Phase Transitions in the $Gd_{0.5}Ba_{0.5}CoO_3$ Perovskite

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Magnetization measurements of a $Gd_{0.5}Ba_{0.5}CoO_3$ perovskitelike compound have revealed an anomalous behavior at $T_i = 240$ K and $T_C = 277$ K that corresponds to appearing and disappearing spontaneous magnetization. The transition at T_i is accompanied by the jump of conductivity and a giant magnetoresistance. Below T_i, $Gd_{0.5}Ba_{0.5}CoO_3$ exhibits metamagnetic behavior. At about $T_M = 370$ K, a transition from a semiconductive to a quasimetallic state has been observed. It is supposed that a ferromagnetic low-spin cobalt state occurs in the temperature range between T_i and T_C. [S0031-9007(98)05789-5]

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$La_{1-x}A_xCoO_3$ (A = Sr, Ba) cobaltites are of considerable interest because of the peculiar way their magnetic and transport properties change with composition and temperature [1–5]. While $LaCoO_3$ shows a high resistivity and antiferromagnetic exchange interaction, the $La_{1-x}Sr_xCoO_3$ solid solutions evolve toward a ferromagnetic intermediate-spin state with itinerant $3d$ electrons as x increases [4–7]. The composition with $x = 0.5$ is a metallic ferromagnet with a moment approximately $1.5\mu_B$ per formula unit and the Curie temperature of 220 K. The size of the Ln ion is well known to influence strongly the magnetic and transport properties of the compounds with the perovskite structure. However, the data on cobaltites of rare earth elements doped by Ba or Sr are quite limited. The studies of $Ln_{1-x}Sr_xCoO_3$ (Ln = Pr, Nd, Sm) 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 [3].

This paper reports the discovery of a new family of magnetic semiconductors exhibiting both antiferromagnet-ferromagnet and metal-insulator first-order phase transitions. The nature of these transitions and properties of $Gd_{0.5}Ba_{0.5}CoO_3$ compound differs from those observed in manganites as well as other related materials studied earlier. We have examined structural, magnetic, and transport properties of the $Gd_{1-x}Ba_xCoO_3$ perovskites in order to investigate the cobaltite properties as a function of lanthanide ionic radii and a variation of the spin state of the cobalt ions with temperature. We have found that $Gd_{0.5}Ba_{0.5}CoO_3$ exhibits a first-order phase transition accompanied by dramatic changes of magnetic properties and an anomalous behavior of electrical transport at about $T_i = 240$ K.

The studied ceramic samples were prepared by a solid state reaction. Mixtures of Gd_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 a rate of 100 K/h. This process was repeated in order to obtain a homogeneous solid solution. 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 symmetry. For $Gd_{0.5}Ba_{0.5}CoO_3$ the lattice parameters were calculated to be $a = 3.909$ Å, $b = 3.876$ Å, and $c = 3.768$ Å. As oxygen content in the specimens was not determined, we use hereafter the chemical formula $Gd_{0.5}Ba_{0.5}CoO_3$. One should note, however, that oxygen nonstoichiometry of the oxide is not zero.

Magnetic properties were studied using a SQUID magnetometer (MPMS 5, Quantum Design) in magnetic fields from 100 Oe to 50 kOe in the temperature range 4.2–330 K. The measurements were performed with zero-field-cooled (ZFC) and field-cooled (FC) samples (in the latter case, measurements were carried out both on cooling and on heating). The electrical resistance was measured in the range $77 \leq T \leq 400$ K by a standard four-probe method.

The temperature dependences of FC magnetization for $Gd_{0.5}Ba_{0.5}CoO_3$ in the fields of 100 Oe, 10.85 kOe, and 50 kOe at heating and cooling are shown in Fig. 1. Taking these curves (Fig. 1) into consideration, one can note some features and distinguish two critical temperatures: (1) A significant increase in magnetization occurs at a low temperature which could be attributed to the paramagnetic contribution of a Gd sublattice. (2) A sharp increase in magnetization is observed at $T_i = 240$ K in the field of $H = 100$ Oe. T_i decreases to 180 K when the field of $H = 50$ kOe is applied (Fig. 1). The transition is accompanied by a temperature hysteresis (Fig. 1). (3) The drop of magnetization at about $T_C = 277$ K (Fig. 1) is caused by another phase transition. Such an anomaly is much more pronounced in low magnetic fields.

