at 500 K was thought to be due to the LS \rightarrow HS transition based on the crystal symmetry considerations as seen from x-ray diffraction studies [5–7]. The neutron diffraction studies on this compound do not fully support the change in crystal symmetry [10]. Abbate *et al* have interpreted the transition in the range 400–650 K as due to an LS \rightarrow HS transition, based on x-ray absorption and x-ray photoelectron spectroscopy measurements [12]. The theoretical calculations are shown to be consistent with this transition. Neutron polarization analysis studies on a single crystal of LaCoO_3 however revealed that the system undergoes the LS \rightarrow HS transition near 90 K and the high-temperature transition near 500 K is not of magnetic origin [11]. Asai *et al* have also shown that the anomalous thermal expansion is in agreement with the theoretical prediction by Bari *et al* [13].

Replacement of La by Sr modifies the properties of the parent system. The compounds exhibit paramagnetic to ferromagnetic and semiconductor to metal transition as the dopant

concentration is increased. These two transitions occur at almost the same concentration of Sr ($x = 0.2$). Jonker *et al* have shown that the mixed system is ferromagnetic for $x \geq 0.15$ [14]. However the magnetic phase diagram by Itoh *et al* reveals that the compounds in the range $0 < x \leq 0.18$ have a spin glass type of behaviour and above $x > 0.18$ the system shows a cluster glass formation [15]. Recent single-crystal neutron polarization analysis measurements on Sr-doped $\text{La}_{0.92}\text{Sr}_{0.08}\text{O}_3$ do not show any spin state transition. Spin glass freezing near 24 K and ferromagnetic correlations up to 600 K are observed in these measurements. The results are explained on the basis of expansion of the cell by Sr doping which allows the presence of the HS state of Co^{3+} having a larger ionic radius [11]. On the other hand $\text{SrCoO}_{2.5}$ has an antiferromagnetic order with a Néel temperature of 570 K and the ordered moment is close to the spin value [16]. The Co^{3+} - Co^{3+} interaction is positive in La-based systems while it is negative in Sr-based compounds. It is thus interesting to study the effect of Sr substitution in LaCoO_3 . The magnetic ordering in these mixed oxides is not yet clear. With a view to understanding the nature of magnetic ordering in the mixed perovskites we have carried out neutron diffraction measurements on the series $\text{La}_{1-x}\text{Sr}_x\text{Co}_3$ as a function of concentration (x) and temperature.

2. Experimental details

The samples were prepared by the solid state reaction method. Spec pure material were used as starting constituents. The solid solution obtained by heating the nitrates of all constituent material was ground and sintered at 930 °C for 24 h. The process of grinding and heating was repeated at least five times. Final sintering was performed in oxygen atmosphere for 24 h. Powder x-ray diffraction patterns showed the formation of a single-phase compound and no impurity line was seen. Transition temperatures (T_C) were obtained from a.c. susceptibility measurements and were found to be 225, 232 and 240 K for $x = 0.2$, 0.3 and 0.4 respectively.

Neutron diffraction measurements were carried out on the PSD-based powder diffractometer [17] at Dhruva reactor at BARC, using a wavelength of 1.09 Å. Samples were well ground and packed in a cylindrical vanadium container for room-temperature and in aluminium cans for low-temperature experiments.

3. Results, data analysis and discussion

The room-temperature data for $x = 0.1, 0.2, 0.3, 0.4$ and 0.5 were analysed by the profile refinement method using the modified version of the profile refinement program by Young *et al* [18]. The parameters varied were atomic positions, occupancies and temperature factors in addition to the instrumental parameters such as zero angle, half-width parameters and scale factor. The observed and the fitted patterns are shown in figure 1 along with the difference plot at the bottom. LaCoO_3 has a rhombohedrally distorted crystal structure. The replacement of La by Sr brings in changes in the crystal structure and it is reported that the system with $x = 0.5$ is cubic. The compounds with $x > 0.5$ have a tendency for oxygen deficiency and the crystal structure depends on the method of preparation and the oxygen deficiency. SrCoO_{3-x} with $x = 0.5$ has an orthorhombic structure of brownmillerite type, while those with $x > 2.7$ prepared under high oxygen pressure are reported to have cubic structure [16, 22, 23]. Harrison *et al* [24] have recently carried out neutron diffraction studies on $\text{Sr}_6\text{Co}_5\text{O}_{15}$. The high-temperature brownmillerite phase of $\text{Sr}_2\text{Co}_2\text{O}_5$ on cooling undergoes phase separation and $\text{Sr}_6\text{Co}_5\text{O}_{15}$ and Co_3O_4 are formed. The analysis of this

