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Low-temperature neutron diffraction study of $La_{0.95}Nd_{0.05}CrO_3$

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Abstract. We have synthesized polycrystalline $La_{0.95}Nd_{0.05}CrO_3$ sample by doping the La-site of $LaCrO_3$ with Nd and its magnetic properties have been studied using DC magnetization and neutron diffraction techniques. DC magnetization study shows a paramagnetic to a weak ferromagnetic-like transition at ∼295 K followed by signatures of a spin reorientation phenomenon at 233 and 166 K and, finally a transition to an antiferromagnetic-like phase at ∼21 K. Low-temperature neutron diffraction measurements confirm a weak ferrimagnetic ordering of Cr^{3+} moments at all temperatures below 295 K.

Keywords. Magnetization; neutron diffraction.

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1. Introduction

Studies of Sr-doped $LaCrO_3$ perovskites have been a subject of great interest [1–3]. This is due to the fact that the Sr-doped perovskites have high electrical conductivity at high temperatures and hence these materials can be used as an electrode material or interconnector for fuel cells, heating elements for high temperature furnaces, etc. Magnetic properties of these Sr-doped perovskites have recently been studied at low temperatures [4]. However, there are no reports on the magnetic properties of Nd-doped $LaCrO_3$ at low temperatures. Here we report the results of DC magnetization and neutron diffraction studies of the polycrystalline $La_{0.95}Nd_{0.05}CrO_3$ compound.

2. Experimental

This 5% Nd^{3+}-substituted $LaCrO_3$ sample was synthesized by the solid state reaction route, namely starting with well heated powders of La_2O_3, Cr_2O_3 and Nd_2O_3 in their appropriate molar ratios. The powders were mixed and ground for 1 h each in an agate mortar pestle and then pelletized and subsequently heated to 1423 K for 48 h in a furnace. The procedure was repeated three times. The color of sample was green, which indicates that there was no change in oxidation state of chromium. X-ray diffraction patterns recorded at room temperature revealed that the prepared sample was in single phase and well crystalline.

DC magnetization measurements were carried out using a commercial vibrating sample magnetometer (Oxford Instruments). Magnetization measurements were carried out for temperatures in the range 310 to 5 K in the cooling cycle with an applied field of 500 Oe. Hysteresis measurements were carried out at temperatures below 310 K with a maximum field of 5 T after cooling the sample from 310 K to the temperature of measurement under zero-field.

Neutron diffraction patterns were recorded using the newly commissioned multi-position sensitive-detector based powder diffractometer at the beam port T1013 in Dhruva reactor, Trombay. Wavelength of neutrons employed was 1.249 Å. The sample was packed in a vanadium can of height 60 mm and diameter 6 mm. The angular range covered was from $2\theta = 10^\circ$ to 130°. For low-temperature diffraction experiments, a closed cycle refrigerator (CCR) was used. The lowest achievable temperature was 12 K with a stability of better than 0.1 K.

3. Results and discussion

Figure 1 shows the temperature dependence of DC magnetization. It indicates a transition from a paramagnetic to a weakly ferromagnetic-type ordering at ~295 K. The transition temperature (295 K) is defined as the point of steepest slope in the M vs. T curve. There are signatures of spin reorientation at ~233 K and ~166 K (inset in figure 1). Thereafter there is an antiferromagnetic-like transition at ~21 K with a sharp drop of magnetization below this temperature.

Figure 2 depicts the hysteresis loops at various temperatures below 295 K. The behaviour of magnetic field dependence of magnetization is typical of an antiferromagnetic-type. However, a small hysteresis is found at all temperatures below ~295 K which indicates the presence of a ferromagnetic component. The observed moment value at 5 K for 5 T field is 1.078 e.m.u./g (0.046 μ_B per formula unit). There was a cross over in these hysteresis loops indicating the presence of

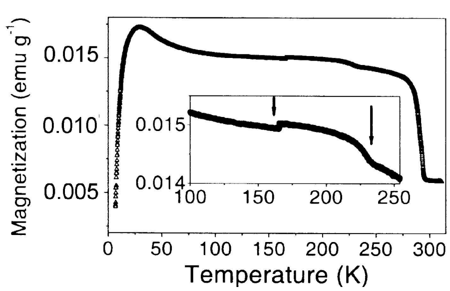

Figure 1. Temperature dependence of DC magnetization. Arrows in the inset indicate the spin reorientation temperatures.

