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Neutron diffraction studies of magnetic ordering in Ni-doped $LaCoO_3$

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ABSTRACT

Research in rare earth cobaltite has recently been intensified due to its fascinating magnetic properties. $LaCoO_3$, an important cobaltite, exhibits two prominent susceptibility features at ~90 K and 500 K in low field measurement. The magnetic behavior below 100 K is predominantly antiferromagnetic (AFM), but absence of pure AFM ordering and emergence of ferromagnetic coupling on further decreasing temperature made situation more intricate. The present work of studying the effect of Ni substitution at Co site in polycrystalline $LaCo_{1-x}Ni_xO_3$ $(0 \le x \le 0.3)$ is motivated by the interesting changes in magnetic and electronic properties. For lucid understanding, temperature dependent neutron diffraction (ND) study was carried out. ND patterns fitted with rhombohedral structure in perovskite form with R-3c space group, elucidated information on phase purity. Further temperature dependent cell parameter, Co–O bond-length and Co–O–Co bond angle were calculated for the series of Ni doped $LaCoO_3$. The results are explained in terms of decrease in the crystal field energy which led to the transition of cobalt from low Spin (LS) state to intermediate spin state (IS).

1. Introduction

Strongly correlated electron systems have generated upsurge in both theoretical as well as experimental research due to the most intriguing and versatile properties such as superconductivity, colossal magneto resistance (CMR), multiferroicity etc; exhibited by this class of compounds [1,2]. Rare earth cobaltite compounds belong to one such class of compounds among strongly correlated electron systems and are being explored for fascinating structural, electrical and magnetic properties [3–5] observed in perovskite type $LaCoO_3$ and similar oxides.

$LaCoO_3$ is an important cobaltite among the rare earth cobaltite which displays exciting properties in the range from low temperature to 500 K. In the low temperature range (< 100 K) $LaCoO_3$ is nonmagnetic semiconductor, and 100 to 500 K it behaves as paramagnetic semiconductor and above 500 K reported as paramagnetic metal [5–9]. Such exciting behavior has been mainly limited to magnetic susceptibility study. Perovskite $LaCoO_3$ is found to be a nonmagnetic insulator in the ground state [10]. Several attempts have been made to understand this phenomenon with the help of numerous models and theories. First of all Goodenough proponed the idea of the existence of two Co spin states: low temperature low spin (LS, $t_{2g}^{6}e^{\circ}{}_{g}$,S=0) and high spin (HS, $t_{2g}^{4}e_{g}^{2}$, S=2). At the first transition, HS Co ions and LS Co ions will coexist equally. Further increase in the temperature would result in the formation of superstructure due to HS and LS Co ions. According to this proposition, second high-temperature anomaly was defined as an order-disorder transition where the superstructure would be decimated due to mobility of e_g electrons. Due to non-observation of such superstructure in the subsequent detailed neutron diffraction studies, the long-range ordering was dropped from the theory [11–14]. Broadly this behavior is explained either in terms of low temperature low spin (LS) ($t_{2g}^{6}e^{\circ}{}_{g,}$ S=0) ground state phase moving to high temperature, high spin (HS) ($t_{2g}^{4}e_{g,}^{2}$ S=2) phase via mixed spin (MS) state where different cobalt ions carrying high and low spin states coexists or in terms of existence of intermediate spins (IS) ($t_{2g}^{5}e_{g,}^{1}$ S=1) between low spin (LS) ground and high spin (HS) state [15,16].

Such unique magnetism which involves thermally driven spin state transition offer a platform to understand the effect on physics upon doping at either of La or Co site. Several reports of doping various elements at La or Co site are available, such as very light Sr doping (x=0.002) has resulted in disappearing of LS to IS transition [17]. Upon increasing Sr doping spin-glass characteristics sets in [18]. Ni doping at Co site has also been investigated for the origin of spin state transition with alloying at transition metal site. The research interests on $LaCo_{1-x}Ni_xO_3$ have been further augmented by presence of glassy ferromagnetism, magneto-resistance and metal insulator transition (MIT) [19,20].

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In the recent past some authors from our research group have carried out detailed study on the effect of Ni substitution on electrical properties, electronics structure, and magnetic properties of perovskite $LaCoO_3$ by employing various experimental viz. x-ray absorption spectroscopy (XAS), resistivity, magnetization etc. [21,22]. Based on these results we could elucidate that Homovalent +3 state and spin state transition of Co^{3+} have been confirmed. The possibility of charge disproportion in doped compounds was also ruled out [21,22]. Ni substitution has been observed to give rise to many interesting features viz. disappearance of thermally driven spin state transitions, magnetic frustration and a different magnetic state at low temperature [21,22].

Neutron diffraction is a widely accepted tool for seeing the structural dynamics at microscopic level. It can also easily sense the long range ordering if any, originated in the compound. In this report we have carried out the detailed temperature dependent neutron diffraction experiments on bulk $LaCo_{1-x}Ni_xO_3$ ($x=0$, 0.1, 0.2, 0.3) between 2.8 and 300 K. In addition to looking for any possible signature of long range ordering, we have focused on determining the microscopic parameters such as Co–O bond length and O–Co–O bond angles in addition to the respective cell parameters as a function of temperature. This study is an attempt to further elucidate and understand how doping at Co site by Ni ion affects the microstructure and these variations are correlated with the previously studied phenomenon using XAS, magnetization etc. It is clearly inferred from the results that systematic increase in the Co–O upon substituting Ni at Co site is consistent with the XAS study, magnetization, AC susceptibility and resistivity measurement reported earlier [22]. These results are further understood in terms of stabilization of intermediate spin state (IS) of Co^{3+}.

