Neutron diffraction study of quasi-one-dimensional spin-chain compounds $Ca_3Co_{2-x}Fe_xO_6$

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Abstract. We report the results of the DC magnetization, neutron powder diffraction and neutron depolarization studies on the spin-chain compounds $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0$, 0.1, 0.2 and 0.4). Rietveld refinement of neutron powder diffraction patterns at room temperature confirms the single-phase formation for all the compounds in rhombohedral structure with space group $R\bar{3}c$. Rietveld refinement also confirms that Fe was doped at the trigonal prism site, 6a (0, 0, 1/4) of Co. The high temperature magnetic susceptibility obeys the Curie–Weiss law; the value of the paramagnetic Curie temperature (θ_p) decreases as the concentration of iron increases and it becomes negative for $x = 0.4$. No extra Bragg peak as well as no observable enhancement in the intensity of the fundamental (nuclear) Bragg peaks has been observed in the neutron diffraction patterns down to 30 K. No depolarization of neutron beam has been observed down to 3 K confirming the absence of ferro- or ferrimagnetic-like correlation.

Keywords. Spin-chain oxides; neutron diffraction.

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1. Introduction

A_3MXO_6-type quasi-one-dimensional spin-chain compounds [1–3], crystallizing in the K_4CdCl_6-type rhombohedral structure, have attracted much interest because of their peculiar magnetic properties. The crystal structure of these compounds consists of chains of alternating face sharing XO_6 octahedara and MO_6 trigonal prism running along the crystallographic c-axis. These chains are arranged on a triangular lattice and each chain is surrounded by six chains. The ferromagnetic intrachain and antiferromagnetic interchain interactions combined with a triangular-lattice arrangement of spin chains give rise to the geometrical spin frustration in these compounds. For example, $Ca_3Co_2O_6$, crystallizing in the rhombohedral K_4CdCl_6 structure (space group $R\bar{3}c$), contains the linear spin chains of face-sharing CoO_6 octahedara and CoO_6 trigonal prism running along the crystallographic c-axis. The chains, separated by Ca^{2+} ions, form a triangular lattice in the ab-plane. Due to different crystalline electric field, the Co^{3+} ions in this compound are in different spin states [2–4], the high spin ($S = 2$) and the low spin ($S = 0$) at trigonal prism

and octahedra sites, respectively. Here, we report the result of the neutron powder diffraction experiments for the compounds $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0$, 0.1, 0.2 and 0.4) in the temperature range from 30 to 297 K. The results of the neutron depolarization study are also presented.

2. Experimental

Polycrystalline samples of $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0$, 0.1, 0.2 and 0.4) were prepared by a conventional solid state reaction method. The stoichiometric mixture of CaO, Co_3O_4 and Fe_2O_3 was calcined at 800°C for 24 h. After thorough grinding of the calcined powder, the powder was pressed in the form of a bar under 2 ton/cm^2 and then heated for 48 h with a few intermediate grindings.

Neutron powder diffraction experiments were performed at Dhruva research reactor, Trombay using a five linear position sensitive detector (PSD) based powder diffractometer ($\lambda = 1.249$ Å) in the angular range $10° < 2\theta < 90°$ (covering a Q-range of 0.53 to 9.398 Å^{-1}). The diffraction data were analysed using the FULLPROF program. Neutron depolarization measurements in the temperature range 3–297 K were carried out using a polarization analysis spectrometer at Dhruva, Trombay with Cu_2MnAl (1 1 1) as a polarizer and Cu_2Fe (2 0 0) as an analyzer.

The DC magnetization measurements were carried out using a commercial (Oxford Instruments) vibrating sample magnetometer. For zero-field-cooled (ZFC) magnetization measurements, the samples were first cooled from room temperature down to 2 K in zero field. After applying a magnetic field of 1 kOe at 2 K, the magnetization was measured in the warming cycle with the field on, whereas, for field-cooled (FC) magnetization measurements, the samples were cooled down to 2 K in the same field (1 kOe) and FC magnetization was measured in the warming cycle under the same field.

