ISSN 1063-7834, Physics of the Solid State, 2012, Vol. 54, No. 1, pp. 79–83. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.A. Dudnikov, D.A. Velikanov, N.V. Kazak, C.R. Michel, J. Bartolome, A. Arauzo, S.G. Ovchinnikov, G.S. Patrin, 2012, published in Fizika Tverdogo Tela, 2012, Vol. 54, No. 1, pp. 74–78.

MAGNETISM

Antiferromagnetic Ordering in REM Cobaltite $GdCoO_3$

V. A. Dudnikov[a,b], D. A. Velikanov[a,c], N. V. Kazak[a], C. R. Michel[d], J. Bartolome[e], A. Arauzo[f], S. G. Ovchinnikov[a,c], and G. S. Patrin[a,c]

[a] *Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences, Akademgorodok 50–38, Krasnoyarsk, 660036 Russia*

[b] *Reshetnev Siberian State Aerospace University, pr. im. Gazety "Krasnoyarskii Rabochii" 31, Krasnoyarsk, 660014 Russia*

[c] *Institute of Engineering Physics and Radio Electronics, Siberian Federal University, ul. Kirenskogo 28, Krasnoyarsk, 660074 Russia*

[d] *Departamenta de Fisica, Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Blvd. Marcelino García Barragán 1421, esq Calzada Olímpica, Guadalajara, Jalisco, C.P. 44430 Mexico*

[e] *Instituto de Ciencia de Materiales de Aragón, Consejo Superior de Investigaciones Científicas (CSIC)—Universidad de Zaragoza Departamento de Fisica de la Materia Condensada, C. María Luna 3, Zaragoza, 50015 Spain*

[f] *Servicio de Instrumentación Científica—Area de Medidas Fisicas, Universidad de Zaragoza, C. Pedro Cerbuna 12, Zaragoza, 50009 Spain*

e-mail: slad63@yandex.ru

Received June 9, 2011

Abstract—Temperature and magnetic-field dependences of the static magnetization of polycrystalline cobaltite $GdCoO_3$ have been measured. The magnetic properties of the $GdCoO_3$ sample have been studied in the paramagnetic and antiferromagnetic states. The magnetic phase diagram has been constructed. The exchange field between the Gd–Gd sublattices and the anisotropy field have been estimated.

DOI: 10.1134/S106378341201009X

1. INTRODUCTION

The nature and the degree of stability of electronic states in cobalt oxide compounds have been discussed up to now. $LnCoO_3$-based rare-earth cobaltites with the valence formula $Ln^{3+}Co^{3+}O_3^{2-}$, where Ln = La, lanthanides, or yttrium, can be considered as model materials for studying the role of strong electron correlations, hybridization, and also charge, orbital, and spin ordering in the formation of electronic states. In these oxides, the cobalt ion has no certain multiplicity and can have various spin states: low-spin (*LS*, $S = 0$, $t_{2g}^6\varepsilon_g^0$), intermediate-spin (*IS*, $S = 1$, $t_{2g}^5\varepsilon_g^1$), or high-spin *HS*, $S = 2$, $t_{2g}^4\varepsilon_g^2$) states [1]. The competition between these states leads to specific features of the magnetic, electrical, and structural properties of the cobaltites.

Like many other oxides, rare-earth cobaltites are characterized by oxygen nonstoichiometry that brings about not only various spin states at a constant valence, but also various valences, which hampers studying these compounds to a greater degree. At the present time, it is reliably established that cobalt ions in $LaCoO_3$ are in a low-spin nonmagnetic ground state at a zero temperature [2]. This state is separated from the magnetic state by a narrow spin gap of ~150 K, which leads to the magnetic properties at $T > 50$ K.

The *LS* state in these states can be stabilized by decreasing the Co–O bond length that can be achieved by a decrease in temperature, by external pressure [3–5], or replacing of lanthanum by other rare-earth element with a smaller ionic radius [6]. This exactly takes place in $GdCoO_3$, where Co^{3+} has $S = 0$ and $L = 0$ at low temperatures.

