

Magnetic and electrical transport properties of orthocobaltites $R_{0.5}Ba_{0.5}CoO_3$ ($R=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy$)

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Magnetization and electrical resistivity studies have established that $La_{0.5}Ba_{0.5}CoO_{3-\gamma}$ (LaBaC) is a metallic ferromagnet whereas $Pr_{0.5}Ba_{0.5}CoO_{3-\gamma}$ (PrBaC) is a magnetic semiconductor. The magnitudes of spontaneous magnetizations are in agreement with intermediate (LaBaC) and low-spin (PrBaC) cobalt states with itinerant $3d$ electrons. $R_{0.5}Ba_{0.5}CoO_{3-\gamma}$ ($RBaC$, $R=Sm, Eu, Gd, Tb, Dy$) exhibit a sequence of phase transitions at temperatures T_i , T_C , and T_M on heating. Below T_i these materials are antiferromagnets, whereas in the temperature interval between T_i and T_C , a ferromagnetic behavior has been revealed. For TbBaC the temperatures T_i and T_C are 245 and 285 K, respectively. The phase transition at T_i is accompanied by a jump of electrical resistivity and peak of magnetoresistance. For TbBaC an external magnetic field of 14 T leads to decreasing T_i from 245 to 85 K. At around T_M (337 K for TbBaC) the first-order phase transition from semiconductive to quasimetallic state (high-temperature phase) has been observed. The transition occurs without changes of orthorhombic symmetry, and the unit-cell volume of the high-temperature phase was shown to be larger as compared to the low-temperature one (approximately 0.2%). It is supposed that the transition at T_M results from oxygen vacancy ordering. [S0163-1829(98)03530-9]

Recently, many investigations have been reported on the $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$ systems because of their interesting and unusual magnetic and transport properties.¹⁻⁶ $LaCoO_3$ exhibits a temperature-dependent transition between low-spin ($S=0$; t_{2g}^6) and high-spin ($S=2$; $t_{2g}^4e_g^2$) states. At around 500 K this compound shows a phase transition from a semiconductive state (below 500 K) to a fairly conductive one with resistivity at about $10^{-3} \Omega \text{ cm}$. The substitution of La^{3+} by divalent Sr^{2+} or Ba^{2+} leads to the appearance of a ferromagnetic intermediate-spin state with itinerant $3d$ electrons. The $La_{0.5}Sr_{0.5}CoO_3$ compound (LaSrC) is a metallic ferromagnet with a magnetic moment approximately $1.5\mu_B$ per formula unit and a Curie temperature of 232 K. The magnetic and transport properties of $La_{1-x}A_xCoO_3$ ($A=Ca, Sr, Ba$) were explained using Zener's double exchange mechanism⁷ or Goodenough's itinerant-electron ferromagnetism model.⁸ The size of the lanthanide ion is well known to influence strongly the magnetic and electrical properties of the compounds with perovskite structure. However, the data on orthocobaltites of rare-earth elements doped by Sr^{2+} or Ba^{2+} are quite limited.⁹⁻¹¹ The studies of $R_{1-x}Sr_xCoO_3$ ($R=Pr, Nd, Sm, Eu$) have shown these materials to be similar to $La_{1-x}Sr_xCoO_3$ with T_C increasing with x as well as with the size of the rare-earth ion.⁷

In the present work, an attempt was made to synthesize the $RBaC$ ($R=Pr, Nd, Sm, Eu, Gd, Tb, Dy$) compounds in order to study the evolution of the magnetic and transport properties as a function of lanthanide ionic radii. We have found that $RBaC$ ($R=Sm, Eu, Gd, Tb, Dy$) are magnetic semiconductors exhibiting both antiferromagnetic-ferromagnetic and insulator-metal transitions.