3. Results and discussion

Figure 1 depicts the neutron powder diffraction patterns for the compounds $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0$, 0.4) at 297 K. Reitveld refinement of the room temperature neutron powder diffraction patterns confirms the single phase formation of these compounds in the rhombohedral structure (space group R$\bar{3}$c). Rietveld refinement also confirms that Fe is doped at trigonal prism site, 6a (0, 0, 1/4) of Co. The refined atomic positions and thermal parameters are given in table 1. The distance between the magnetic ions along the chain is ~2.59 Å which is half of the interchain distance (~5.52 Å) for $Ca_3Co_2O_6$. No significant change in the lattice parameters (only slight increase in lattice constant a), unit cell volume, bond angles and bond lengths has been observed by Fe doping.

As shown in figure 2, the high temperature magnetic susceptibility for all compositions obeys the Curie–Weiss law [$\chi_{mol} = C_{mol}/(T - \theta_p)$]. Here C_{mol} and θ_p are the molar Curie constant and the paramagnetic Curie temperature, respectively. The value of θ_p decreases as the concentration of iron increases; reaching 7.5 K for $x = 0.2$ against 27.9 K for $x = 0$ and it becomes negative (-1.6 K) for $x = 0.4$. The
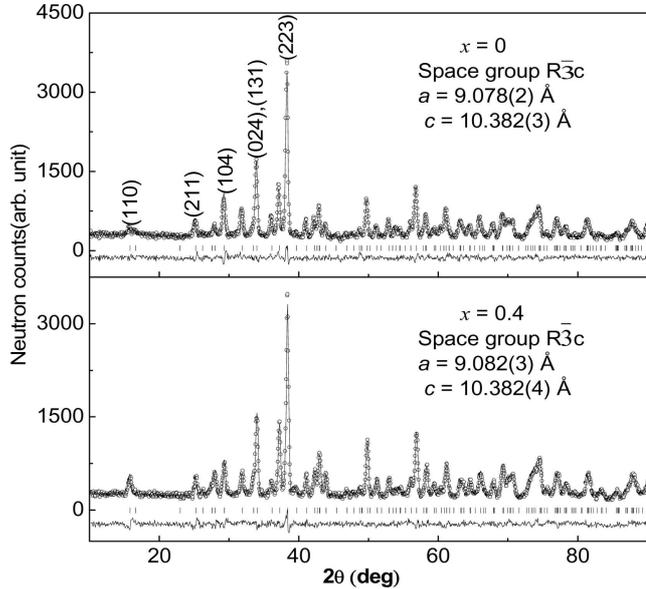
Figure 1. Observed (open circles) and calculated (solid lines) neutron diffraction patterns for $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0$, 0.4) at 297 K. Solid line at the bottom of each panel shows the difference between the observed and the calculated patterns. The $(h\,k\,l)$ values corresponding to strong Bragg peaks are also listed.

Table 1. Atomic positions and thermal parameters for $Ca_3Co_{2-x}Fe_xO_6$ samples.

x	Atom	Site	x	y	z	B_{iso}
0	Ca	18e	0.3698(2)	0	1/4	0.39(4)
	Co1	6b	0	0	0	0.37(8)
	Co2	6a	0	0	1/4	0.48(9)
	O	36f	0.1774(4)	0.0257(5)	0.1145(3)	0.53(2)
0.4	Ca	18e	0.3692(2)	0	1/4	0.55(4)
	Co1	6b	0	0	0	0.39(9)
	Co2	6a	0	0	1/4	0.54(7)
	Fe	6a	0	0	1/4	0.49(7)
	O	36f	0.1759(3)	0.0235(3)	0.1139(2)	0.85(4)

