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Magnetic and crystal structure phase transitions in $R_{1-x}Ba_xCoO_{3-y}$ ($R = Nd, Gd$)

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Abstract. Perovskites of the $R_{1-x}Ba_xCoO_{3-y}$ type where R is Nd or Gd have been prepared and characterized. The substitution of Nd by Ba ions up to $x = 0.4$ leads to a nonhomogeneous ferromagnetic state appearance similar to that found for the $La_{1-x}Sr_xCoO_3$ system studied earlier. Structural refinement of $Nd_{0.5}Ba_{0.5}CoO_{3-y}$ reveals the chemical ordering of Nd and Ba ions. The magnetic properties of $Nd_{0.5}Ba_{0.5}CoO_{3-y}$ depend drastically on oxygen content. Reduced samples ($y > 0.2$) exhibit magnetic phase transitions at around $T_i \sim 200$ K and $T_C \approx 280$ K as well as a crystal structure transition at $T_M \approx 350$ K which leads to a drop in the electrical conductivity. The transitions at T_i and T_M are more pronounced in the $Gd_{1-x}Ba_xCoO_{3-y}$ series. The decrease of Ba content below $x = 0.5$ leads to decreasing T_i whereas the increase of Ba ions above $x = 0.5$ leads to a suppression of both spontaneous magnetization and phase transition at T_M . It is supposed that the transition at T_M results from the oxygen vacancy ordering whereas at T_i the antiferromagnetic state (low temperature phase) transforms into a weak ferromagnetic one with spontaneous magnetization around $0.2 \mu_B$ per cobalt ion.

1. Introduction

The discovery of the ‘colossal’ magnetoresistance (CMR) in the manganites with perovskite structure has stimulated the search for new compounds exhibiting large magnetic resistance. The magnetic and electrical properties of $La_{1-x}A_xCoO_3$ ($A = Ca, Sr, Ba$) perovskites and CMR materials such as $La_{1-x}A_xMnO_3$ ($A = Ca, Sr, Ba$) have some common features [1–5]. In both systems the substitution of La by divalent ions creates a metallic ferromagnetic state. The magnetic superexchange interactions taking place between $Co^{3+}-O-Co^{4+}$ are ferromagnetic. However, ferromagnetic ordering in $La_{1-x}Sr_xCoO_3$ does not lead to a metal–insulator transition like that in CMR materials. In contrast to CMR materials $La_{0.5}Sr_{0.5}CoO_3$ exhibits weak positive magnetoresistance [6].

It is well known that the size of lanthanide ion influences strongly the magnetic and electrical transport properties of perovskites. It was found that the properties of $R_{0.5}Ba_{0.5}CoO_{3-y}$ ($R =$ rare earth) differ dramatically from those of $La_{0.5}Ba_{0.5}CoO_3$ apparently due to large deviation from stoichiometry [7–9]. The $Gd_{0.5}Ba_{0.5}CoO_{3-y}$ and

$\text{Tb}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ exhibit antiferromagnet–ferromagnet and metal–insulator transitions the nature of which is still a matter of discussion. In [10] it was shown by HREM and electron diffraction techniques that $\text{RBaCo}_2\text{O}_{6-\delta}$ ($R = \text{rare earth}$) have crystal structure similar to the 112 type perovskite structure with oxygen vacancies ordered. Recently it was reported [11] that orthorhombic and tetragonal samples of $\text{YBaCo}_2\text{O}_{5.5}$ exhibit an antiferromagnet–ferromagnet transition whereas only the orthorhombic one shows a metal–insulator transition. It is interesting to find out the influence of both oxygen content and the ordering of A-site cations on the properties of rare earth cobaltites. In addition there are no systematic data in the literature on properties of rare earth cobaltites with different content of barium ions. We have examined the structural, magnetic and transport properties of $\text{R}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ ($R = \text{Nd, Gd}$) depending on barium and oxygen content.

