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Properties of Nd Doped $La_{0.5}Ba_{0.5}CoO_3$ Pervoskite

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***Abstract*—The properties of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ ($0 \leq x \leq 0.425$) has been investigated. All samples show a cubic structure at room temperature. The Curie temperature T_C and the estimated molecular magnetic moment of the samples at 5K decrease monotonically with increasing Nd-doping level. The results are discussed in terms of the double exchange (DE) interaction associated with the variation of Co-O bond length and Co-O bond angle due to the substitution of smaller Nd^{3+} ions for larger La^{3+} ions. At low temperature, the ferromagnetic (FM) interaction is greatly suppressed by the Nd-doping, illustrating a special noncollinear spin structure. The spin state of Co ions derived from the Curie constant is not affected by the Nd doping and remains an intermediate spin state. The electric resistance measurements show that the conduction of the materials belongs to the thermal activation process below T_C, while it belongs to the variable range hopping conduction of polarons over T_C except for parent $La_{0.5}Ba_{0.5}CoO_3$.**

***Keywords*—$La_{0.5-x}Nd_xBa_{0.5}CoO_3$; immediate spin state; noncollinear spin structure; electron transport**

I. INTRODUCTION

In the past few years, the intensive research on perovskite cobaltites has revealed unusual magnetic and transport properties [1–3]. The Co ions in an octahedral symmetry are found in a high (HS, S=2), intermediate (IS, S=1) or low spin state (LS, S=0) as the energies of the crystal-field split of the Co 3d states (E_{cf}) and the Hund's rule exchange energy (E_{ex}) are comparable. The $LaCoO_3$ has a charge transfer insulator type non-magnetic ground state with Co^{3+} ion in the LS state at low temperature. With increasing temperature, the spin state of Co ions thermally activates to an IS state or HS state developing magnetic moment above approximately 30K and exhibiting a paramagnetic-like behavior above 100 K [1,4].

In the hole doped cobaltites $La_{1-x}A_xCoO_3$ (A =alkaline earth metal: Ca, Sr or Ba)[4], the additional Co^{4+} ion increases the complexity of the system as it is susceptible to exist in several spin-state configurations as well. Among doped cobaltites, the system $La_{1-x}Sr_xCoO_3$ is the most extensively investigated[5,6]. Below x=0.2, a spin-glass- or a cluster-glass-like magnetic behavior has been noted due to coexistence of the spin-glass phase with percolating ferromagnetic clusters. However, for x>0.25, the system becomes metallic and shows a long-range ferromagnetic ordering. Similar metallic ferromagnetic state was observed in barium doped cobaltites with the barium content x >0.2 [7].

The nature of the ferromagnetic state in magnetic state in $La_{1-x}Ba_xCoO_3$ (LBCO) with Ba^{2+} having a larger ionic radius than Sr^{2+} (ionic radii of La^{3+}= 1.216Å, Ba^{2+}=1.47 Å, Sr^{2+}= 1.31 Å) [8] is less studied. Substitution of the large ionic radius of Ba^{2+} for La^{3+} (a) enhances the local disorder due to larger size mismatch between the Ba^{2+} and La^{3+} ions, (b) reduces the rhombohedral distortion present in the undoped $LaCoO_3$ compound, and (c) strengthens the concentration of the Jahn–Teller (JT) which is assumed to be favored by the IS state[7]. In addition, LBCO does not show the occurrence of charge ordering with x close to 0.50 [10].

So far, much work has been reported on the ordered/disordered $La_{0.5}Ba_{0.5}CoO_3$ and its oxygen non-stoichiometry in $La_{0.5}Ba_{0.5}CoO_{3\pm\delta}$[8,11-13]. Rautama et al.[10] observe that the method of synthesis precursor reactivity and oxygen pressure play a crucial role for controlling the cationic order or disorder phenomena in the stoichiometric perovskites $La_{1-x}Ba_xCoO_3$. Troyanchuk and his coworkers[11] show that the decrease of the oxygen content leads to a transformation of the ferromagnetic structure into G-type antiferromagnetic one via an intermediate region of the compositions demonstrating a macroscopic phase separation into different structural and magnetic phases. Whereas, applied pressure can induce a gradual transition from the antiferromagnetic into a ferromagnetic state [12].

In this paper, a systematic study was made on the effect of Nd dopant content on structural, electrical and magnetic properties of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ perovskite oxides ($0 \leq x \leq 0.425$), with an aim to understand its magnetically ordered state and transport mechanism.

II. EXPERIMENTAL PROCEDURE

Polycrystalline samples with nominal composition of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ ($0 \leq x \leq 0.425$) were prepared by the standard solid state reaction. Stoichiometric amounts of La_2O_3, Nd_2O_3, Co_2O_3 and $BaCO_3$ were mixed, ground and pressed into pellets forms. And then the pellets were sintered at 1080ºC for 3 hours and furnace cooled in air. The crystal structures were examined by X-ray diffractometer using Cu Ka radiation at room temperature. The magnetic measurements were carried out with a quantum design superconducting quantum interference device (SQUID) system. The resistance measurements were performed by using the standard four-probe method from 77K to 320K.