It is of interest to study the contribution of the magnetism of rare-earth elements themselves to the physical properties of cobaltites in which lanthanum is replaced by other rare-earth element, along with the problem of the spin state of the Co^{3+} ions. When there are no magnetic moments of the Co^{3+} ions, the magnetism of $GdCoO_3$ at low temperatures can be due to ordering the magnetic moments of Gd. The magnetic properties of $GdCoO_3$ in the paramagnetic region at $T > 4.2$ K are described in [7, 8] where the paramagnetic Curie temperature was estimated to be $\Theta_C = -6$ K, but no antiferromagnetic state was achieved in the temperature range under study. However, the transition of $GdCoO_3$ to the antiferromagnetic state at $T_N = 3.05$ K was indicated in [9], but this phenomenon was not considered in detail.

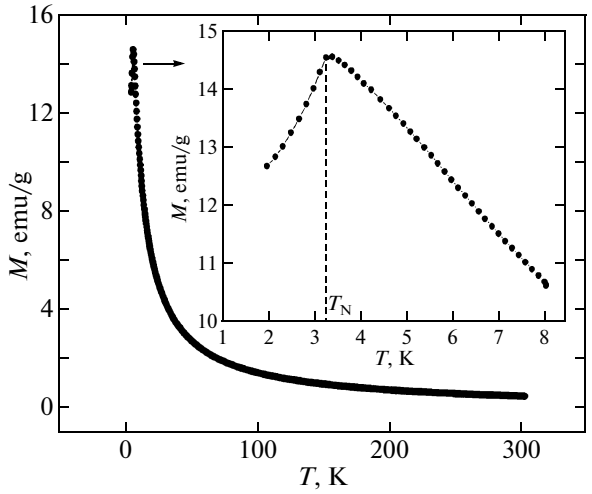

Fig. 1. Temperature dependence of the magnetization of $GdCoO_3$ measured at $H = 5$ kOe. The inset shows the $M(T)$ curve segment in the range 2–8 K.

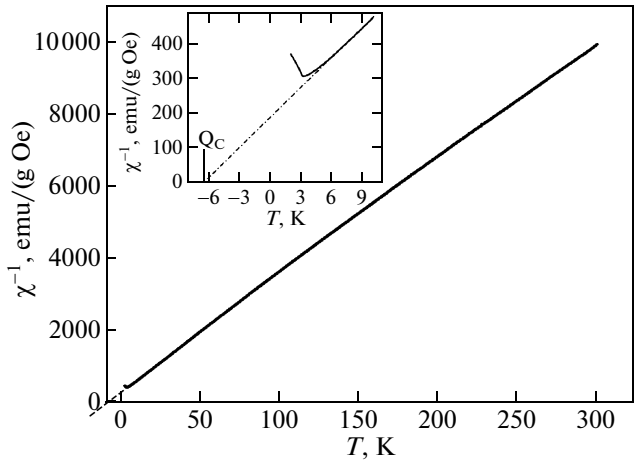

Fig. 2. Temperature dependence of the reciprocal of the magnetic susceptibility for $GdCoO_3$ measured in magnetic field of 5 kOe. The inset shows the dependence $\chi^{-1}(T)$ in the range 2–10 K.

In this work, the magnetic properties of polycrystalline $GdCoO_3$ at temperatures $T \geq 2$ K have been studied in more detail. We have also been studied the transition to the antiferromagnetic state and the spin-oriented transition in an external magnetic field.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The polycrystalline $GdCoO_3$ samples were prepared by the solution sol–gel method [10], in which stoichiometric amounts of cobalt and gadolinium nitrates were dissolved in deionized water and then were dried at a temperature of 90°C for 6 h. The thus-prepared powders were annealed at a temperature of 300°C in air, were pressed into pellets 12 mm in diameter, and were subjected to repeated annealing. We measured the temperature dependences of the static magnetization in the temperature range from 2 to 300 K and magnetic-field dependences of the magnetization in magnetic fields to 50 kOe at various temperatures using a Quantum Design MPMS-XL SQUID magnetometer at the Joint Usage Center of the Siberian Federal University. The crystal structure was studied at room temperature using a DRON-4 diffractometer in [7].