$R_{1-x}Ba_xCoO_{3-\gamma}$ ($R=La, Pr-Dy$; $0.4 \leq x \leq 0.66$) samples were prepared by a solid-state reaction. The powders of R_2O_3 , $BaCO_3$, and Co_3O_4 were weighed in the desired proportions and milled with acetone. The resulting solids were pressed into pellets, heated at 1200 K, reground, and then fired at 1490 K in air to form hard, dense bars. All the samples were cooled to room temperature at a rate of 100 K/h. The oxygen-deficient samples of $RBaC$ ($R=Eu, Gd, Tb, Dy$) obtained in this way were annealed in air at 1100 K for 12 h. We failed to obtain a $Y_{0.5}Ba_{0.5}CoO_{3-\gamma}$ sample with perovskite structure. However, we have managed to obtain a $Y_{0.46}Dy_{0.04}Ba_{0.5}CoO_{3-\gamma}$ (YBaC) single phase sample. Oxygen content in the TbBaC sample was determined by thermogravimetric analysis in high vacuum. One should note also that oxygen nonstoichiometry of the other studied samples is not zero. Magnetization measurements were done with a commercial superconducting quantum interference device magnetometer (MPMS 5, Quantum Design). The measurements were performed with zero-field-cooled (ZFC) and field-cooled (FC) samples. The electrical resistivity was measured by a standard four-electrode technique in a steady magnetic field up to 140 kOe. X-ray-diffraction (XRD) patterns of all the $RBaC$ samples were completely indexed as the perovskite-type structure and their lattice parameters are listed in Table I. The crystal-structure distortions increase as the lanthanide ionic radius decreases. The values of T_C for various $RBaC$ compounds are listed in Table I. The values of M_s and T_C found by us for LaBaC are close to those reported by Patil and co-workers.¹⁰ The magnitude of spontaneous magnetization (36 emu/g at 4.2 K) is in agreement with an intermediate spin state of cobalt with itinerant $3d$

TABLE I. Symmetry, the unit-cell parameters at room temperature, and T_i , T_C , T_M temperatures (that were indicated in the text) of $RBaC$ compounds.

Lanthanoid ion	Symmetry ^a	a (Å)	b (Å)	c (Å)	V (Å ³)	T_i (K) ^b	T_C (K) ^c	T_M (K)
La	C	3.893			59.00		225	
Pr	T	3.900		3.813	57.99		150	
Nd	T	3.899		3.804	57.83		140, 260	360
Sm	O	3.915	3.890	3.784	57.63	120–200	280	370
Eu	O	3.910	3.884	3.775	57.33	150–240	280	350
Gd	O	3.909	3.876	3.768	57.09	225	280	360
Tb	O	3.911	3.872	3.760	56.94	245	285	337
Dy	T	3.889		3.756	56.81		265	330
Y	T	3.884		3.748	56.54		250	

^aC - cubic, T - tetragonal, O - orthorhombic.

^bFor SmBaC and EuBaC the ranges of T_i are given (see text).

^cFor NdBaC two Curie temperatures are presented (see text).

electrons. However, PrBaC shows a much less magnetization at 4.2 K, approximately 5 emu/g or $0.2\mu_B$ per formula unit (Fig. 1). Magnetization increases as temperature increases up to 100 K, likely due to Pr-sublattice contribution. The drops of the magnetization of NdBaC at $T_{C1}=140 \text{ K}$ and $T_{C2}=260 \text{ K}$ are probably caused by the phase transition into the paramagnetic state in different magnetic phases. The fraction of the magnetic phase with higher T_C increases markedly in SmBaC and especially in EuBaC compounds (Fig. 1). The large temperature hysteresis of FC magnetization of EuBaC (Fig. 1) is associated with a first-order magnetic phase transition. Such a transition is much more pronounced in the

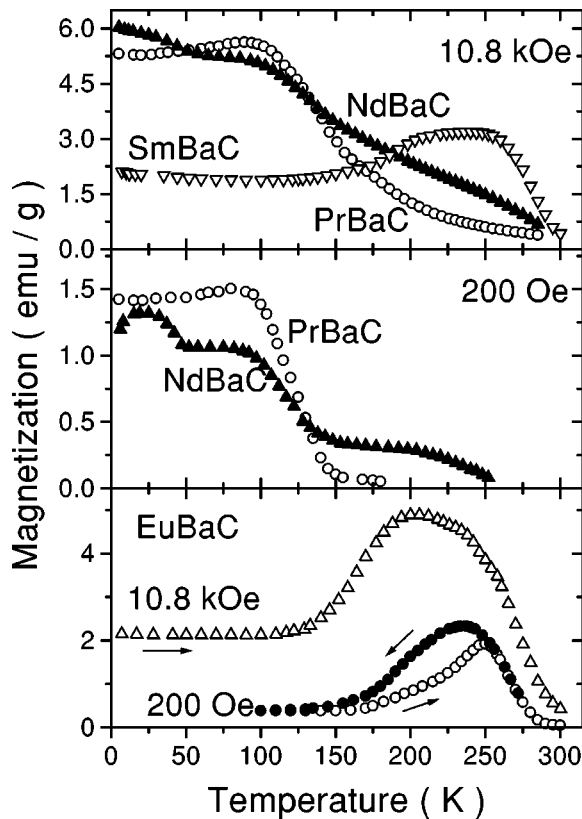


FIG. 1. Temperature dependence of FC magnetization for $RBaC$ ($R=\text{Pr, Nd, Sm, Eu}$) at the field of 10.8 kOe and 200 Oe.