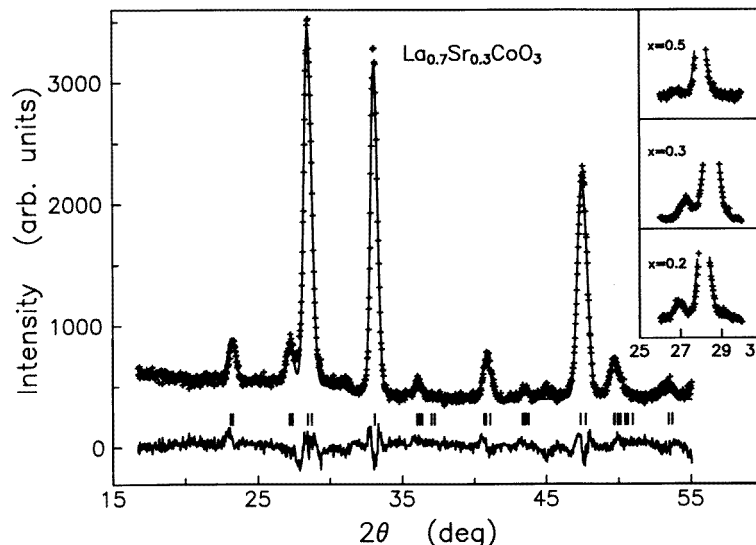


Figure 1. The observed and fitted patterns along with the difference curve for $x = 0.3$. The inset shows the $(1, -1, 1)$ peak for $x = 0.2$, $x = 0.3$ and $x = 0.5$.

system, with Co_3O_4 as impurity phase, reveals that the compound has trigonal crystal structure, isostructural with $\text{Ba}_6\text{Ni}_5\text{O}_{15}$ [25]. The two Sr ions have eightfold coordination of oxygen while there are two octahedrally and one trigonally oxygen coordinated Co ions. The compounds reported in the present paper have Sr concentration $x \leq 0.5$. All these compounds have rhombohedral crystal structure with two formula units per unit cell. Out of the two possible space groups $R\bar{3}C$, having only one Co site, gave a better fit than $R\bar{3}$, which has two Co sites. The variation of occupancy parameters for the different atoms, not all in the same cycle of refinement, showed no significant change in these parameters, confirming the stoichiometry of the compounds. Table 1 gives the values of the refined parameters for these compositions.

Table 1. Various parameters obtained from the Rietveld refinement and the agreement factors.

Parameter	$x = 0.0^a$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$
Cell parameters a (Å)	5.37	5.32(0.06)	5.36(0.04)	5.32(0.02)	5.35(0.05)	5.35(0.03)
Unit cell volume		107.95(0.05)	110.41(0.07)	108.03(0.05)	108.79(0.04)	109.28(0.11)
Rhombohedral cell angle	60.79	60.49(0.04)	60.45(0.04)	60.47(0.08)	60.30(0.02)	60.27(0.03)
Temperature factors La {Sr}		0.85(0.06)	0.98(0.09)	0.92(0.1)	0.95(0.06)	0.95(0.1)
Co		0.70(0.04)	0.78(0.07)	0.72(0.09)	0.66(0.07)	0.85(0.1)
O		1.15(0.05)	1.03(0.06)	0.98(0.08)	1.09(0.05)	1.09(0.1)
$d(x)^b$	0.049	0.042(0.005)	0.039(0.001)	0.028(0.001)	0.024(0.008)	0.014(0.002)
R_p		5.0	5.70	4.85	5.6	5.1
R_{wp}		7.7	7.04	6.53	8.03	7.9
R_{exp}		4.7	5.72	3.92	5.2	4.99

^a Values as reported in [10].