negative value of θ_p for $x = 0.4$ compound indicates the presence of a dominant antiferromagnetic interaction for this compound. Figure 3 shows the temperature dependence of the observed neutron powder diffraction patterns for the $x = 0$ and $x = 0.4$ compounds at 30, 50 and 100 K. No extra Bragg peak as well as no observable enhancement in the intensity of the fundamental (nuclear) Bragg peaks has been found down to 30 K. The same behaviour has been observed for all other compounds. Neutron depolarization measurements were carried out to investigate the
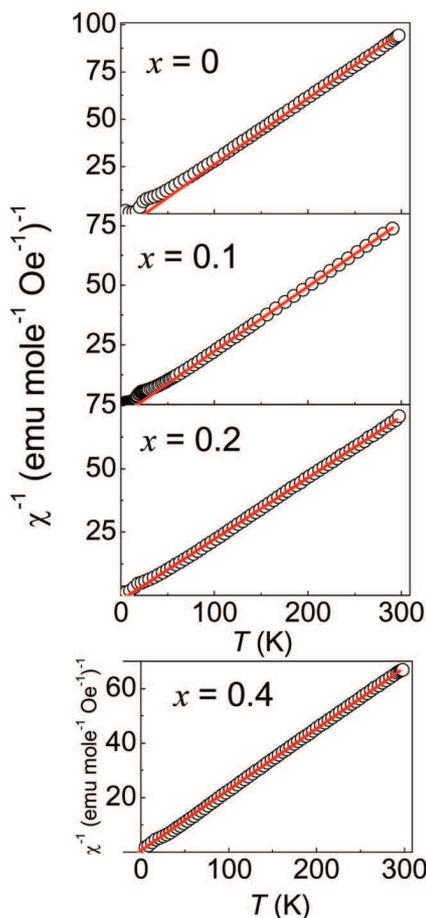
Figure 2. χ^{-1} vs. T for $Ca_3Co_{2-x}Fe_xO_6$.

existence of any ferromagnetic-like domains. However, no depolarization of neutron beam has been observed down to 3 K for all the samples confirming the absence of ferro- or ferrimagnetic-like correlation down to 3 K for these compounds.

4. Summary and conclusions

We have prepared single phase polycrystalline samples of quasi-one-dimensional spin-chain compounds $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0$, 0.1, 0.2 and 0.4). The Rietveld refinement of the neutron diffraction patterns for each of these compositions confirms the single phase formation of these compounds in the rhombohedral structure (space group R$\bar{3}$c). Refinement of the neutron diffraction patterns also confirmed that Fe was doped at the trigonal prism site, 6a (0, 0, 1/4) of Co. No significant change in the lattice parameters (only slight increase in lattice constant a), unit cell
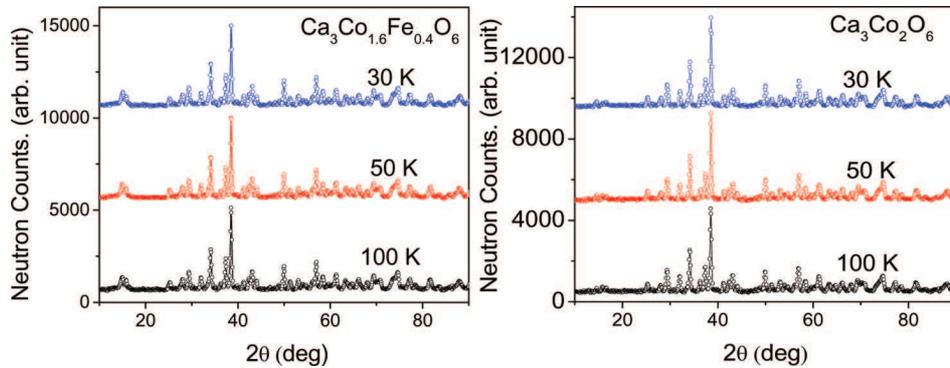
Figure 3. Neutron diffraction patterns for $Ca_3Co_2O_6$ and $Ca_3Co_{1.6}Fe_{0.4}O_6$ at 30, 50 and 100 K using a neutron wavelength of 1.249 Å.

volume, bond angles and bond lengths has been observed by Fe doping. The high temperature magnetic susceptibility obeys the Curie–Weiss law, the value of θ_p decreases as the concentration of iron increases; reaching 7.5 K for $x = 0.2$ against 27.9 K for $x = 0$ and it becomes negative (-1.6 K) for $x = 0.4$. In the neutron diffraction patterns, no extra Bragg peak as well as no observable enhancement in the intensity of the fundamental (nuclear) Bragg peaks has been found down to 30 K for these compounds. No depolarization of neutron beam has been observed down to 3 K confirming the absence of ferro or ferrimagnetic-like correlation. Low temperature (below 30 K) neutron powder diffraction experiments using long wavelength neutrons are required to further investigate the nature of magnetic interaction at low temperatures in these compounds.

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