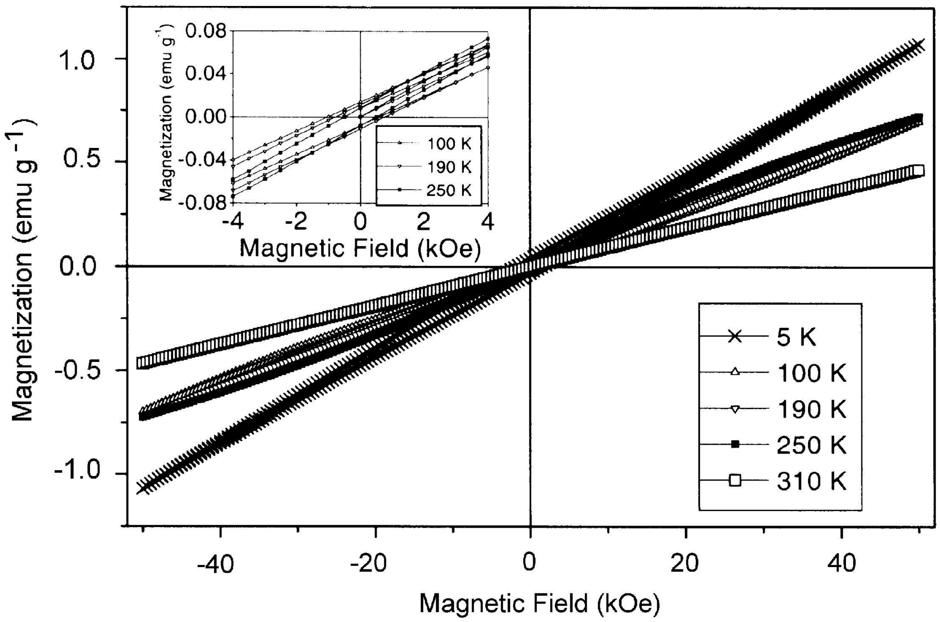

Figure 2. Magnetization over all four quadrants of applied magnetic field.

a magnetocrystalline anisotropy. An ordering of Nd moment in $NdCrO_3$ was reported in an earlier neutron diffraction study at 4.2 K [5]. Theoretical calculation of collinear antiparallel alignment of Nd^{3+} and Cr^{3+} moments leads to a net moment per formula unit of 2.84 μ_B which is much larger than the value obtained from the magnetization studies. It therefore, indicates that the present system does not have such a collinear antiferromagnetic-like structure.

Figure 3 shows the observed and Rietveld refined neutron powder diffraction patterns at 12, 250, and 300 K for the compound. The Rietveld refinement was carried out using the WINPLOTR suite of programs [6]. Various structural parameters are shown in table 1. Refinement shows an orthorhombic perovskite structure (space group Pbnm) at all temperatures. The room temperature diffraction pattern could be fitted with only nuclear intensities confirming the paramagnetic nature of the sample at this temperature. Rietveld refinement of diffraction data recorded at 12 and 250 K showed ferrimagnetic ordering of moments on the two sets of magnetically inequivalent Cr sites [First set: (1/2, 0, 0) and (0, 1/2, 1/2); second set: (1/2, 0, 1/2) and (0, 1/2, 0)]. At 12 K, an ordered moment per ion of Cr of magnitude 3.8 ($\pm$0.1) μ_B and 2.8 ($\pm$0.1) μ_B, has been obtained along the crystallographic c-axis. The magnetic R-factor was 13.5%. At 250 K, the observed moments are 2.3 ($\pm$0.1) μ_B and 2.2 ($\pm$0.1) μ_B along the crystallographic c-axes for the two Cr sites respectively with the magnetic R-factor of 11.2%. The net moments at 250 and 12 K are 0.06 and 1.07 μ_B, respectively. No ordering of Nd site was found in our neutron diffraction experiments.

Table 1. Structural parameters obtained from neutron diffraction study.

	12 K	250 K	300 K
La/Nd			
x	−0.0036(8)	−0.0033(10)	−0.0039(12)
y	0.0215(4)	0.0200(6)	0.0190(7)
z	0.25	0.25	0.25
B (Å^2)	0.01	0.08(2)	0.22(3)
n	0.475/0.025	0.475/0.025	0.475/0.025
Cr			
x	0.5	0.5	0.5
y	0	0	0
z	0	0	0
B (Å^2)	0.01	0.05	0.1
n	0.5	0.5	0.5
O1			
x	0.0609(8)	0.0607(10)	0.0619(12)
y	0.4887(8)	0.4910(10)	0.4942(13)
z	0.25	0.25	0.25
B (Å^2)	0.08(6)	0.14(6)	0.33(8)
n	0.5	0.5	0.5
O2			
x	0.2750(5)	0.2751(6)	0.2753(7)
y	−0.2787(5)	−0.2761(6)	−0.2745(7)
z	−0.0366(3)	−0.0367(4)	−0.0373(5)
B (Å^2)	0.14(3)	0.23(5)	0.34(5)
n	1.0	1.0	1.0
a (Å)	5.5044(6)	5.5104(6)	5.5110(7)
b (Å)	5.4737(5)	5.4790(7)	5.4806(8)
c (Å)	7.7475(8)	7.7582(9)	7.7634(11)
V (Å^3)	233.43	234.23	234.48
R_{p} (%)	4.12	4.58	4.88
R_{wp} (%)	5.22	5.81	6.14
R_{e} (%)	4.61	4.60	4.76
R_{Bragg} (%)	5.26	4.45	5.66
R_{mag} (%)	13.5	11.2	–
χ^2	1.28	1.60	1.67
$\mu\mathrm{Cr}_1$ (μ_{B})	3.86(14)	2.32(10)	–
$\mu\mathrm{Cr}_2$ (μ_{B})	2.79(14)	2.26(10)	–