2. Experimental procedure

The Ni doped $LaCoO_3$ samples ($LaCo_{1-x}Ni_xO_3$, $x=0.0$, 0.1, 0.2, 0.3) were prepared in polycrystalline form using the solid state reaction method. The high purity (>99.9%) ingredients La_2O_3, Co_2O_3 and NiO were taken in stoichiometric ratio and used in the sample preparation. The details of the sample preparation are discussed elsewhere [21,22]. The other higher concentrations $x=0.4$, 0.5 described in these references could not be prepared in the single phase considering the higher quantity requisite for powder neutron diffraction. Peaks of un-reacted Co_2O_3 were observed as secondary phase in higher concentrations $x=0.4$, 0.5 and hence were not considered for neutron diffraction studies. The phase purity of the prepared samples, $x=0$, 0.1, 0.2, and 0.3, was first confirmed with XRD analysis prior to detailed study. Temperature dependent Neutron diffraction experiments were performed at a wavelength of 1.48 Å, using the position sensitive detector (PSD) based focusing crystal diffractometer (FCD) installed by UGC-DAE CSR Mumbai Center at National Beam Facility for Neutron Research (NFNBR), Dhruva Reactor, BARC, India, [23]. Neutron diffraction (ND) patterns were recorded at various temperatures such as 2.8, 10, 25, 50, 75, 100, 150, 200, 250 and 300 K in the warming cycle. For low temperature measurements, vanadium *cans* filled with the powder sample was loaded in a commercial Closed Cycle Refrigerator (CCR) based cryostat [23]. The sample was kept at constant temperature for sufficient time to achieve the equilibrium temperature condition and then the diffraction pattern was recorded at that temperature. For the room temperature (300 K) ND patterns, sample placed in vanadium *cans* were directly exposed to neutron beam. The obtained neutron diffraction data was analyzed using Rietveld method and the refinement of both crystal and magnetic structures, was carried out using the FullProf program, and BondStr in FullProf suite was further used determining the various bond length and angle [24].

3. Results and discussion

For clear understanding of structural and magnetic behavior of the samples in this series of compounds, detailed temperature dependent neutron diffraction (ND) study was carried out ($\lambda=1.48$ Å). Fig. 1 shows the Rietveld fitted pattern of all the samples at room temperature. ND patterns fitted with R-3c space group (space group no. 167) revealed the phase purity and also pointed out that structure remains intact up to the Ni-doping of $x=0.3$, at Co site in the ambient conditions. The cell parameters a and c were found to be 5.4445 Å and 13.0933 Å for pure $LaCoO_3$ at room temperature in the hexagonal symmetry which is close to the values reported in the literature [6,26]. Upon looking in Figs. 1 and 3 we also observed that the relative intensity corresponding to the peaks indexed as 202 and 024 at $2\theta=39.15$ and 45.77 varies upon doping at Co site. The variations in the relative intensities of these peaks are ascribed to the variation in the cell parameters, which are shown in Fig. 4(a) and (b).

In the crystal structure of $LaCo_{1-x}Ni_xO_3$, $x=0$, 0.1, 0.2, 0.3, Wyckoff position for La, Co and O atoms were taken at 6a (0, 0, 0.2500), 6b (0, 0, 0) and 18e (p, 0, 0.2500) site. It is clear that except x co-ordinate of Oxygen (denoted as p) at 18e all the positions corresponding to all three atoms are special positions and thus cannot be refined. For $LaCoO_3$, in the rhombohedral crystal symmetry the value of x co-ordinate of O atom 'p' is reported to be 0.54975 [7]. While analyzing the temperature dependent neutron diffraction data it was observed that no additional peak or modification in the spectrum was seen which could be attributed to lowering of the symmetry. This points out that up to $x=0.3$ the crystal symmetry does not alter from R-3c, as the structure was fitted by only one oxygen position. It further signifies that even after doping Ni at Co site, the corner sharing CoO_6 octahedra along all three crystallographic axes does not alter. It was further observed that in addition to the variation in the cell parameter corresponding to various samples at different temperature, the x co-ordinate of oxygen atom (p) at 18e was used for the variation but the value of p was not found to change significantly, thus ruling out the scope of major distortion in the Co–O_6 octahedra. The goodness of fitting parameters for various fitted patterns was within the satisfactory limit. The schematic diagram of $LaCo_{1-x}Ni_xO_3$ unit cell is shown in Fig. 2 which shows various atomic positions in the compound. The alternating rotating corner sharing CoO_6 octahedra along the principle axes is also shown in the crystal structure.

The temperature dependent magnetization and isothermal magnetization hysteresis at various constant temperatures on these samples were studied in detail, and have been previously described elsewhere [21]. The magnetization study is clearly in accordance with previous reports and further indicates that in pure $LaCoO_3$, Co ion is in mixture of LS state and excited state (IS/HS), and at low temperature it undergoes spin state transition. But for $0 \le x \le 0.3$, magnetization increases with decreasing temperature and thermally driven spin state transition are found to disappear, indicating stabilization of excited spin state at even low temperature [21].

The neutron diffraction pattern at 2.8 K for all four samples is shown in Fig. 3. We can clearly observe that within the instrumental resolution of the diffractometer there is neither any signature of structural transition nor appearance of any of superlattice peaks or increment in the pre-existing peak, which indicates that AFM/FM ordering is not set down to the lowest temperature, 2.8 K at the wavelength 1.48 Å, in all the samples for $x=0$, 0.1, 0.2 and 0.3. Similar result of non-appearance of any