Figure 2 demonstrates further evidence of the two magnetic phase transitions. According to the results obtained, the magnetic phase transition can be induced by the field.

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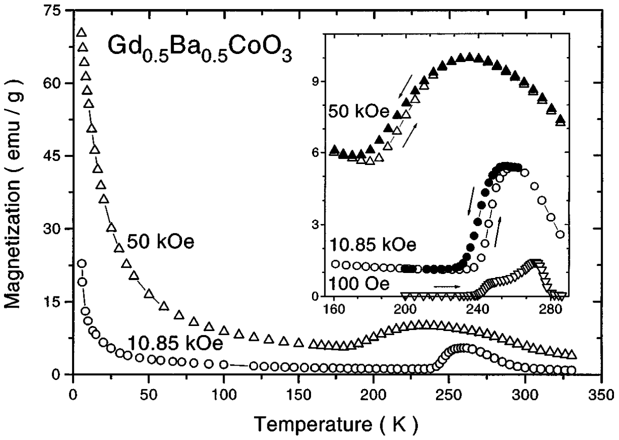

FIG. 1. Temperature dependence of FC magnetization for $Gd_{0.5}Ba_{0.5}CoO_3$ at 100 Oe, 10.85 kOe, and 50 kOe. The inset shows the temperature hysteresis of the magnetization.

At $T \leq 150$ K, the $M(H)$ curve shows a behavior typical of either paraferromagnets or antiferromagnets. The noticeable feature of the $M(H)$ curve at 220 and 225 K is the appearing anomaly at magnetic field H_i, which indicates the metamagnetic phase transition. The transition is accompanied by the field hysteresis (Fig. 2). The spontaneous magnetization develops above 240 K (Fig. 2). The high paraprocess within the temperature range of $240 \leq T \leq 277$ K is probably a result of the Gd-sublattice contribution. The coercive field decreases rapidly with increasing temperature (420 Oe at $T = 250$ K, and 45 Oe at $T = 271$ K). The magnetization versus temperature curve at $T = 250$ K shows rather low spontaneous magnetization, approximately 5 emu/g.

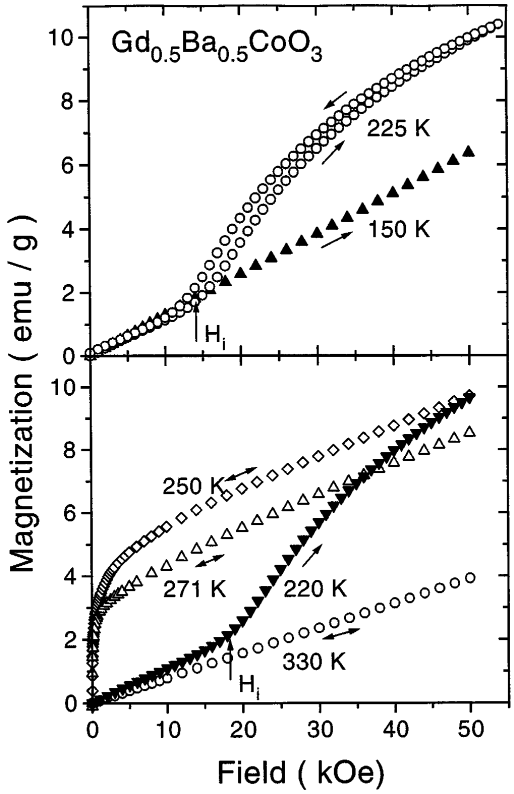

FIG. 2. Field dependence of the magnetization for $Gd_{0.5}Ba_{0.5}CoO_3$ at various temperatures.