2. Experimental procedure

The $\text{R}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ samples were prepared from a stoichiometric mixture of high-purity R_2O_3 , BaCO_3 and Co_3O_4 at 1200°C in an aluminum oxide crucible. After repeated grinding and firing for 5 h in air, the samples were found to be single phase by x-ray diffraction.

Magnetization was measured with a Foner vibrating sample magnetometer. Zero-field cooled runs were taken after cooling the sample in a residual field typically less than 1 Oe. No corrections for demagnetization were applied. Resistivity data were determined with a standard four-probe method using indium as contacts. The oxygen content for some samples was determined by thermogravimetric analysis in high vacuum.

Neutron diffraction data were collected with a high-resolution powder diffractometer at the NIST Center for Neutron Research (USA). A wavelength of 1.5401 \AA was used on the BT-1 spectrometer and all the data were obtained at 295 K to determine the nuclear structure in the paramagnetic range.

3. Results and discussion

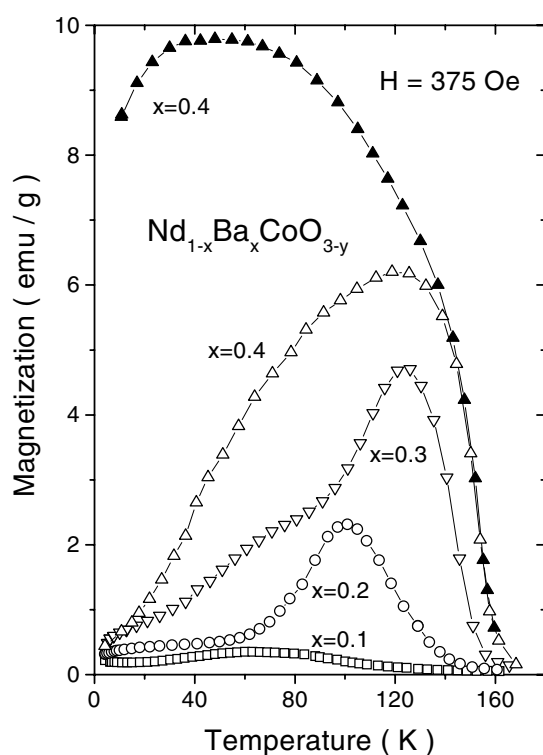
The crystal structure parameters of $\text{R}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ ($R = \text{Nd, Gd}$) taken from x-ray data are shown in table 1. $\text{Nd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ ($x \leq 0.4$) are orthorhombic whereas $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ prepared in oxidative conditions is tetragonal. Reduction in a vacuum first leads to the appearance of the orthorhombic structure while strongly reduced compounds are tetragonal (table 1). Solid solutions of $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ exist in our preparation conditions in the range $x \geq 0.44$.

Table 1. Unit cell parameters a , b , c and volume per formula unit calculated from x-ray data.

Chemical formula	a (\AA)	b (\AA)	c (\AA)	V (\AA^3)
$\text{Nd}_{0.9}\text{Ba}_{0.1}\text{CoO}_{3-y}$	3.807	3.841	3.793	55.46
$\text{Nd}_{0.8}\text{Ba}_{0.2}\text{CoO}_{3-y}$	3.812	3.848	3.804	55.80
$\text{Nd}_{0.7}\text{Ba}_{0.3}\text{CoO}_{3-y}$	3.826	3.849	3.811	56.12
$\text{Nd}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-y}$	3.895		7.602	115.33
$\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.81}$	3.900		7.604	115.66
$\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.74}$	3.902	3.937	7.594	116.66
$\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.68}$	3.922		7.608	117.03
$\text{Gd}_{0.56}\text{Ba}_{0.44}\text{CoO}_{3-y}$	3.874	3.907	7.523	113.88
$\text{Gd}_{0.53}\text{Ba}_{0.47}\text{CoO}_{3-y}$	3.874	3.909	7.530	114.03
$\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.77}$	3.888	3.919	7.537	114.80
$\text{Gd}_{0.48}\text{Ba}_{0.52}\text{CoO}_{3-y}$	3.878	3.911	7.536	114.30

Table 2. Final structural parameters of $NdBaCo_2O_{5.76}$ from neutron diffraction data. Lattice parameters are $a = 3.90362(13)$ Å; $b = a$; $c = 7.60938(30)$ Å; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 90^\circ$; cell volume = $115.956(7)$ Å³.