TbBaC compound (Fig. 2). The temperature T_i , at which the first-order magnetic phase transition starts, decreases strongly with the increase of an external magnetic field. TbBaC also exhibits an anomalous behavior of the magnetization near $T_C=285 \text{ K}$ and $T_M=337 \text{ K}$ (Fig. 2). T_C is just the Curie temperature, because $M(H)$ dependences are linear above 285 K.

The magnetization behavior of $RBaC$ ($R=\text{Gd, Dy, Y}$) is presented in Fig. 3. GdBaC exhibits transitions at $T_i=225 \text{ K}$ and $T_C=280 \text{ K}$, whereas the magnetic behavior of DyBaC is more complicated. FC magnetization in the field of 200 Oe shows a minimum at $T=45 \text{ K}$, and a large temperature hysteresis within the temperature range of 70–200 K. The magnetic susceptibility of YBaC is much less than that for $RBaC$ ($R=\text{Pr - Dy}$). ZFC and FC magnetizations do

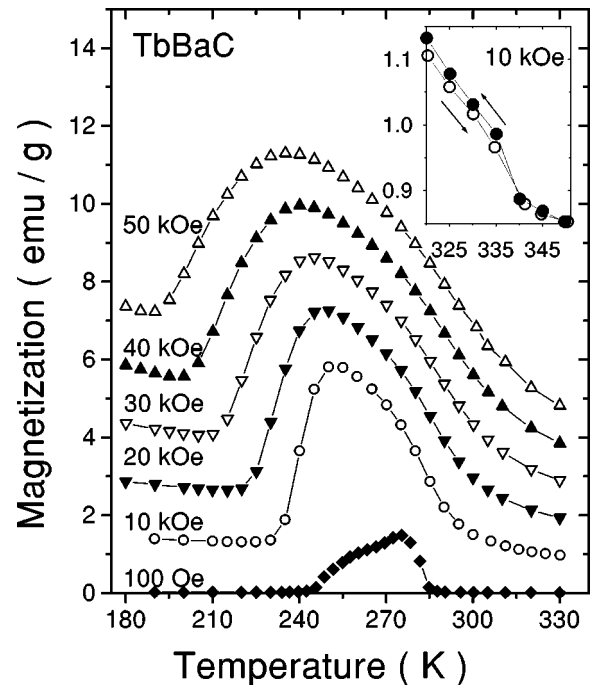


FIG. 2. Temperature dependence of FC magnetization of TbBaC on heating at various fields. The inset shows magnetization behavior on heating and on cooling in the temperature range 320–350 K at the field of 10 kOe.

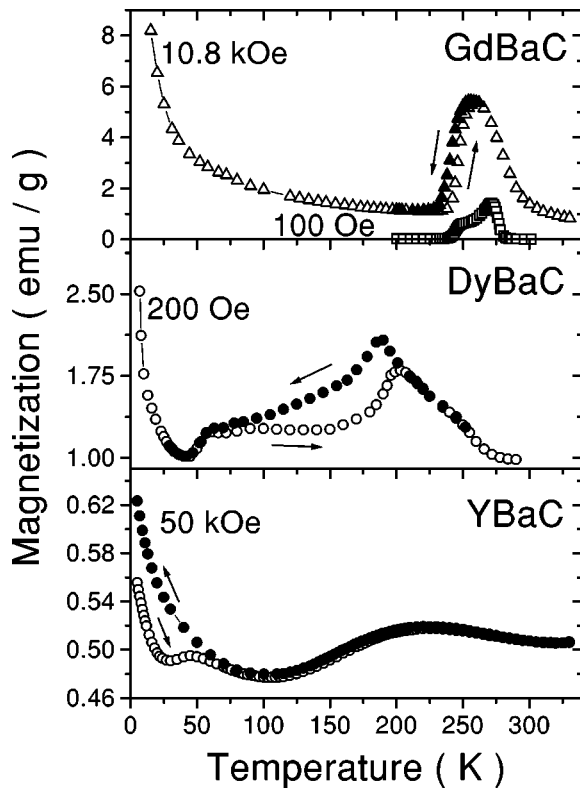


FIG. 3. Temperature dependence of FC magnetization for RBaC ($R = \text{Gd, Dy, Y}$).

not coincide below 250 K even in the magnetic field of 50 kOe, apparently due to a large magnetic anisotropy. ZFC magnetization of YBaC shows two peaks: the first one at 50 K and the broad second one in the vicinity of 225 K. Below 60 K the difference between ZFC and FC magnetizations increases sharply. It is worth noting that the magnetization at 330 K (paramagnetic regime) is larger than at 100 K.