The magnetic phase transitions are accompanied by anomalies in the transport properties. The data on electrical resistance are shown in Fig. 3. One can select a number of characteristic steps of the temperature dependence of resistance:

(i) At temperatures below $T_i = 240$ K, $Gd_{0.5}Ba_{0.5}CoO_3$ is a semiconductor with a low activation energy. There is no appreciable magnetoresistance.

(ii) Between 240 and 250 K, the resistance decreases sharply indicating the phase transition. The giant magnetoresistance effect develops at temperatures above 240 K. In this paper, the magnetoresistance is defined as $MR(H) = [\rho(H) - \rho(0)] \times 100\%/\rho(0)$. Magnetoresistance is observed to reach a maximum at $T = 250$ K (15% in the field of 10 kOe) and then decreases rapidly.

(iii) At about 275 K, the slope of the $\rho(T)$ curve changes due to another magnetic phase transition. Therefore, no magnetoresistance peak is observed.

(iv) In the temperature range $360 \leq T \leq 370$ K, the resistivity falls rapidly down to 10^{-3} Ω cm. This value is typical of the metallic $La_{0.5}A_{0.5}CoO_3$ (A = Ba, Sr) compounds [4] and the high-temperature metallic phase of $LaCoO_3$ [1–3].

Figure 4 shows the field dependences of the magnetoresistance ratio at different temperatures (top panel) and the H-T phase diagram (bottom panel) of $Gd_{0.5}Ba_{0.5}CoO_3$. The sharp increase of magnetoresistance is associated with the first-order phase transition into the state with spontaneous magnetization. The external field of 140 kOe leads to decreasing T_i down to 85 K.

The XRD studies revealed, at T_M, an abrupt increase of the a and c unit cell parameters and a decrease of the b parameter with increasing temperature. At room temperature, the a, b, c parameters are equal to 3.909,

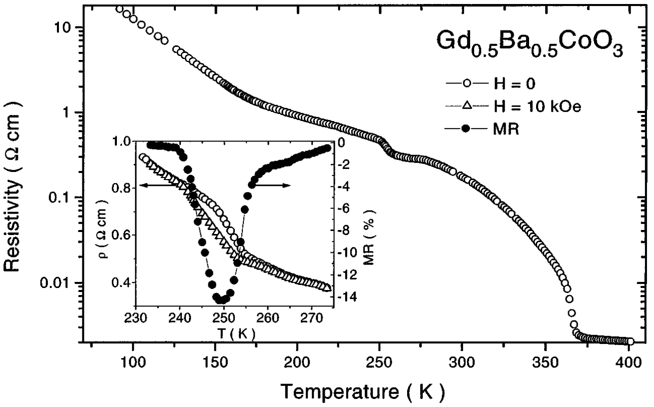

FIG. 3. Temperature dependence of the resistivity for $Gd_{0.5}Ba_{0.5}CoO_3$. The inset shows the resistivity and the magnetoresistance at $H = 10$ kOe as a function of temperature at about T_i.