Name	X	Y	Z	Site sym.	Mult.	Type	Fraction
Ba1	0.000 000	0.000 000	0.000 000	4/ <i>MMM</i> 001	1	BA	0.073(21)
Nd1	0.000 000	0.000 000	0.000 000	4/ <i>MMM</i> 001	1	ND	0.927(21)
Ba2	0.000 000	0.000 000	0.500 000	4/ <i>MMM</i> 001	1	BA	0.927(21)
Nd2	0.000 000	0.000 000	0.500 000	4/ <i>MMM</i> 001	1	ND	0.073(21)
Co	0.500 000	0.500 000	0.250 8(7)	4/ <i>MM</i> (001)	2	CO	1.0000
O1	0.500 000	0.500 000	0.000 000	4/ <i>MMM</i> 001	1	O	0.756(21)
O2	0.500 000	0.500 000	0.500 000	4/ <i>MMM</i> 001	1	O	1.0000
O3	0.500 000	0.000 000	0.217 88(21)	<i>MM</i> 2(001)	4	O	1.0000

**Figure 1.** Temperature dependence of the zero-field cooled magnetization (open symbols) and field cooled magnetization (dark symbols) for $Nd_{1-x}Ba_xCoO_{3-y}$.

Compositions in the range $0.44 \leq x \leq 0.52$ prepared by slow cooling in air show orthorhombic distortions at room temperature. $Gd_{0.5}Ba_{0.5}CoO_{2.5}$ obtained in vacuum is tetragonal.

Rietveld analysis of the room-temperature neutron diffraction data for the $Nd_{0.5}Ba_{0.5}CoO_{3-y}$ sample prepared in air was carried out using a tetragonal cell in the space group $P4/mmm$. The model gave the best fit to the collected data. The results of structural refinement are given in table 2. In accordance with neutron diffraction data, the Nd and Ba ions are ordered forming the Nd and Ba containing planes along the c -axis so the true chemical formula is $NdBaCo_2O_{6-y}$. The position 0(1) is not completely occupied by oxygen.

Figure 1 shows the field cooled and zero-field cooled magnetization behaviour of $Nd_{1-x}Ba_xCoO_{3-y}$ ($x \leq 0.4$) compounds. Below the critical temperature T_C a sudden

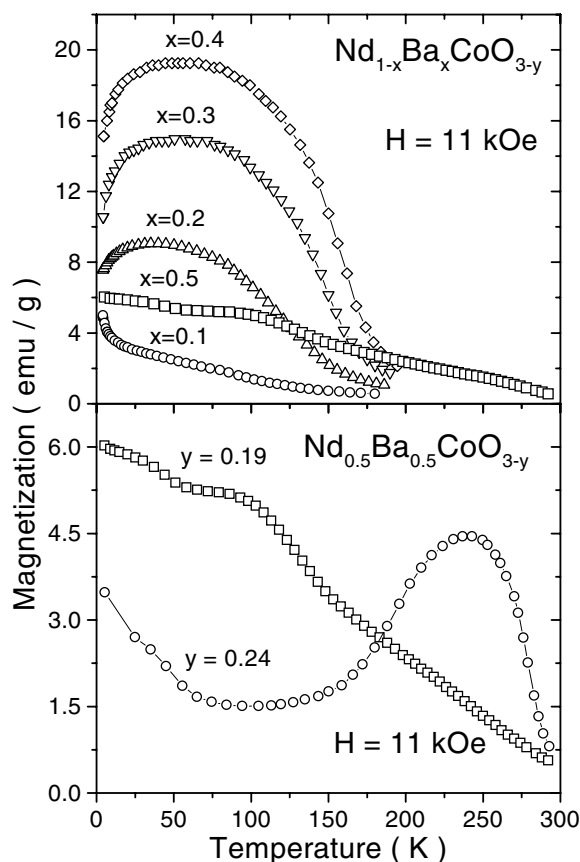


Figure 2. Temperature dependence of the field cooled magnetization for $\text{Nd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ (top panel) and for $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ with different oxygen contents (bottom panel).

