Magnetic and structural phase transitions in some orthocobaltites doped by Ba or Sr ions

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Abstract. It has been found that reduction of $La_{0.5}Ba_{0.5}CoO_3$ perovskite in vacuum leads to collapse of the ferromagnetic state without changes of cubic symmetry. $R_{0.5}Ba_{0.5}CoO_{3-x}$ (R = Nd, Tb) oxygen deficit orthorhombic phases undergo phase transitions approximately at temperatures $T_i \sim 240$ K, $T_C \sim 280$ K and $T_M \sim 350$ K. The first order antiferro–ferromagnet transition at T_i is accompanied by a jump of conductivity, and the negative magnetoresistance reaches 25% in a field of 1 T. The magnetization data indicate a low-spin state of cobalt ions. Spontaneous magnetization develops at T_i and disappears at T_C. The first order transition from a semiconductive to quasi-metallic state occurs at T_M with a drop of resistivity of more than one order of magnitude. The transitions are most pronounced at $x = 0.25$. It is supposed that the transition at T_M results from oxygen vacancies ordering. The $R_{0.5}Sr_{0.5}CoO_3$ perovskites are metallic ferromagnets with an intermediate-spin state of Co ions. The properties of $R_{0.5}Ba_{0.5}CoO_{3-x}$ compounds drastically differ from those of $R_{0.5}Sr_{0.5}CoO_{3-x}$ apparently due to rare-earth and barium ions ordering.

1. Introduction

The discovery of the 'colossal' magnetoresistance (CMR) in the manganites with perovskite structure [1] has stimulated the research of the compounds exhibiting large magnetoresistance. The magnetic and transport properties of $La_{1-y}Sr_yCoO_{3-x}$ cobaltites with perovskite structure and CMR materials such as $La_{1-y}Sr_yMnO_{3-x}$ have common features [2–6]. In both systems the substitution of La with divalent ion creates the metallic ferromagnetic state. The ferromagnetic interactions taking place between Co^{3+}/Co^{4+} are supposed to arise from a double exchange mechanism like that in $La_{1-y}Sr_yMnO_{3-x}$ materials. However, the detailed mechanism of the ferromagnetism and the metal–insulator transition in cobaltites are not well understood. It was found that in the metallic samples of $La_{1-y}Sr_yCoO_3$ ($y > 0.2$) the magnitude of the magnetoresistance is typically small whereas it is becomes larger in the composition range $y \leqslant 0.2$, where the system is close to the metal–insulator transition [7]. In contrast to manganite, there is no temperature driven insulator–metal transition in the cobaltites.

It is well known that the magnetic and transport properties of the rare-earth metal oxides with perovskite structure depend strongly on the size of the rare-earth ion as well as the

oxygen content [8]. However, there are few data concerning cobaltites of rare earth elements doped by Ba or Sr. The studies of $R_{1-y}Sr_yCoO_{3-x}$ (R = Pr, Nd, Sm) have shown these materials to be similar to $La_{1-y}Sr_yMnO_{3-x}$ with T_C decreasing with decreasing size of the rare-earth ion [7, 8]. It is well established that properties of manganites depend markedly on oxygen nonstoichiometry. The dependence of the magnetic and transport properties of cobaltites on oxygen content has not been studied yet. We have examined the structural, magnetic and transport properties of the $R_{1-y}A_yCoO_{3-x}$ (A = Ba, Sr) perovskites in order to investigate the evolution of the cobaltite properties as a function of lanthanoid ionic radii as well as oxygen content. It was found that both the lanthanoid ion type and the oxygen nonstoichiometry x influence markedly the magnetic ground state of the barium doped cobaltites.

2. Experiments

The studied samples were polycrystalline pellets produced by a solid state phase reaction. Mixtures of R_2O_3, $BaCO_3$, Co_3O_4 were pressed into pellets, sintered at 1473 K for 5 h in air and then cooled to room temperature at 100 K h^{-1}. This process was repeated in order to produce a homogeneous solid solution. As-prepared samples were treated in oxygen or vacuum in order to investigate the effect of oxygen content on magnetic and transport properties. According to the powder x-ray diffraction (XRD) patterns, the specimens were single phase. The XRD data at room temperature were indexed on the basis of a distorted perovskite-type structure with orthorhombic or tetragonal symmetry. The crystal structure parameters are listed in table 1. Oxygen content in the samples was determined by thermogravimetric analysis in high vacuum.