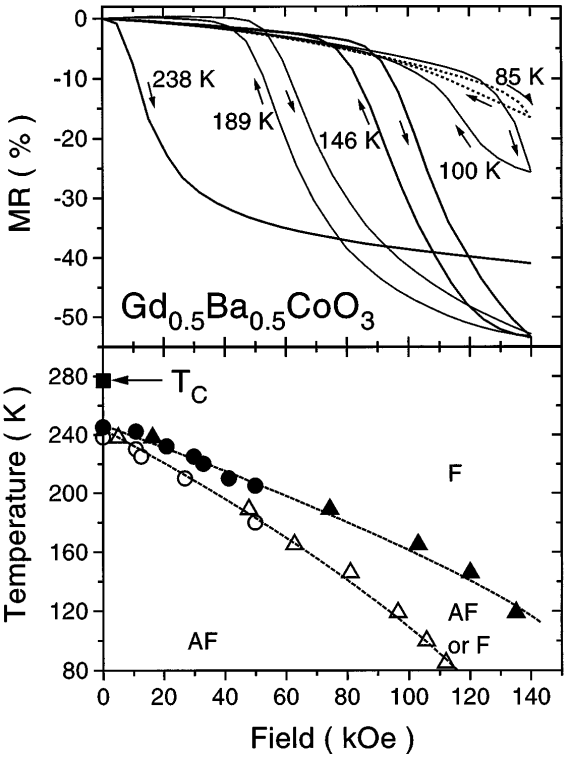

FIG. 4. Field dependence of magnetoresistance at various temperatures (top panel) and the *H*-*T* phase diagram (bottom panel) for $Gd_{0.5}Ba_{0.5}CoO_3$ (AF: antiferromagnet; F: ferromagnet; circles: data obtained from magnetization measurement; triangles: data obtained from magnetoresistance measurement; closed symbols: the end of the transition from AF to F; open symbols: from F to AF).

3.876, and 3.768 Å, respectively, whereas at 380 K they are 3.925, 3.859, and 3.782 Å. The unit cell volume of the high-temperature phase was shown to be larger as compared to the low-temperature phase (approximately 0.2%). The transition occurs without changes of orthorhombic symmetry.

The phase transitions at T_i and T_M are much less pronounced in the solid solutions with a deviation from an ideal ratio Gd:Ba to be 1:1 (Fig. 5). Such oxide compounds were found to exhibit the spontaneous magnetization within the whole temperature range 4.2–277 K. It should also be pointed out that the spontaneous magnetization of $Gd_{1-x}Ba_xCoO_3$ reaches a maximum for $x = 0.5$, whereas the temperature T_C depends slightly on composition.

The annealing of $Gd_{0.5}Ba_{0.5}CoO_3$ sample in air at 1100 K leads to decreasing T_i, whereas the specimen reduced in vacuum does not exhibit the spontaneous magnetization within the temperature range of 4.2–300 K.

The magnetic properties of the cobaltites 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 state. They also depend on the indirect exchange interactions between the cobalt ions through an intermediate oxygen ion. Because of this interaction, the Co^{3+}-O-Co^{4+} systems show different magnetic properties. In the $Ln_{1-x}A_xCoO_3$ (Ln = La, Pr, Nd) the exchange of Co^{3+}-O-Co^{4+} is ferromagnetic, whereas for semiconducting $Gd_{0.5}Ba_{0.5}CoO_3$ the situation is more complicated (Figs. 1 and 2).

The anomalous behavior of magnetization at about 277 K could be attributed to a collapse of a long-range magnetic order. The spontaneous magnetization developing above 240 K is too low for the ferromagnetic ordering of localized magnetic moments of the Co^{3+} and Co^{4+} ions. Therefore, the $Gd_{0.5}Ba_{0.5}CoO_3$ above 240 K can be expected to be ferromagnetic or nonhomogeneous magnetic. In the first case, the spontaneous magnetization arises from an antialignment of Co^{3+} and Co^{4+} ion magnetic moments. However, according to the Goodenough-Kanamori

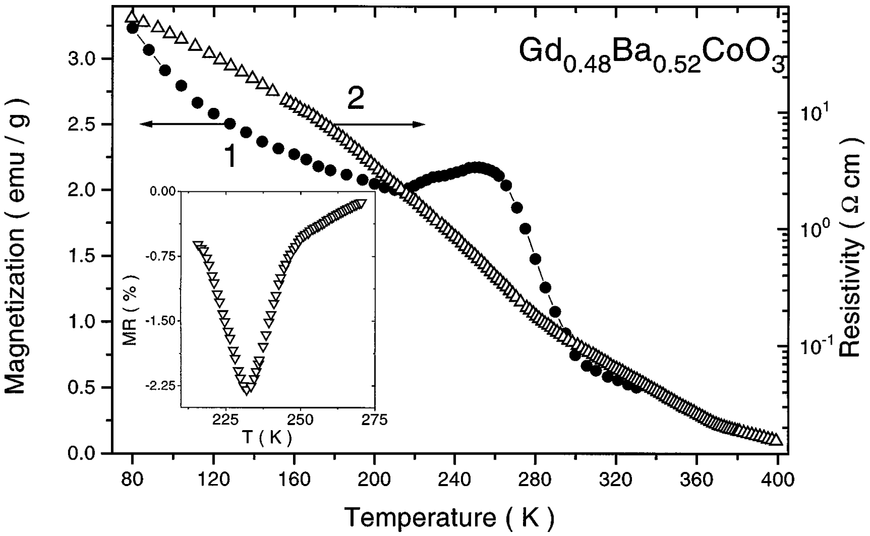

FIG. 5. Temperature dependence of the magnetization at 10.85 kOe (1), resistivity (2), and magnetoresistance at 10 kOe (inset) for $Gd_{0.48}Ba_{0.52}CoO_3$ composition.