rise in the magnetization is seen but the data depend strongly on the thermal history and the applied magnetic field. A marked splitting of the ZFC and FC magnetization data is observed for relatively small fields $H \leq 1$ kOe. While FC magnetization shows a broad maximum with decreasing temperature, the ZFC data go through a sharp maximum and tend to zero as $T \rightarrow 0$. The maximum shifts to lower temperatures and the splitting of FC and ZFC data is reduced upon increasing field. The magnetization increases strongly upon increasing barium content up to $x = 0.4$ (figure 2 top panel); however, the magnetization and Curie point of $\text{Nd}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-y}$ are lower than those for the well studied $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ [5, 12].

The magnetic properties of $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ depend dramatically on oxygen content (figure 2 bottom panel). The sample with relatively large oxygen content shows a broad transition into the paramagnetic state with anomalous behaviour at $T_{C1} = 180$ K and $T_C = 280$ K where the spontaneous magnetization disappears (figure 2). The magnetization of samples reduced in vacuum has maximal shifting to higher temperature with decreasing oxygen content down to $y = 0.25$. All the $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ samples have relatively low spontaneous magnetization in comparison with $\text{Nd}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-y}$, whereas the Curie point of $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.75}$ is much higher.

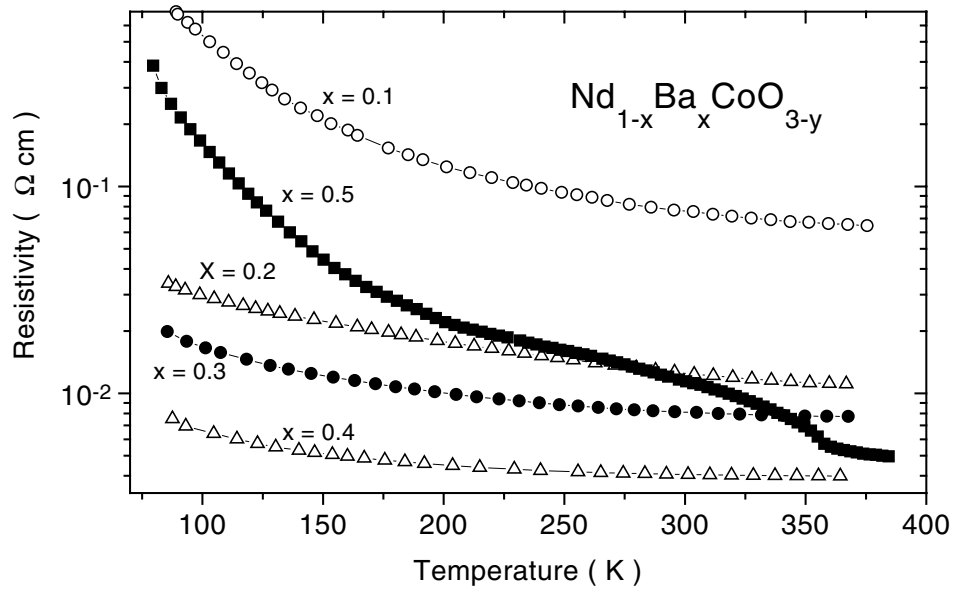


Figure 3. Temperature dependence of the resistivity for $Nd_{1-x}Ba_xCoO_{3-y}$.