III. RESULTS AND DISCUSSION

Powder X-ray diffraction shows all the samples are single phase and crystallize in simple cubic structure. The lattice constant of the sample with x=0 is 3.894 Å, close to that of $La_{0.5}Ba_{0.5}CoO_3$ (3.8863 Å)[13]. When La^{3+} ion is partially substituted by smaller Nd^{3+} ion (Nd^{3+} has a radius of 1.115 Å[14]), the lattice constant decreases slightly with Nd dopant.

Figure I displays magnetization M as a function of temperature T for $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ with magnetic field up to 0.4 T. Consistent with previous report[8], the Curie temperature T_C of the undoped compound is 202K. The value of T_C for all samples is listed in Table I. We could see very clearly that T_C decreases monotonously with increasing Nd dopant. It is worth noting that there is a downward trend in M - T curves at low temperature for the doped samples. For the samples with x=0.375, 0.425, the paramagnetic (PM) – ferromagnetic (FM) transition is substituted by a peak, suggesting the Nd doping greatly suppresses the FM interaction in the system, which seems to be the transition for either the magnetic or the spin state. In order to understand the magnetic behavior at low temperature, we measured the magnetization versus applied field at 5K and 77K in the magnetic field of 5T and 1T, respectively. The molecular magnetic moment derived from the M - H curve at 5K of all samples is also listed in Table I. One can see that the molecular moment of the parent $La_{0.5}Ba_{0.5}CoO_3$ is 1.9 μ_B, similar to the other reports[9,12]. Meanwhile, the molecular moment of the other doped samples decreases monotonously with Nd dopant. We suggest that the decrease of T_C and the molecular moment should be attributed to the decrease in double exchange (DE) interaction due to the increase in Co-O bond length and the decrease in Co–O bond angle caused by the substitution of smaller Nd^{3+} ions for larger La^{3+} ions.

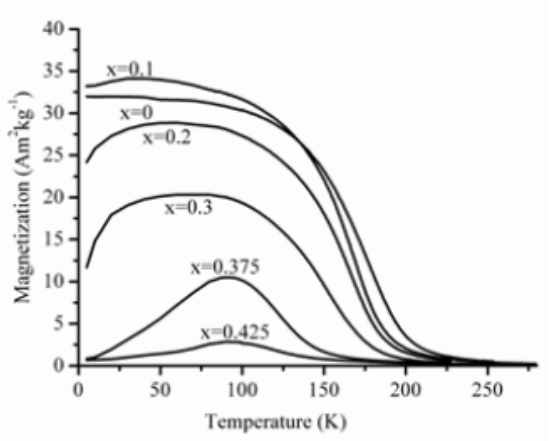

FIGURE I. DEPENDENCES OF MAGNETIZATION M FOR La0.5-XNdXBa0.5CoO3 ON TEMPERATURE T IN A MAGNETIC FIELD OF 0.4 T

TABLE I. Tc IS THE CURIE TEMPERATURE, u_{mole} IS RELATED TO THE MOLECULAR MOMENT, u_{eff} DENOTES THE EXPERIMENTAL EFFECTIVE MAGNETIC MOMENT OF CO^{3+}/CO^{4+}, AND Θ IS THE WEISS TEMPERATURE

Sample	x=0	x=0.1	x=0.2	x=0.3	x=0.375	x=0.425
Tc (K)	202	195	186	170	128	123
u_{mole} (μ_B)	1.90	1.87	1.65	1.09	0.57	0.51
u_{eff} (μ_B)	3.55	3.33	3.08	3.17	3.23	3.33
Θ (K)	184	173	169	160	125	116

The hysteretic loop for the sample with x=0.375 at 77K is shown in Figure II. One can see from Figure II that the coercivity of the sample is very small and the high field part of the loop raises linearly with increasing magnetic field. The special magnetic state is probably ascribed to the noncollinear spin structure[8], arising from the competition between disordered crystal field caused by random distribution of the 4f orbits of Nd^{3+} ions and the exchange interaction of Co3d electrons.