For comparison, we also use the results of the magnetic measurements performed on polycrystalline $GdCoO_3$ samples obtained by solid-phase synthesis described in [9].

3. EXPERIMENTAL RESULTS AND DISCUSSION

The X-ray diffraction data show that the $GdCoO_3$ samples under study have the rhombohedrally distorted perovskite-type structure with space group P_{bnm} which is typical of compounds of the $LnCoO_3$ series. The lattice parameters correspond to the data available in the literature [11].

Figure 1 shows the temperature dependence of the magnetization $M(T)$ of the $GdCoO_3$ sample measured in a magnetic field of 5 kOe.

The magnetization increases monotonically as temperature decreases. The $M(T)$ curve has a maximum near 3 K that can be due to a transition to the antiferromagnetic state. We found that $T_N = 3.3$ K.

Figure 2 depicts the temperature dependence of the reciprocal of the magnetic susceptibility $\chi^{-1}(T)$. At high temperatures, the $\chi^{-1}(T)$ curve is well approximated by a linear dependence according to the Curie–Weiss law:

$$\chi = \frac{C}{T + \Theta_C}, \quad (1)$$

where C is the Curie constant, Θ_C is the asymptotic Curie temperature. The quantity $\Theta_C \approx -6.4$ K that agrees well with the data of [7–9].

At temperatures higher than 6 K, $C \approx 7.84$ cm^3 K/mol, which corresponds to the effective magnetic moment $\mu_{eff} \approx 7.91\mu_B$ per formula unit whose value almost coincides with the theoretical value $\mu_{eff} \approx 7.94\mu_B$ for free Gd^{3+} ion, but it is somewhat higher than that in [7, 8].

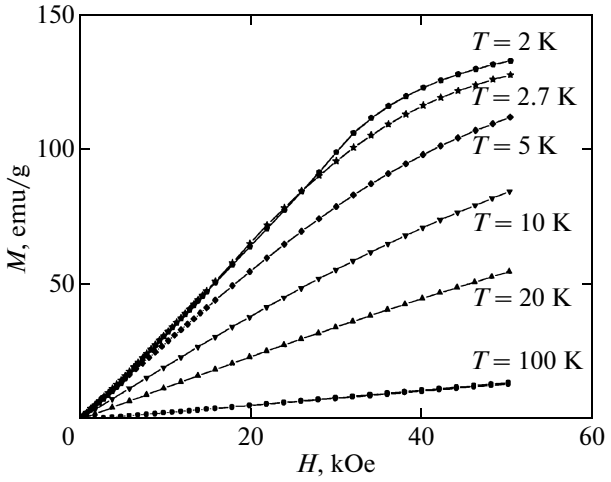

Fig. 3. Magnetization curves of $GdCoO_3$ measured at various temperatures.

Using the medium-field theory, we estimated the exchange interaction $J_{Gd-Gd}/k \approx -0.11$ K by the formula

$$kT_N = \frac{zJS(S+1)}{3}, \quad (2)$$

where z is the number of the nearest neighbors, $S = 7/2$ for Gd^{3+}, k is the Boltzmann constant, and J is the exchange integral.