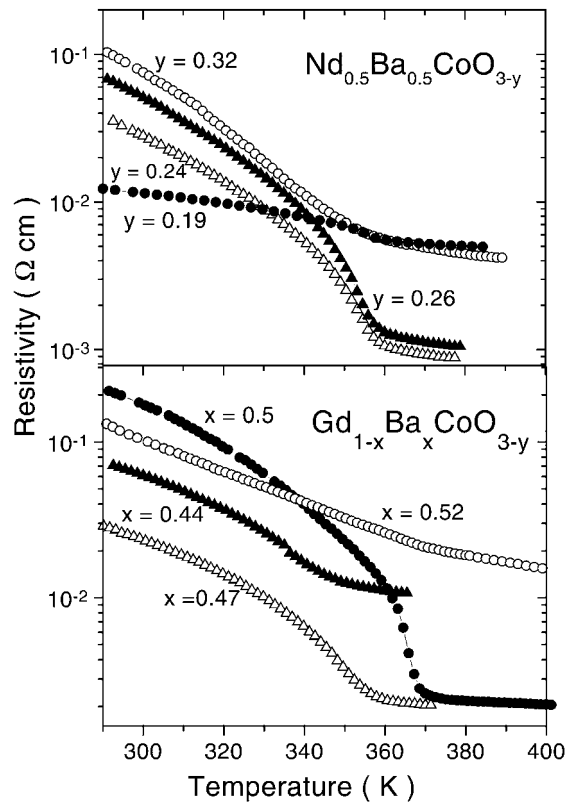


Figure 4. Temperature dependence ($290 < T < 370$ K) of the resistivity for $Nd_{0.5}Ba_{0.5}CoO_{3-y}$ (top panel) and $Gd_{1-x}Ba_xCoO_{3-y}$ (bottom panel).

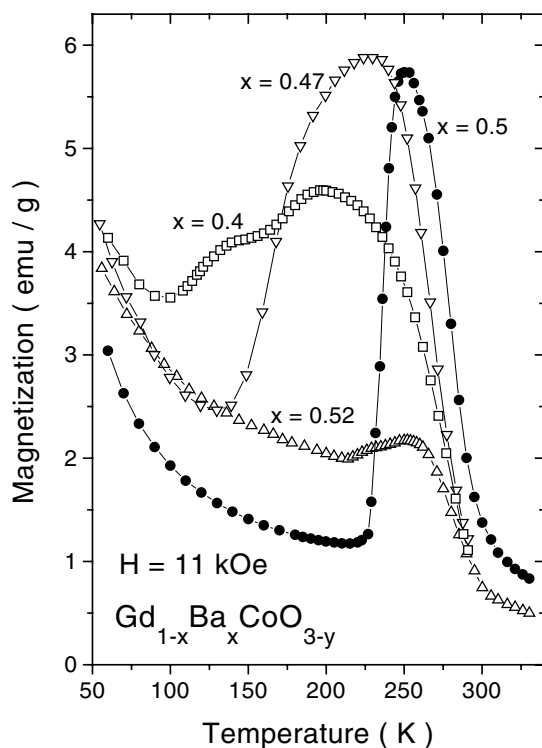


Figure 5. Temperature dependence of the field cooled magnetization for $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$.

The substitution of Nd by Ba ions leads to decreasing activation energy of charge carriers, but there is no concentrational insulator–metal transition (figure 3). Such a transition has been observed in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system at $x > 0.2$ [5]. The electrical resistivity of $\text{Nd}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-y}$ is relatively low and shows a very small temperature dependence with negative $\partial\rho/\partial T$. Apparently this composition is close to the concentrational metal–insulator transition. Oxidized samples of $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ exhibit also semiconductive behaviour (figure 4 top panel). The reduced sample $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ shows relatively large resistivity which drops at around $T_M = 350$ K. The electrical resistivity behaviour of the high temperature phase $T > T_M$ of $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ resembles that for the high temperature phase of LaCoO_3 [13]. Both phases exhibit temperature independent resistivity behaviour with resistivities close to $10^{-3} \Omega \text{ cm}$.