The magnetic phase transitions are accompanied by anomalies in the electrical resistivity (Fig. 4). Below T_i , RBaC ($R = \text{Sm} - \text{Tb}$) are semiconductors with a small activation energy. At around T_i the resistivity drops, indicating a phase transition. The temperature T_i depends strongly on the external magnetic field, thus leading to a giant magnetoresistance. This effect is very pronounced in TbBaC. At around T_C the slope of the $\rho(T)$ curve changes due to another magnetic phase transition. The transition at T_C is accompanied by a peak of the magnetoresistance for a number of orthocobaltites (Fig. 4). Near T_M the resistivity falls from $10^{-2} \Omega \text{ cm}$ to $10^{-3} \Omega \text{ cm}$. The metallic phase of LaCoO_3 exhibits the same magnitude of resistivity.³ Above T_M the resistivity changes very slowly with temperature.

The field dependence of the magnetoresistance for TbBaC at various temperatures is shown in Fig. 5 (upper panel). The magnetoresistance increases steeply above the critical field corresponding to the transition into a state with spontaneous magnetization. The critical field depends linearly on temperature. The results of the magnetization measurements correspond to the magnetoresistance data.

It is worth pointing out that the spontaneous magnetization of $R_{1-x}\text{Ba}_x\text{CoO}_3$ ($R = \text{lanthanide ion}$, $0.4 \leq x \leq 0.66$) solid solutions is maximal for $x = 0.5$ compounds. The deviation from the ideal ratio $R:\text{Ba}$ to 1:1 leads to the broadening

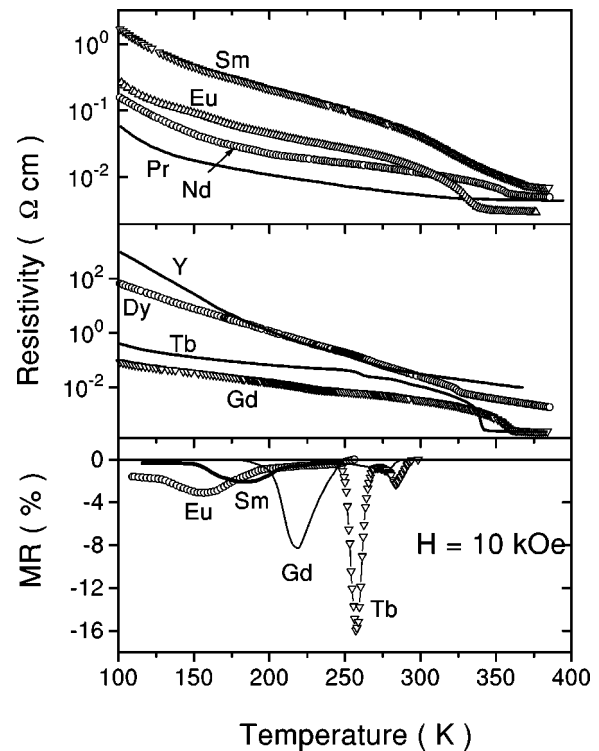


FIG. 4. Temperature dependences of resistivity (top and middle panels) and magnetoresistance $MR = [R(10 \text{ kOe}) - R(0)] \times 100\% / R(0)$ (bottom panel) for RBaC.

of the transition at T_i , whereas the transition at T_M is vanished. However, the Curie temperature T_C depends slightly on a barium content. The samples reduced in vacuum do not show a spontaneous magnetization and insulator-metal transition. They are semiconductors with a relatively large activation energy of charge carriers. The XRD studies revealed at T_M an abrupt increase of the unit-cell parameters a , c , and a decrease of the parameter b as the temperature increases. For TbBaC at 300 K the a , b , c parameters are equal to 3.911, 3.872, 3.760 Å, respectively, whereas at 350 K they are 3.932, 3.846 and 3.852 Å. The transition occurs without change of orthorhombic symmetry, and the unit-cell volume of the high-temperature phase was shown to be smaller as compared to the low-temperature one (approximately 0.05%). According to the dilatometric studies, the temperature hysteresis reaches 10 K.