Figure 3 shows the isotherms of the magnetization of $GdCoO_3$ measured at various temperatures. At $T =$ 2.0 and 2.7 K, the magnetization curves have inflections in weak fields (Figs. 3, 4); the inflection can be interpreted as a spin-reorientation process. At $T = 2$ K, the spin-flop-transition field H_{SF} can be determined as a point of intersection of approximations of the rectilinear sections of isotherms of the magnetization (Fig. 4a). In this case, $H_{SF} = 4.7$ kOe. At $T = 2.7$ K, the thus-found similar value is $H_{SF} = 2.8$ kOe. Figure 4b shows, for comparison, the curve of magnetization of the $GdCoO_3$ sample prepared by solid-phase synthesis. The magnetic properties of the $Gd_{1-x}Ca_xCoO_3$ system are described in [9]; however, the spin-flop transition in undoped $GdCoO_3$ sample was not discussed in [9]. We see that the spin-flop transition takes place in $GdCoO_3$ samples prepared by various technologies. The transition fields H_{SF} are different, which is likely due to differences in anisotropy related to the sample microstructures. It is seen that the spin reorientation is a smeared process; and it is likely related to the fact that the measurements were carried out on polycrystalline samples, and the magnetization is that averaged over all directions.

Figure 3 shows that, at temperatures higher than 5 K, the field dependences of the magnetization have

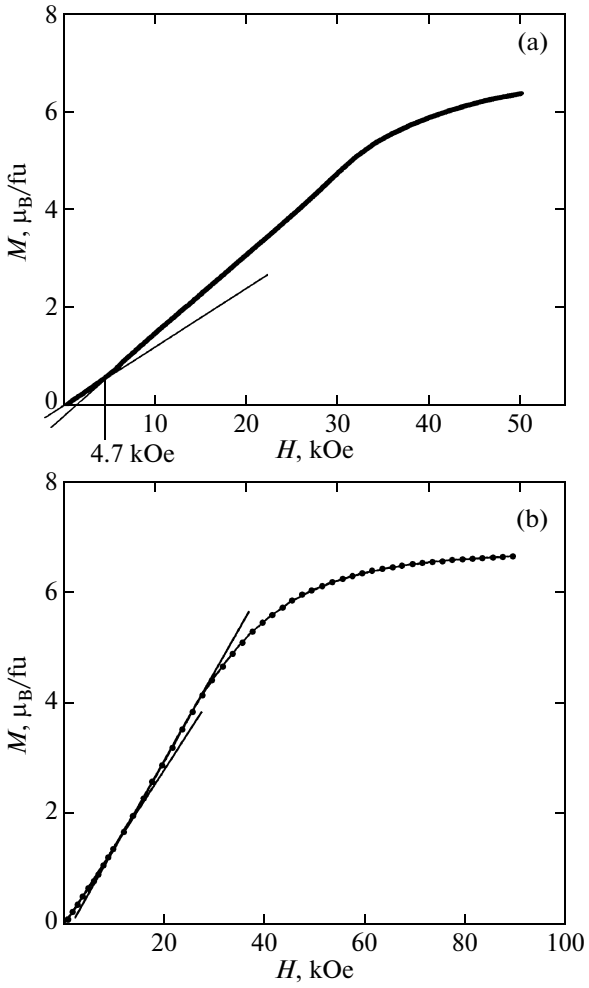

Fig. 4. Magnetization curves of $GdCoO_3$ measured (a) at $T = 2$ K for the sample prepared by the sol–gel method and (b) at $T = 25$ K for the sample prepared by the solid-phase method. $H_{SF} = 12$ kOe.

no inflections characteristic of the spin-reorientation process, and this fact corresponds to the paramagnetic behavior of $GdCoO_3$.

Figure 5 depicts the temperature dependences of the magnetization measured over a wide field range of 5–50 kOe. It is seen that the maxima in the $M(T)$ curves corresponding to the Néel temperatures are shifted toward lower temperatures with increasing field.

As a result, we obtained the magnetic phase diagram of $GdCoO_3$ (Fig. 6) that demonstrates the field dependence of the Néel temperature $T_N(H)$ and the spin-flop transition temperature $T_{SF}(H)$.