^b $d(x)$ is the deviation of the x and y coordinates of the oxygen ion from its special position $0.25 \{-d(x)\}$, $0.25 \{+d(x)\}$ respectively. For cubic symmetry $d(x) = 0.0$.

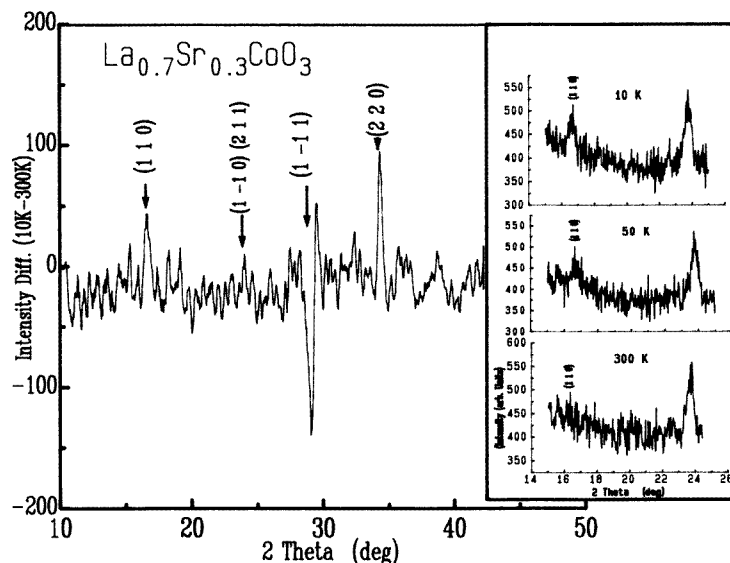


Figure 2. The difference curve of 300 and 10 K neutron diffraction patterns for $x = 0.3$. The inset shows the (1, 1, 0) peak at 300, 50 and 10 K.

The rhombohedral distortion decreases with increase in x . The effect is similar to the thermal expansion reported in the parent compound LaCoO_3 . The ionic radius of the Sr ion, being larger than that of La ion, effectively expands the unit cell. The decrease in distortion is also indicated by the intensity of the (1, -1, 1) (rhombohedral index) peak in the profiles (shown in the inset) of figure 1. The intensity of this peak was found to be sensitive to the asymmetry of the oxygen octahedra (indicated by $d(x)$ in table 1) and it decreases with decrease in the asymmetry. It will completely vanish if the system becomes cubic. In the present series the asymmetry exists even for $x = 0.5$ (cell angle $\alpha = 60.27^\circ$) which had been reported to be cubic in the earlier work with x-ray diffraction [1, 19]. An anomaly in cell parameters and cell volume is observed at $x = 0.2$, the values for this concentration being higher than those for others as seen from table 1. It has been reported in the literature that a small Sr doping results in increase in cell parameter and decrease in rhombohedral angle [11]. It is worth noting here that at the dopant concentration $x \cong 0.2$ we observe ferromagnetic ordering at low temperatures.

In order to observe the magnetic ordering, diffraction profiles were recorded at 10, 50 and 100 K in addition to those at 300 K. The samples were packed in an aluminium container and were attached to the cold finger of the closed cycle refrigerator (CCR). The temperature variation of the (1, 1, 0) peak at various temperatures for $x = 0.3$ is shown in the inset of figure 2. This peak is not observable for any of the samples at 300 K, where its intensity is extremely small. On cooling neither (1, 1, 0) nor any other additional peak is seen for the $x = 0.1$ sample. For higher compositions the (1, 1, 0) peak develops on cooling and is clearly seen at 10 K. The intensities of all other peaks remain unchanged, except for the thermal parameter effect. No additional line corresponding to any antiferromagnetic type of ordering was seen.