Table 1. Symmetry, the unit cell parameters (a, b, c) and volume (V) of $R_{0.5}Ba_{0.5}CoO_{3-x}$.

Chemical formula	Symmetry[a]	a (Å)	b (Å)	c (Å)	V (Å^3)
$La_{0.5}Ba_{0.5}CoO_{2.95}$	C	3.885			58.62
$La_{0.5}Ba_{0.5}CoO_{2.82}$	C	3.923			60.29
$La_{0.5}Ba_{0.5}CoO_{2.80}$	C	3.924			60.46
$La_{0.5}Ba_{0.5}CoO_{2.76}$	C	3.933			60.86
$La_{0.4}Y_{0.1}Ba_{0.5}CoO_{3-x}$	T	3.901		3.875	58.97
$La_{0.4}Y_{0.1}Ba_{0.5}CoO_{3-x}$	T	3.897		3.858	58.58
$La_{0.4}Y_{0.1}Ba_{0.5}CoO_{3-x}$	T	3.891		3.790	57.36
$Nd_{0.5}Ba_{0.5}CoO_{2.81}$	T	3.900		3.802	57.83
$Nd_{0.5}Ba_{0.5}CoO_{2.76}$	O	3.927	3.902	3.792	58.11
$Nd_{0.5}Ba_{0.5}CoO_{2.74}$	O	3.937	3.902	3.797	58.33
$Nd_{0.5}Ba_{0.5}CoO_{2.68}$	O	3.954	3.917	3.804	58.92
$Tb_{0.5}Ba_{0.5}CoO_{2.80}$	O	3.886	3.860	3.737	56.05
$Tb_{0.5}Ba_{0.5}CoO_{2.75}$	O	3.905	3.864	3.755	56.67
$Tb_{0.5}Ba_{0.5}CoO_{2.71}$	O	3.901	3.881	3.763	56.96
$Tb_{0.5}Ba_{0.5}CoO_{2.69}$	T	3.894		3.761	57.03

[a] C—cubic, T—tetragonal, O—orthorhombic.

Magnetic properties were studied using a Foner vibrating sample magnetometer. The electrical resistivity was measured in the range $77 \leqslant T \leqslant 400$ K by a standard four-probe method.

3. Results and discussion

All the $La_{0.5}Ba_{0.5}CoO_{3-x}$ samples have a simple cubic unit cell independent of oxygen content. The oxygen loss leads to increasing unit cell parameter (table 1). The $Nd_{0.5}Ba_{0.5}CoO_{2.81}$ cooled slowly in air has tetragonal structure whereas the samples reduced slightly in vacuum are characterized by orthorhombic distortions of the unit cell (table 1). The samples of $Tb_{0.5}Ba_{0.5}CoO_{3-x}$ treated in oxidative conditions are orthorhombic. In contrast with Nd-based compounds, reduced Tb-based samples have tetragonal symmetry. The replacement of La ions with Y leads to lowering symmetry down to tetragonal.

In accordance with magnetization data $La_{0.5}Ba_{0.5}CoO_{2.95}$ is a ferromagnet with $T_C = 210$ K (figure 1). The magnitude of spontaneous magnetization is in agreement with the intermediate spin state of cobalt ions. The decrease of oxygen content down to 2.82 leads to a drop of magnetization without appreciable change of Curie temperature (figure 1). The $La_{0.5}Ba_{0.5}CoO_{2.80}$ sample exhibits a peak of magnetization slightly below Curie temperature. $La_{0.5}Ba_{0.5}CoO_{2.76}$ does not show spontaneous magnetization above 20 K (figure 1). Such a magnetization behaviour could be attributed to the formation of ferromagnetic clusters associated with microdomains enriched by Co^{4+} ions because Co^{3+}–O–Co^{3+} exchange interaction (for cobalt ions in intermediate- or high-spin state) is antiferromagnetic in