In the mean-field approximation, the magnetization of a system with one type of spins is known to be [12]

$$M_Z = Ng\mu_B\langle S^Z\rangle, \quad (3)$$

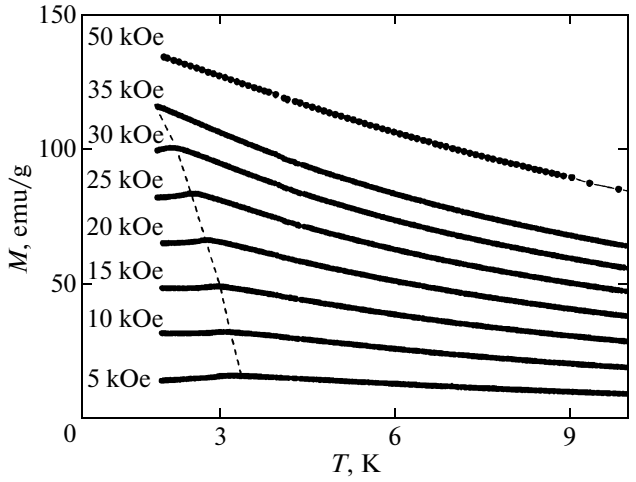

Fig. 5. Temperature dependences of the magnetization of $GdCoO_3$ measured in various magnetic fields. The dashed line shows the shift of the Néel temperature with increasing magnetic field.

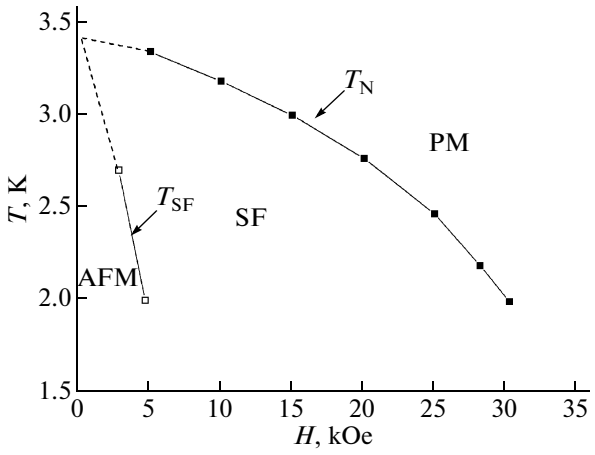

Fig. 6. Field dependence of the Néel temperature T_N and the spin-flop transition temperature T_{SF}. AFM is the antiferromagnetic region, PM is the paramagnetic region, and SF is the spin-flop transition region.

where $\langle S^Z \rangle = SB_S(Sy)$ is the average magnetic moment and

$$y = \frac{g\mu_B H + k(0)\langle S^Z \rangle}{kT}. \quad (4)$$

In the nearest neighbor approximation, $k(0) = Iz$. As a result, we have $M_Z = Ng\mu_B SB_S(Sy)$, where $B_S(Sy)$ is the Brillouin function, N is the number of atoms per volume unit, g is the g-factor, μ_B is the Bohr magneton, and k is the Boltzmann constant.

In strong magnetic fields at $T < T_N$, we have $B_S(Sy) \longrightarrow 1$, and the saturation magnetization (net magnetization) of sublattices in $GdCoO_3$ must be $M_{sat} = g\mu_B\langle S_Z \rangle = 2(7/2)\mu_B = 7\mu_B \approx 147.5$ emu/g; this value is much more than the maximum magnetization 134.05 emu/g measured at $H = 50$ kOe. This fact indicates that the state, in which the magnetizations of the Gd^{3+} sublattices become parallel (spin-flop transition), appears in higher fields, and, because of this, we did not obtain such a state.