In figure 2 the difference pattern of 300 and 10 K for $x = 0.3$ is shown. The (1, 1, 0) peak is clearly visible with its intensity increasing at 10 K. The $\{(1, -1, 0)(1, 0, -1)$ and

(2, 1, 1)} peak does not show any increase. The major intense peaks {(2, 0, 0), (2, 2, 2)} and (2, 1 1) do show a difference, but it can be attributed to temperature effects as the magnetic contribution to these peaks is extremely small as compared to the nuclear intensity. Also it may be mentioned here that the magnetic form factor reduces the magnetic intensities at higher angles. This is not the case with the {(1, -1, 0), (1, 0, -1), (2, 1, 1)} reflections. As the rhombohedral distortion is very small the peaks are not well separated. In such a situation we can only consider the sum of the intensities of the contributing reflections. The ratio of the sum of the calculated magnetic contribution to the nuclear contribution for {(1, -1, 0), (1, 0, -1), (2, 1, 1)} peaks is found to be 18%. The absence of this magnetic peak can only be explained by choosing the proper direction of the magnetic moment of the Co ion. We attempted various directions for the magnetic moment of Co ion but the ratio of the magnetic intensity to nuclear intensity was found to be above 10% except for the (1, 0, 0) direction. If we assume the moment direction to be along the (1, 0, 0) direction then the ratio is found to be 6%, which is close to the observed value. The effective site magnetic moment was obtained from the intensity of (1, 1, 0) reflection after normalizing the intensity of (2, 2, 0) with the calculated intensity. The normalized intensities are given in table 2. The temperature dependence of the magnetic moment is plotted in figure 3 along with the Brillouin function for $J = 2$ and $3/2$.

Table 2. The normalized intensities and effective magnetic moment of the Co ion obtained for $x = 0.3$ and $x = 0.2$.

hkl (Rhom.)	Normalized intensity			
	300 K	100 K	50 K	10 K
For $x = 0.3$				
(1 1 0)	—	9.5	15.5	18.8
(1 $\bar{1}$ 0), (1 0 $\bar{1}$), (2 1 1)	35	41	46	45
(200), (202)	290	284	289	295
(220)	273	273	273	273
μ_{eff} (μ_B)	—	1.33(0.08)	1.7(0.1)	1.89(0.11)
For $x = 0.2$				
(1 1 0)	—	12.1	—	7.5
(1 $\bar{1}$ 0), (1 0 $\bar{1}$), (2 1 1)	40	42	—	39
(200), (202)	286	282	—	288
(220)	273	273	—	273
μ_{eff} (μ_B)	—	1.18(0.07)	—	1.5(0.09)

The appearance of the (1, 1, 0) peak shows that the ordering is ferromagnetic in nature. The temperature dependence of the moment deviates from the Brillouin function (figure 3), indicating that the magnetic behaviour of HS Co^{3+} in these compounds is different from that in other ionic systems. The mixed system has been reported to have ferromagnetic and antiferromagnetic interactions resulting in magnetic frustration [15]. $SrCoO_3$ is a ferromagnet [20] while $SrCoO_{2.5}$ has an antiferromagnetic ordering [16]. These results indicate that $Co^{4+}-Co^{4+}$ exchange is ferromagnetic and $Co^{3+}-Co^{3+}$ exchange is antiferromagnetic, but the neutron diffraction measurements on $LaCoO_3$ [11] have shown the presence of ferromagnetic interaction in this system, implying a positive $Co^{3+}-Co^{3+}$ exchange. These observations then suggest that the $Co^{3+}-Co^{3+}$ interaction is sensitive to the inter-ionic distance and $Co^{3+}-O-Co^{3+}$ bond angles. The oxygen deficiency also seems

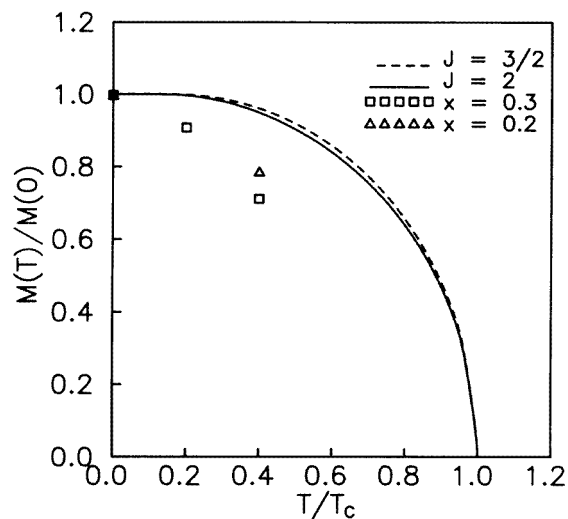


Figure 3. The reduced magnetization against reduced temperature for $x = 0.2$ and $x = 0.3$ of the compound $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$.

to affect the sign of the exchange integral involved.