4. Summary and conclusion

We have studied structural and magnetic properties of polycrystalline $La_{0.95}Nd_{0.05}CrO_3$ sample by carrying out DC magnetization and neutron diffraction measurements. The crystal structure of 5% Nd-doped $LaCrO_3$ remains orthorhombic from 300 to 12 K as for the parent system. The parent system has been reported

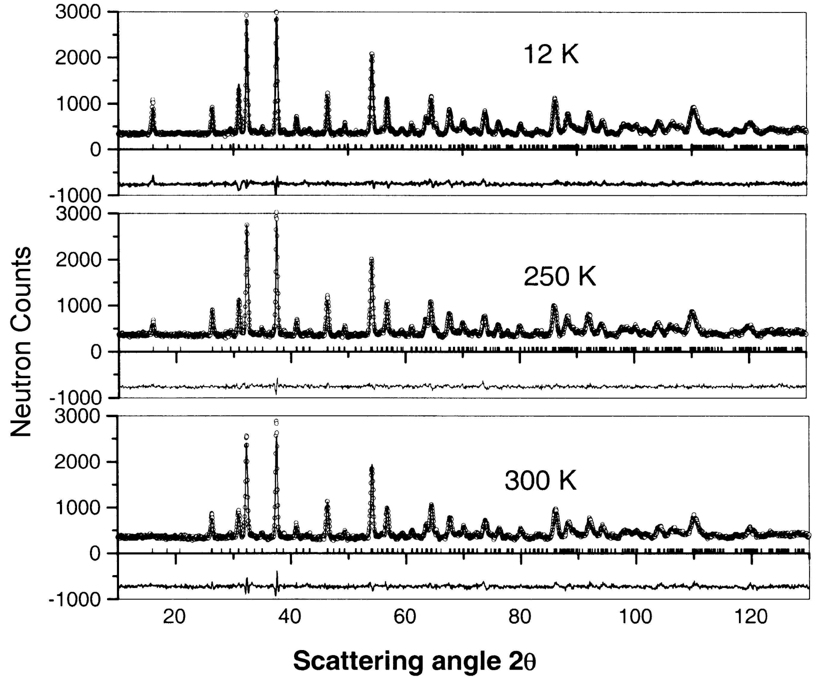

Figure 3. Observed (open circles) and calculated (solid line) neutron diffraction patterns at three temperatures. The difference patterns are also shown. The vertical bars indicate allowed Bragg peak positions of each curve by solid bars.

to be weakly ferromagnetic with a Curie temperature of ∼271 K. However, with the 5 at% Nd doping, the ordering temperature is found to increase to 295 K. DC magnetization study shows a paramagnetic to a weak ferrimagnetic-like transition at ∼295 K followed by signatures of a spin reorientation phenomenon at 233 and 166 K and, finally a transition to an antiferromagnetic-like phase at ∼21 K. Low-temperature neutron diffraction measurements confirm a net weak ferrimagnetic ordering of Cr^{3+} moments along the crystallographic *c*-axis at all temperatures below 295 K. Nd site does not show any magnetic ordering down to 12 K. Understanding of spin reorientation phenomena observed at 233 and 166 K for the Nd-doped sample needs further investigations.

References

[1] C P Khattak and D E Cox, *Mater. Res. Bull.* **12**, 463 (1977)
[2] D B Meadowcroft, *Brit. J. Appl. Phys. (J. Phys.)* **D2**, 1225 (1969)
[3] D P Karim and A T Aldred, *Phys. Rev.* **B20**, 2255 (1979)
[4] K Tezuka and Y Hinatsu, A Nakamura, T Inami, Y Shimjo and Y Morii, *J. Solid State Chem.* **141**, 404 (1998)
[5] N Shamir, H Shaked and S Shtrikman, *Phys. Rev.* **B24**, 6642 (1981)
[6] Juan Rodriguez-Carvajal, *Physica* **B192**, 55 (1993).