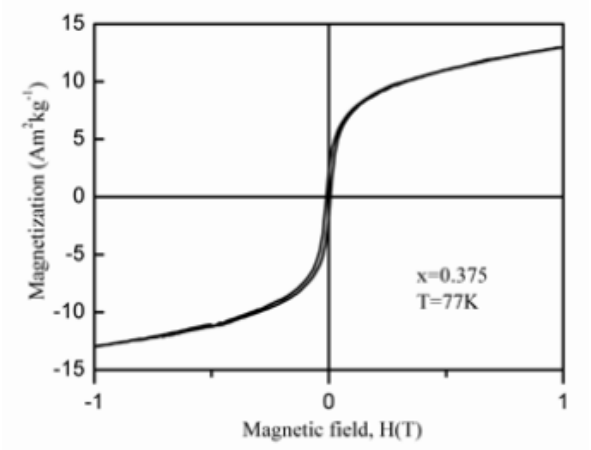

FIGURE II. HYSTERETIC LOOP OF La0.125Nd0.375Ba0.5CoO3 AT 77 K

For the sake of comprehend whether the nature of the peak on M-T curves for the $x \geq 0.375$ samples is the magnetic transition or the spin transition, We fitted the inverse magnetic susceptibility χ^{-1} with T above T_C to determine the spin state of the Co ions in the high temperature paramagnetic state. The effective magnetic moment u_{eff} of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ deduced from the Curie-Weiss equation can be obtain as 3.55, 3.52, 3.48, 3.12, 3.84, 3.51 u_B for the samples with x=0, 0.1, 0.2, 0.3, 0.375, and 0.425, respectively. On the hypothesis of simple spin configuration, the experimental effective magnetic moment of Co^{3+}/Co^{4+}can be calculated by[15]

$$u_{eff}(Co^{3+}/Co^{4+}) = \sqrt{(u_{eff}(La_{0.5-x}Nd_xBa_{0.5}CoO_3))^2 - x[u_{eff}(Nd^{3+})]^2} \quad (1)$$

The magnetic moment of Nd^{3+} ion is supposed to be 3.62 u_B (J=9/2, g=8/11). The experimental effective numbers and the Weiss temperature are shown in Table I, too. One can see clearly that the experimental u_{eff} of all the sample are approximate to the theoretical one (3.39 u_B), suggesting the intermediate spin state of Co ions. The similar result was reported in the $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ compound[16].

Temperature (T) dependence of resistivity (ρ) for the all samples were systematically studied in the temperature range of 77-135K and 225-300K. The resistivities of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ perovskite decrease exponentially with the increase in temperature in the range of 77-135 K, indicating that the samples have typical semiconductor behavior at low temperatures (seen in Figure III)[17].

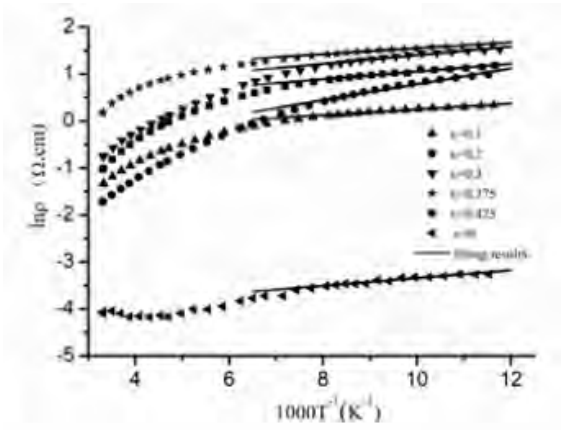

FIGURE III. DEPENDENCE OF LN (ρ) WITH T^{-1} FOR ALL SAMPLES. THE CIRCLES SHOW THE EXPERIMENTAL DATA AND THE SOLID LINE IS THE BEST LINEAR FIT

In order to certify the transport mechanisms of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$, we try to fit ρ -T the curves according to several possible models. It is observed that the resistivity of the doped samples could be fitted well by Mott's law for variable range hopping (VRH) model of polarons[18,19] except for that of the parent $La_{0.5}Ba_{0.5}CoO_3$. The measurement and fitting results are shown in Figure IV, respectively. For the sample with $x = 0$, the conduction belongs to the metal type beyond the Curie temperature.

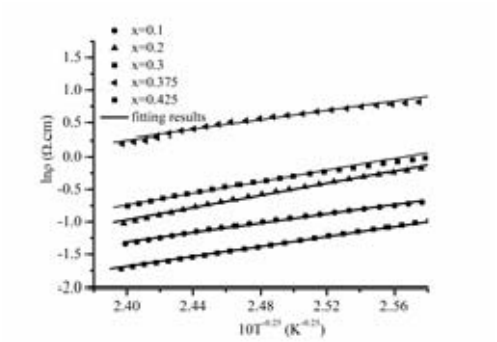

FIGURE IV. VARIATION OF Ln (ρ) WITH $T^{-0.25}$ FOR DOPED SAMPLES. THE CIRCLES SHOW THE EXPERIMENTAL DATA AND THE SOLID LINE IS THE BEST LINEAR FIT

IV. CONCLUSION

The properties of $La_{0.5-x}Nd_xBa_{0.5}CoO_3$ have been studied ($0 \leq x \leq 0.425$). The Curie temperature and the molecular magnetic moment of the compounds decrease monotonically with increasing Nd dopant demonstrating the size effect of rare-earth ions at A-site on the magnetic properties. At low temperature, the ferromagnetic interaction is greatly decreased by Nd doping, illustrating a special noncollinear spin structure. The spin state of Co ions derived from the Curie constant is in the intermediate spin state. The electric resistance results show that the conduction of the materials belongs to thermal activation process below T_C, while it belongs to the variable range hopping conduction of polarons over T_C except for parent $La_{0.5}Ba_{0.5}CoO_3$.

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