The magnetic properties of the orthocobaltites with the perovskite structure depend upon the spin states of Co^{3+} and Co^{4+} , whether they are in the low-, intermediate-, or high-spin states. The magnetic properties of $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ are similar to those for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ where the ferromagnetic intermediate spin state with itinerant $3d$ electrons is realized.³ In our opinion, the most appropriate explanation of magnetic and electrical properties of the RBaC series could be based on the assumption that cobalt ions are in the low-spin state and $3d$ electrons are itinerant, due to a strong hybridization of t_{2g} orbitals of cobalt and $2p$ orbitals of oxygen. This assumption is in agreement with both the strong dependence of T_i on the external magnetic field and low spontaneous magnetization of the samples. It was established that the samples of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\gamma}$ prepared in air were characterized with the magnitude of γ up to 0.12.^{3,11} Accord-

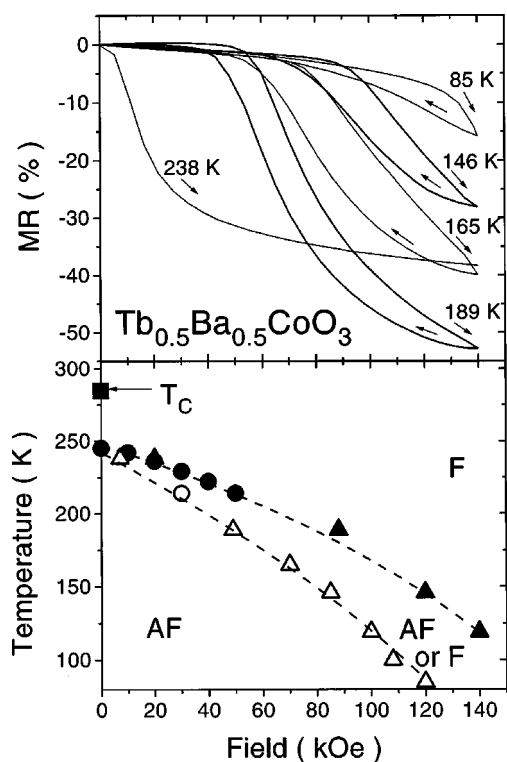


FIG. 5. Field dependence of magnetoresistance $MR = [R(10 \text{ kOe}) - R(0)] \times 100\% / R(0)$ at various temperatures (top panel) and the H - T phase diagram (bottom panel) for TbBaC (AF - antiferromagnet, F - ferromagnet, circle - data obtained from magnetization measurement, triangle - data obtained from magnetoresistance measurement, closed symbols - finish of the transition from AF to F, open symbols - from F to AF).

ing to the thermogravimetric analysis data, the true chemical formula of TbBaC is $\text{Tb}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.87}$. Hence, the average magnetic moment can be calculated to be $0.25\mu_B$ per formula unit at $T=0$, whereas the observed magnetic moment at 250 K is close to $0.22\mu_B$ per formula unit. We suppose

that the sign of exchange interactions depends strongly on interatomic distances, thus leading to the antiferromagnetic-ferromagnetic transition at T_i . The chemical inhomogeneity (associated apparently with a complex distribution of oxygen vacancies and rare-earth ions over the crystal lattice) leads to the broadening transition at T_i , that occurs in a wide temperature range in $R\text{BaC}$ ($R=\text{Nd, Sm, Eu}$) compounds. The low-temperature phase of the $R\text{BaC}$ ($R=\text{Sm, Eu, Gd, Tb, Dy}$) specimens is dominantly antiferromagnetic (Fig. 1). The drop of the magnetization observed in YBaC originates apparently from an oxygen deficit increasing with decreasing lanthanide ionic radii. In this compound the dependence of magnetization from magnetic prehistory exists at temperatures up to 250 K, being comparable to that for rare-earth compounds. The anomalous behavior could be attributed to the freezing of magnetic moments of clusters associated with microdomains with a different content of Dy ions. Relatively high magnetic susceptibility in a paramagnetic phase indicates a possible spin state transition.

The insulator-metal transition at T_M leads to decreasing magnetic susceptibility (Fig. 2). So we suppose that this transition is not dominantly magnetic in origin. The oxygen content in the TbBaC sample corresponds to the chemical formula $\text{Tb}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-1/n}$, where $n=8$. From this point of view the transition at T_M could be attributed to oxygen vacancy ordering. Most likely, the transition at T_M leads to an overlapping of π^* narrow band and wide valence one. This assumption is supported by spectroscopic studies of LaCoO_3 indicating a small energy difference between the p band of ligand anions and the upper Hubbard band of cobalt metal.¹² We suppose that at T_M some of the Co-O distances decrease abruptly because the unit-cell parameter b decreases markedly.

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