Table 3. Effective spin only moment of Co ion for two compounds in μ_B .

Spin state	$x = 0.2$	$x = 0.3$
1 Co^{3+} HS	4.2	4.3
Co^{4+} HS		
2 Co^{3+} LS	0.2	0.3
Co^{4+} LS		
3 Co^{3+} HS	3.4	3.1
Co^{4+} LS		
4 Co^{3+} LS	1.0	1.5
Co^{4+} HS		
5 Co^{3+} mixed low and high spin	1.0	1.5
Co^{4+} LS		

We now consider various models to explain the observed magnetic structure. The Co ions can exist in 3+ or/and 4+ state with either high- or low-spin configurations as shown in table 3. For ferromagnetic ordering (figure 4), the structure factors of all the reflections have the form $M_{hkl} = p_3M_3 + p_4M_4$ where M_3 and M_4 represent the magnetic moments and p_3 and p_4 represent the fractional occupancies of the 3+ and 4+ ions, respectively. This is under the assumption of a random distribution of the two types of ion on the lattice sites [21]. Table 3 gives the expected magnetic moment for various possible spin states of the two ions. A comparison with the observed value of the moment ($1.89 \mu_B$ for $x = 0.3$) rules out the possibility of the first three configurations. Cases 4 and 5 give same value for the moment. For Co^{3+} to be in an LS state, the Co–O overlap integral should be large. The observed increase in Co–O bond length with Sr doping indicates, on the other hand, a low value for the overlap. The unit cell volume also increases with the concentration of the dopant (Sr), which has a larger ionic radius and then the Co^{3+} (HS) ion with a larger

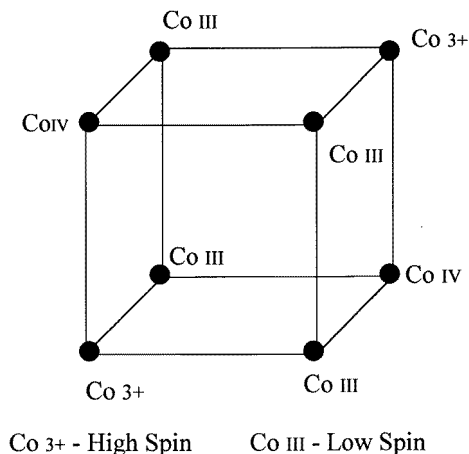


Figure 4. The magnetic unit cell of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$: $x = 0.25$.

orbital spread will be preferred. Similarly the Co–O overlap will be more for 4+ ions than 3+ ions, which, in turn, will squeeze the Co–O bond length, resulting in making the crystal field effect on Co^{4+} more dominant. This will make the LS state of Co^{4+} energetically favourable. The possibility of case 4 is thus ruled out. The system will then have Co^{4+} in the LS state and a mixed low- and high-spin configuration for the Co^{3+} ions as given in case 5. Assuming that the lattice is divided into an La rich region with Co^{3+} ions in the LS state and Sr rich regions with Co^{3+} ions in an HS state, the magnetic structure factor has been calculated and is in agreement with the observed values.

4. Summary

In this work the chemical and magnetic structure aspects of the series $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ are studied by powder neutron diffraction. Ferromagnetic order is confirmed by the observation of a magnetic peak below the Curie temperature for compounds with $x \geq 0.2$. The effective moments of the Co ions obtained have values close to those observed by other macroscopic techniques. The results are explained by considering various spin configurations. We have not seen any antiferromagnetic superlattice lines in the diffraction patterns. This suggests that the antiferromagnetic contributions if present at all is very weak compared to the double-exchange $\text{Co}^{4+}\text{--O--Co}^{3+}$ mechanism responsible for the ferromagnetic ordering in this system.

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