There is no spontaneous magnetization in $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.77}$ below T_i (figure 5). All the $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ samples exhibit maximum magnetization above T_i which shifts to higher temperature with increasing barium content up to $x = 0.5$ (figure 5). Above $x = 0.5$ the magnetization decreases strongly. All the samples have a Curie point around 280 K. The magnetic moment of $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.77}$ is close to $0.2 \mu_B$ at 260 K.

The $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ compounds are semiconductors up to 360 K where a drop of resistivity by more than one order of magnitude occurs (figure 4 bottom panel). Above 360 K the resistivity depends weakly on temperature. The DTA measurements indicate that the transition of T_M is first order with temperature hysteresis of 3 K (figure 6). The transition at T_i into the phase with spontaneous magnetization leads to a drop of resistivity by a factor of two.

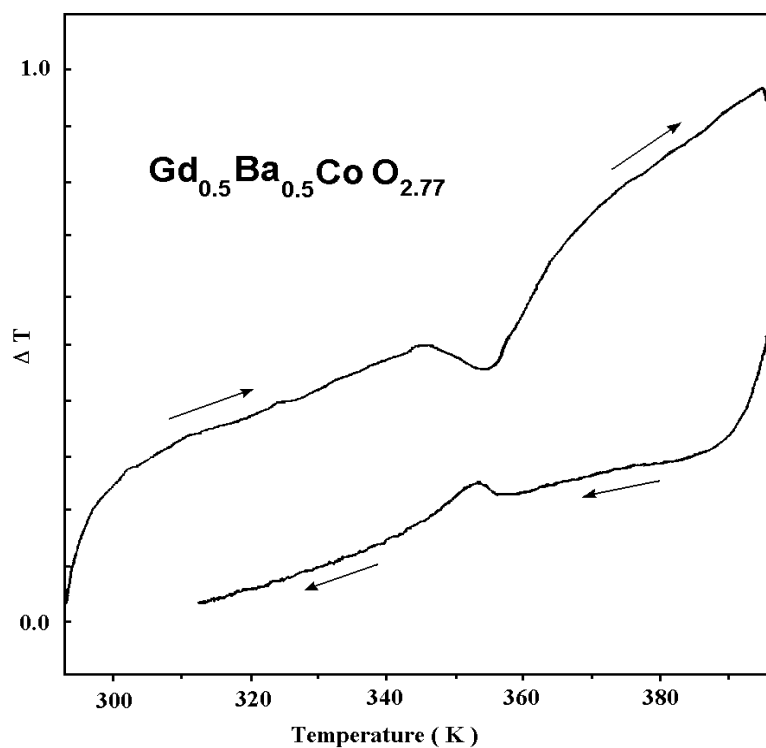


Figure 6. DTA data for $Gd_{0.5}Ba_{0.5}CoO_{2.77}$.

We have found that $Gd_{0.5}Ba_{0.5}CoO_{2.77}$ exhibits a large magnetoresistance at around T_i where the effect reaches 15% in a field of 10 kOe (figure 7 bottom panel). The magnetoresistance is much less pronounced at T_C . The deviation from a Gd/Ba ratio of 1:1 leads to a smaller effect (figure 7 bottom panel).

The ferromagnetism of $La_{1-x}Sr_xCoO_{3-y}$ has been explained by Goodenough in terms of the band magnetism [3, 12]. In this model narrow π^* and σ^* cobalt bands are overlapped. The metallic conductivity results from an overlapping upper Hubbard band of π^* type and a wide oxygen band [14]. The spontaneous magnetic moment per formula unit corresponds to a high spin state of Co^{4+} ions [4, 5] or intermediate-spin state of all cobalt ions [3, 12]. The properties of $La_{1-x}Sr_xCoO_3$ and $Nd_{1-x}Ba_xCoO_3$ in the range $0 < x < 0.4$ are similar in many aspects whereas the properties of $La_{0.5}Sr_{0.5}CoO_{3-y}$ and $R_{0.5}Ba_{0.5}CoO_{3-y}$ are strongly different. The large mismatch between the rare-earth ions and barium leads to the long-range ordering of these ions and large deviation from stoichiometry. Apparently anomalous magnetic properties of $R_{0.5}Ba_{0.5}CoO_{3-y}$ ($R = Nd, Gd$) may be attributed to these effects. The spontaneous magnetization depends strongly on oxygen content and reaches a maximal magnitude at around 2.75 oxygen content. For this composition all cobalt ions adopt the three-valent state. The spontaneous magnetic moment of $Gd_{0.5}Ba_{0.5}CoO_{2.77}$ is approximately eight times lower than that of $La_{0.5}Sr_{0.5}CoO_3$ and could not be attributed to parallel alignment of all three-valent cobalt ions if they adopt an intermediate-spin state. By contrast with [7–9] in this work we suggest that between T_i and T_C $R_{0.5}Ba_{0.5}CoO_{2.75}$ are weak ferromagnets whereas in [7–9] the true ferromagnetic state has been postulated. There are some reasons supporting our assumption:

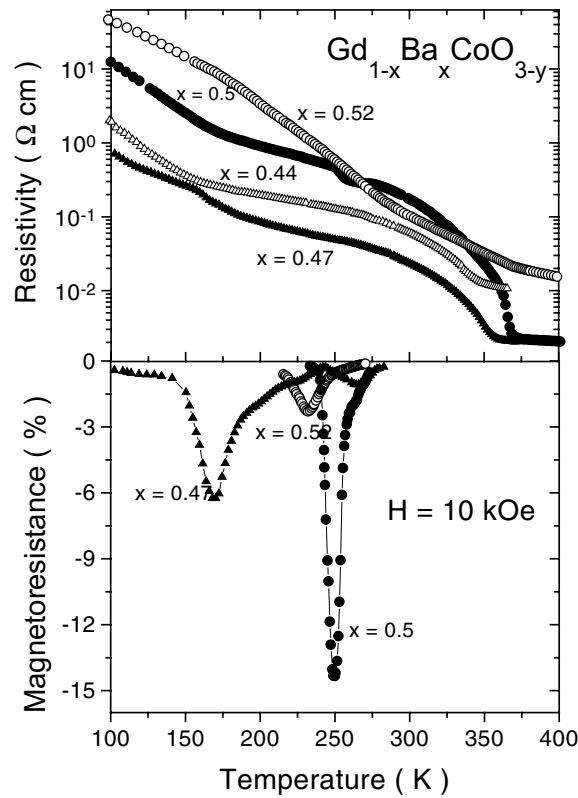


Figure 7. Temperature dependence of the resistivity (top panel) and magnetoresistance (bottom panel) for $\text{Gd}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$.

- (1) The $\text{Co}^{3+}\text{--O--Co}^{3+}$ superexchange interaction is always antiferromagnetic in cobaltites with perovskite structure [2, 12].
- (2) The appearance of Co^{4+} ions, in contrast with the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ system, suppresses the ferromagnetic contribution for the $\text{R}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-y}$ compositions.
- (3) The antiferromagnet–weak ferromagnet transition has been observed in the $\text{DyFe}_{1-x}\text{Co}_x\text{O}_3$ perovskites [15].

According to [10] oxygen vacancies are not distributed randomly in a crystal lattice. The transition at T_M could be attributed to the rare-earth and barium ion disordering or oxygen vacancies disordering. However, the transition at T_M occurs only in orthorhombic samples whereas rare-earth and barium ions are also ordered in tetragonal samples. So we think that this transition results from oxygen vacancies ordering. The deviation from ideal composition $x = 0.5$ and oxygen content 2.75 leads to a suppression of both transitions at T_i and T_M . The temperature T_i is more sensitive to changes of chemical composition than temperature T_M (figure 5). So we think the deviation of oxygen content from 2.75 does not destroy long-range oxygen ordering in some domains. Apparently, the samples are divided into relatively large domains with different oxygen concentration. It is worth noting that oxygen ordering in the $\text{SrFeO}_{3-1/n}$ perovskite where $n = 8, 4, 2$ respectively occurs as a first order phase transition [16].

Acknowledgment

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