rules, the Co^{3+}-O-Co^{4+} superexchange interaction should be ferromagnetic [8]. In the second case only a part (approximately 25%) of the sample is truly ferromagnetic, assuming the intermediate-spin state of Co^{3+} and Co^{4+} ions. Furthermore, the deviation from Gd:Ba ratio as 1:1 leads to decreasing of spontaneous magnetization. Such behavior cannot be explained adequately by the two-phase model.

In our opinion, the most appropriate explanation of magnetic and electrical properties of the $Gd_{0.5}Ba_{0.5}CoO_3$ compound could be based on the assumption that all of the $3d$ electrons of Co ions occupy a d_ε (π^*) band, which is equivalent to the low-spin configuration. It was established that $Ln_{0.5}Ba_{0.5}CoO_3$ nominal compositions exhibit oxygen nonstoichiometry increasing strongly with decreasing lanthanide ion size [5,9]. According to Refs. [5,9], the samples of $Ln_{0.5}Sr_{0.5}CoO_{3-\gamma}$ (Ln = La, Gd) prepared in air were characterized with the magnitude of γ up to 0.12. Assuming that the true chemical formula is $Gd_{0.5}Ba_{0.5}CoO_{2.9}$, the average magnetic moment can be calculated to be $0.3\mu_B$ per formula unit at $T = 0$, whereas the observed magnetic moment at 250 K is close to $0.23\mu_B$ per formula unit.

The metamagnetic transition in $Gd_{0.5}Ba_{0.5}CoO_3$ is very reminiscent of the charge-ordering transition in $Nd_{0.5}Sr_{0.5}MnO_3$ perovskite [10]. In both systems, a deviation from an ideal ratio rare earth to alkaline earth ion concentration as 1:1 leads to suppressing metamagnetic transition. However, in contrast to $Nd_{0.5}Sr_{0.5}MnO_3$ perovskite, the ferromagnetic phase of $Gd_{0.5}Ba_{0.5}CoO_3$ is not metallic. Both antiferromagnetic and ferromagnetic phases of $Gd_{0.5}Ba_{0.5}CoO_3$ exhibit semiconductive behavior with close-related activation energies of charge carriers. Therefore, there is no charge ordering in this compound.

The transition at T_i arises apparently from the inversion of an exchange interaction from antiferromagnetic to ferromagnetic on heating. We suppose that the low-spin state of the itinerant $3d$ electrons is also kept in the low-temperature phase because the activation energies of charge carriers are very close in both phases. The exchange interaction sign inversion may be a result of thermal expansion of the sample. Such a situation is realized in the Mn_2Sb compound studied in detail.

Most likely, the crystal-structure phase transition at T_M leads to the overlapping of π^* narrow bonds and the valence oxygen one. The spectroscopic studies of $LaCoO_3$ have revealed a small energy difference between the p band of ligand anions and upper Hubbard bands of cobalt metal [11]. We suppose that at T_M some of the Co-O distances decrease abruptly because the unit cell parameter b decreases significantly.

Recently, we found the antiferromagnet-ferromagnet as well as the metal-insulator transitions in the whole series $Ln_{0.5}Ba_{0.5}CO_{3-\gamma}$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy). Magnetoresistance in these compounds reaches up to 40% in the field of 1 T. A moderate replacement of Co by Fe leads to an increasing Curie point above room temperature.

The structural determination in a wide temperature range along with magnetic resonance studies may shed new light on the understanding of these new observations, and further studies are in progress.

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