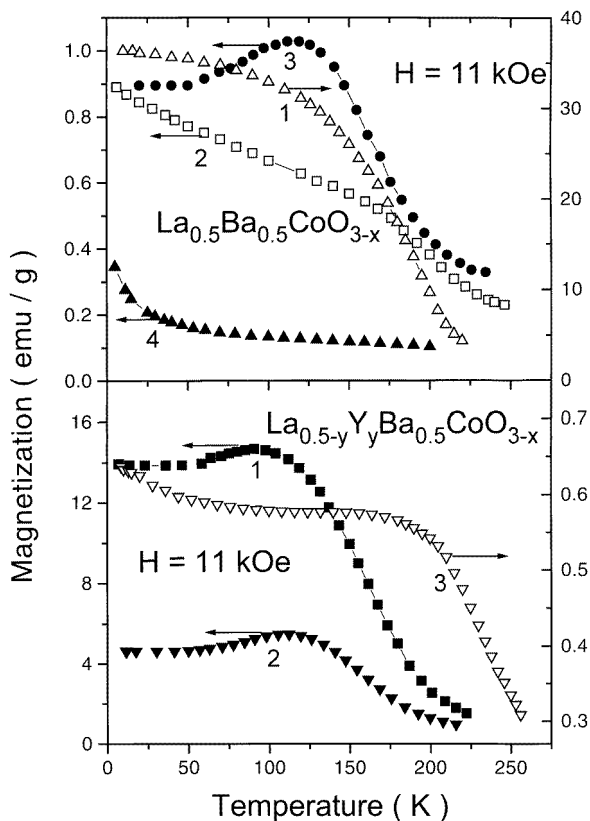**Figure 1.** Magnetization as a function of temperature for $La_{0.5}Ba_{0.5}CoO_{3-x}$ where $x = 0.05$ (1); $x = 0.18$ (2); $x = 0.20$ (3); $x = 0.24$ (4) (top panel) and $La_{0.5-y}Y_yBa_{0.5}CoO_{3-x}$ where $y = 0.1$ (1); $y = 0.2$ (2); $y = 0.3$ (3) (bottom panel).

perovskites [6]. The magnetic properties of $La_{0.5-y}Y_yBa_{0.5}CoO_{3-x}$ in part resemble those of $La_{0.5}Ba_{0.5}CoO_{3-x}$ samples. Some samples with $y \leqslant 0.3$ exhibit a slightly pronounced peak of magnetization (figure 1).

$Nd_{0.5}Ba_{0.5}CoO_{2.81}$ is characterized by a broad transition into the paramagnetic state (figure 2). In spite of a relatively high Curie temperature ($T_C \sim 280$ K) this compound shows a very low spontaneous magnetization incompatible with intermediate-spin state of cobalt ions. Apparently the broad transition results from magnetic inhomogeneity because the reduced samples show a peak of magnetization at around 250 K (figure 2, top panel). There is no spontaneous magnetization below $T_i \sim 260$ K for $Tb_{0.5}Ba_{0.5}CoO_{2.75}$ (figure 2, bottom panel). Spontaneous magnetization develops at temperature above T_i. The spontaneous magnetic moment at 272 K is 0.18 μ_B per formula unit, and the Curie temperature T_C is 286 K. It is interesting to note that both oxidation and reduction lead to a decrease of T_i and T_C of this compound.
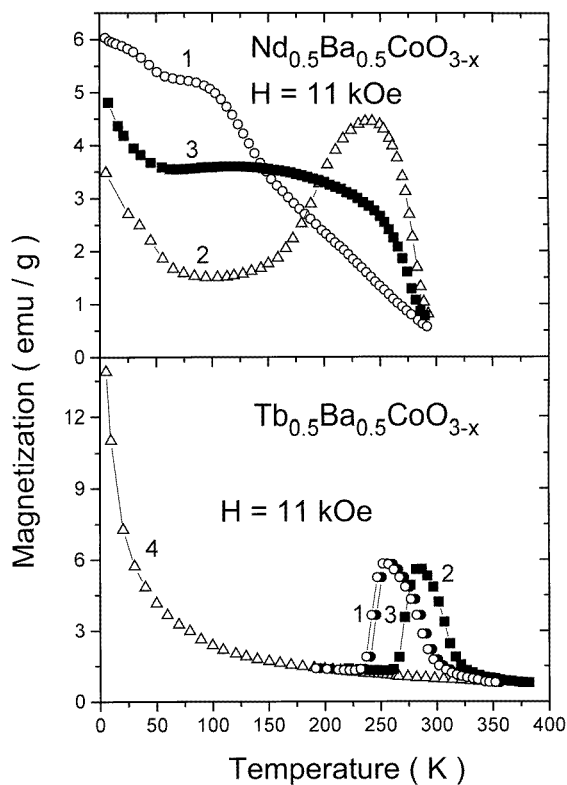

Figure 2. Magnetization as a function of temperature for $Nd_{0.5}Ba_{0.5}CoO_{3-x}$ where $x = 0.19$ (1); $x = 0.24$ (2); $x = 0.32$ (3) (top panel) and $Tb_{0.5}Ba_{0.5}CoO_{3-x}$ where $x = 0.2$ (1); $x = 0.25$ (2); $x = 0.31$ (3) (bottom panel).

Both reduction of $La_{0.5}Ba_{0.5}CoO_{3-x}$ and replacement of La ions with rare earth or Y give rise to a transition from metallic to semiconductive behaviour. All the $R_{0.5}Ba_{0.5}CoO_{3-y}$ compounds are semiconductors. Figure 3 (top panel) displays resistivity–temperature behaviour of $Nd_{0.5}Ba_{0.5}CoO_{3-x}$ samples with different oxygen content. At $T_M \sim 350$ K all the Nd-based samples show a drop of the electrical resistivity becoming more pronounced
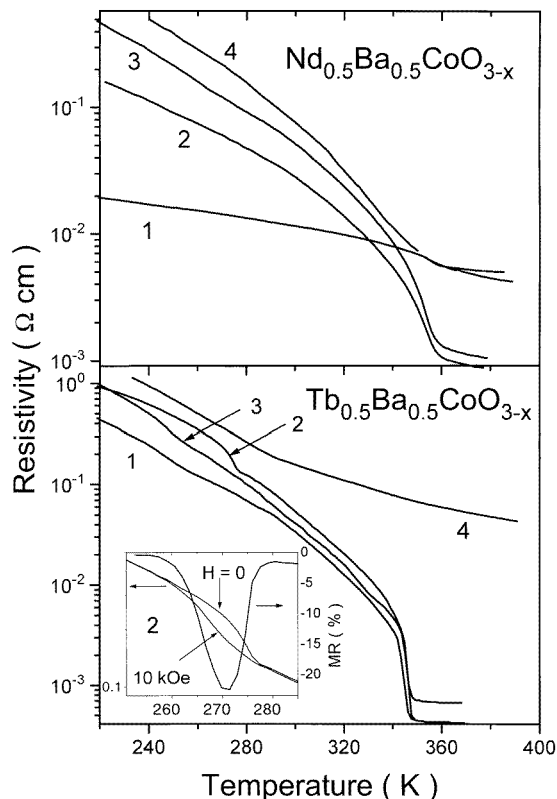
Figure 3. Resistivity as a function of temperature for $Nd_{0.5}Ba_{0.5}CoO_{3-x}$ where $x = 0.19$ (1); $x = 0.24$ (2); $x = 0.26$ (3); $x = 0.32$ (4) (top panel) and $Tb_{0.5}Ba_{0.5}CoO_{3-x}$ where $x = 0.2$ (1); $x = 0.25$ (2); $x = 0.29$ (3); $x = 0.31$ (4) (bottom panel).

for reduced samples. The temperature T_M depends only slightly on oxygen content and is not connected with magnetic phenomena, because T_M is higher than T_C. The anomalous behaviour is much more pronounced for $Tb_{0.5}Ba_{0.5}CoO_{3-x}$ compositions (figure 3). At $T_i \sim 260$ K the resistivity drops by a factor of two. At T_C there is a small resistivity anomaly whereas at T_M the electrical resistivity drop reaches more than one order of magnitude. Both reduction and oxidation of $Tb_{0.5}Ba_{0.5}CoO_{2.75}$ lead to suppression of the anomalous behaviour.

We have found that $Tb_{0.5}Ba_{0.5}CoO_{3-x}$ exhibits a large magnetoresistance around T_i that reaches 25% in a field of 1 T (figure 4). The magnetoresistance peak is much less pronounced at T_C. Both oxidized and reduced samples exhibit the relatively broad peak of magnetoresistance at lower temperatures.

The study of elastic properties of $Tb_{0.5}Ba_{0.5}CoO_{2.75}$ has revealed the anomalous behaviour near the phase transitions (figure 5). The transition at T_i leads to sharp increase of Young's modulus whereas there is a minimum near T_M. The DTA measurements indicate that the transition at T_M is first order (figure 6). The temperature hysteresis reaches 6 K. XRD study has revealed a strong decrease of b and increase of both a and c unit cell parameters around T_M without changes of orthorhombic symmetry. The unit cell volume of the low-temperature phase is larger by approximately 0.035%.
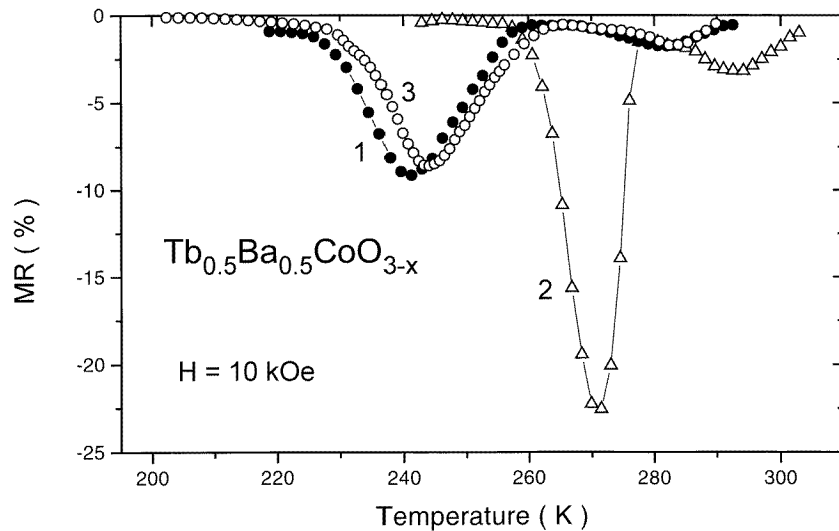
Figure 4. Magnetoresistance as a function of temperature for $Tb_{0.5}Ba_{0.5}CoO_{3-x}$ where $x = 0.2$ (1); $x = 0.25$ (2); $x = 0.29$ (3).

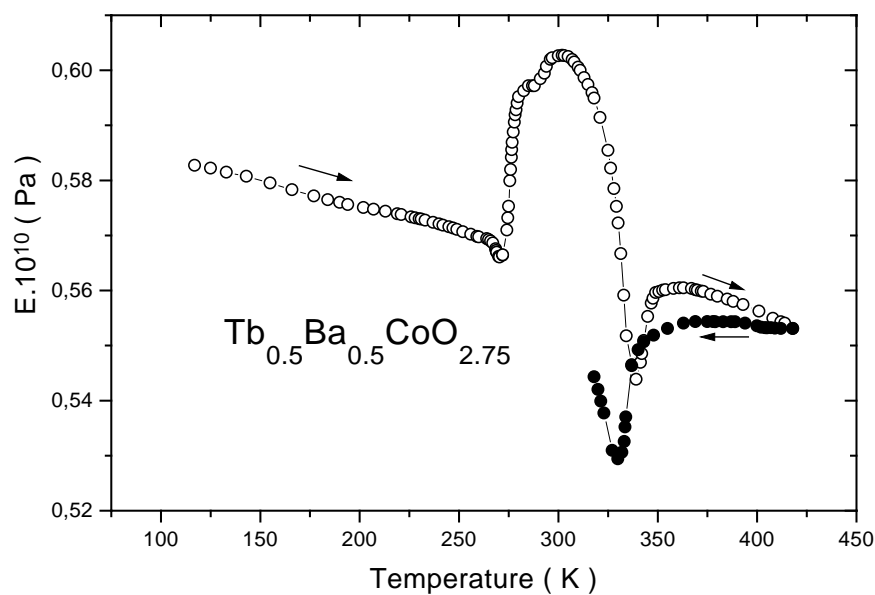**Figure 5.** Young's modulus as a function of temperature for $Tb_{0.5}Ba_{0.5}CoO_{2.75}$.

It is worth noting that properties of Ba-containing rare-earth cobaltites differ strongly from those of Sr-containing ones. For example $Eu_{0.5}Sr_{0.5}CoO_{3-x}$ and $Gd_{0.5}Sr_{0.5}CoO_{3-x}$ have cubic unit cells (table 2). Sr-containing compounds are metallic below room temperature and exhibit ferromagnetic behaviour with a rather large spontaneous magnetic moment at 4.2 K associated with the intermediate-spin state of cobalt ions (figure 7). In spite of the large spontaneous magnetization the Curie temperatures are much lower than those
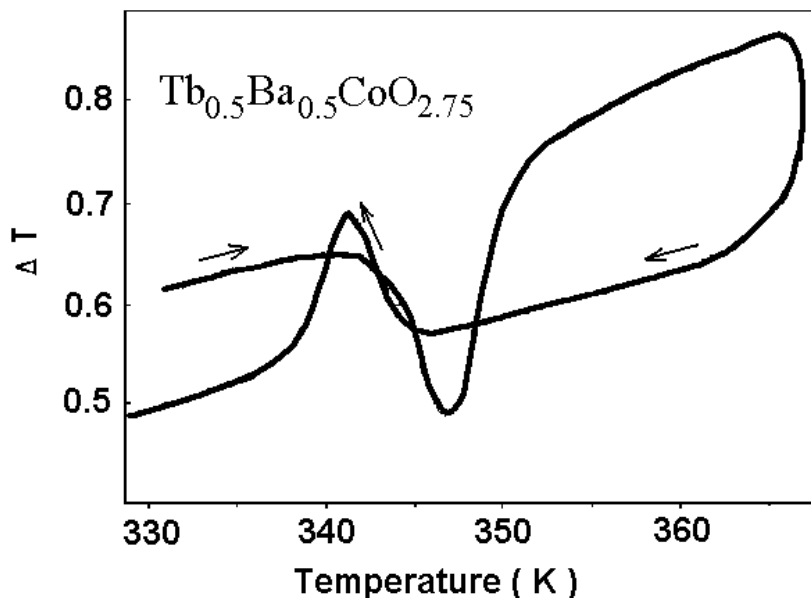
Figure 6. DTA curves obtained on heating and cooling of $Tb_{0.5}Ba_{0.5}CoO_{2.75}$.

Table 2. Symmetry, the unit cell parameters (a, b, β) and volume (V) of $R_{0.5}Sr_{0.5}CoO_{3-x}$.

Chemical formula	Symmetry[a]	a (Å)	b (Å)	β (°)	V (Å^3)
$La_{0.5}Sr_{0.5}CoO_{3-x}$	R	3.835		90.11	56.40
$Pr_{0.5}Sr_{0.5}CoO_{3-x}$	M	3.825	3.800	90.55	55.56
$Nd_{0.5}Sr_{0.5}CoO_{3-x}$	M	3.819	3.793	90.63	55.35
$Sm_{0.5}Sr_{0.5}CoO_{3-x}$	M	3.811	3.795	90.42	55.01
$Eu_{0.5}Sr_{0.5}CoO_{3-x}$	C	3.796			54.70
$Gd_{0.5}Sr_{0.5}CoO_{3-x}$	C	3.798			54.79

[a]C—cubic, R—rhombohedral, M—monoclinic.

for the corresponding compounds of Ba-based series. These compounds show rather small positive magnetoresistance without any peak at the Curie temperature. Both spontaneous magnetic moment and the Curie temperature decrease with decreasing lanthanoid ionic radii apparently due to increasing oxygen nonstoichiometry. There is no metal–insulator transition.

The ferromagnetic properties of $La_{1-y}Sr_yCoO_{3-x}$ have been explained by Raccah and Goodenough in terms of band magnetism [2]. In this model narrow π^* and σ^* cobalt bands are overlapped. The metallic conductivity results from overlapping of the upper Hubbard band of π^* type and the wide oxygen valence band [8]. The properties of $La_{1-y}Sr_yCoO_{3-x}$ and $La_{1-y}Ba_yCoO_{3-x}$ systems are similar in many aspects whereas properties of rare-earth cobaltites of both series are strongly different (figures 1, 2–7). We think that the large size mismatch between rare-earth and barium ions favours the effect of ordering of these ions. Apparently, large crystal-structure distortions of Ba-based compounds in comparison with the Sr-based series could be attributed to this effect. Below T_M, $R_{0.5}Ba_{0.5}CoO_{3-x}$ is a semiconductor, so the upper Hubbard band of π^* type is not overlapped with the valence band. Low magnetic moment is incompatible with the intermediate- or high-spin state
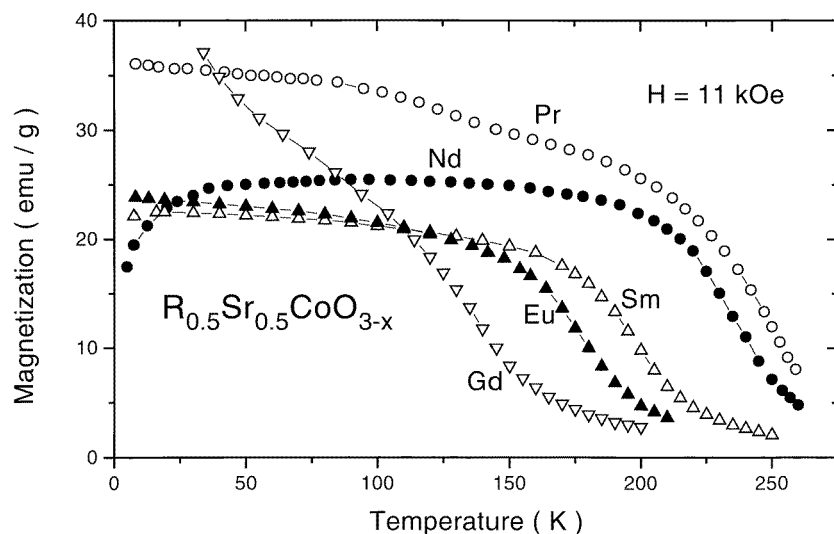
Figure 7. Magnetization as a function of temperature for $R_{0.5}Sr_{0.5}CoO_{3-x}$ compounds.

of both Co^{3+} and Co^{4+} ions. The most appropriate model ascribes the low spontaneous magnetization to holes (Co^{4+} ions) in the narrow π^* band. In this model 3d (d_ε) electrons are itinerant, π^* and σ^* bands are not overlapped, and cobalt atoms have low-spin state. It is necessary to note that transitions at T_M and T_i are most pronounced in samples with oxygen content close to 2.75. This value corresponds to chemical formula $R_{0.5}Ba_{0.5}CoO_{3-1/n}$ where $n = 4$. It is known that the vacancy ordered phases of $SrFeO_{3-1/n}$ where $n = 8$, 4 and 2 show first-order transition to their disordered structures at 523, 598 and 1103 K correspondingly [10]. It is possible that oxygen vacancies in the terbium cobaltite are long-range ordered. Results obtained on samples with different oxygen content show that T_M depends slightly on the oxygen content in contrast with strong changes of resistivity at T_M against oxygen content (figure 3). One can expect such a behaviour in a two-phase model. The deviation of oxygen content from the optimal value ($x \sim 0.13$) leads to decreasing content of the phase exhibiting the metal–insulator transition. It is possible that the phase transition at T_M results from the oxygen vacancies ordering. It is necessary to undertake a neutron diffraction study to clarify this hypothesis. Apparently at T_M some Co–O bonds become shorter thus leading to an overlap of the upper Hubbard band of π^* type with the oxygen valence band.

The antiferromagnet–ferromagnet transition at T_i in $Tb_{0.5}Ba_{0.5}CoO_{2.75}$ resembles that for $Pr_{0.5}Sr_{0.5}MnO_3$ [11]. In later compound this transition arises from competition of antiferromagnetic and ferromagnetic parts of exchange interaction without charge order–disorder transition and radical change of electrical transport. We think that antiferromagnetic and ferromagnetic parts of exchange interactions are very close in the $R_{0.5}Ba_{0.5}CoO_{3-x}$ series.

Acknowledgments

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