Estimate the exchange field through the Néel temperature. In the mean-field theory,

$$\mu_B H_E(\mathrm{Gd}) = zIS = \frac{3kT_N}{S+1} = \frac{2}{3}kT_N. \quad (5)$$

Using known relationship $H_{SF} = \sqrt{2H_A \times H_E}$ that relates the exchange field H_E and the field of magnetic anisotropy H_A, we can estimate the value of the latter.

For $GdCoO_3$ prepared by the sol–gel method (Fig. 4a), $H_E = 34$ kOe, $H_A = 0.33$ kOe.

For the sample prepared by solid-phase synthesis (Fig. 4b), $H_E = 31$ kOe, $H_A = 2.3$ kOe.

These data can be compared with similar characteristics for $GdAlO_3$ single crystal [13] where $H_E = 21$ kOe, $H_A \approx 3$ kOe. The difference is related to polycrystalline character of our samples.

The samples prepared by solid-phase synthesis are more anisotropic as compared to the samples prepared by the sol–gel method.

4. CONCLUSIONS

The measured effective magnetic moment per formula unit $\mu_{eff} \approx 7.91\mu_B$ coincides practically with the theoretical value μ_{eff} for free Gd^{3+} ions. Once again, this fact confirms that Co^{3+} ions are in nonmagnetic state over the temperature range under consideration, and this result agrees with those reported in [7, 8, 14–16]. At temperatures below 3.4 K, the gadolinium sublattice undergoes the transition to the antiferromagnetic state.

The negative asymptotic Curie temperature is indicative of the antiferromagnetic character of the Gd–Gd exchange interaction. Small difference between $|\Theta_C|$ and T_N shows that the exchange field H_E and the anisotropy field H_A can be estimated with allowance for only sublattice interaction.

The very low Néel temperature $T_N \leq 3.5$ K brings about low critical fields: the spin-flop transition field is on an order of 10 kOe, the exchange field $H_E \approx 20$–35 kOe, and the anisotropy field is $H_A \approx 0.1$–3.0 kOe.

ACKNOWLEDGMENTS

The authors are grateful to N.B. Ivanova, A.I. Pankrats, and A.M. Vorotynov for the assistance in the discussion of the results.

This study was supported by the program of the Branch of Physical Sciences of the Russian Academy of Sciences "Strong Electron Correlations," the Russian Foundation for Basic Research (project no. 09-02-00171-a), and Federal Agency for Science and Innovations (grant no. MK-5632.2010.2).

REFERENCES

1. N. B. Ivanova, S. G. Ovchinnikov, M. M. Korshunov, I. M. Eremin, and N. V. Kazak, Phys.–Usp. **52** (8), 789 (2009).
2. S. Noguchi, S. Kawamata, and K. Okuda, Phys. Rev. B: Condens. Matter **66**, 094404 (2002).
3. T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B: Condens. Matter **67** 140401(1) (2003).
4. R. Lengsdorf, M. Ait-Tahar, S. S. Saxena, M. Ellerby, D. I. Khomskii, H. Micklitz, T. Lorenz, and M. M. Abd-Elmeguid, Phys. Rev. B: Condens. Matter **69** 140403 (2004).
5. G. Vanco, J. P. Rueff, A. Mattila, X. Nemeth, and A. Shukla, Phys. Rev. B: Condens. Matter **73**, 024434 (2006).
6. I. A. Nekrasov, S. V. Streltsov, M. A. Korotin, and V. I. Anisimov, Phys. Rev. B: Condens. Matter **68**, 235223 (2003).
7. N. B. Ivanova, N. V. Kazak, C. R. Michel, A. D. Balaev, S. G. Ovchinnikov, A. D. Vasil'ev, N. V. Bulina, and E. B. Panchenko, Phys. Solid State **49** (8), 1498 (2007).
8. N. B. Ivanova, N. V. Kazak, C. R. Michel, A. D. Balaev, and S. G. Ovchinnikov, Phys. Solid State **49** (11), 2126 (2007).
9. N. B. Ivanova, J. Bartolome, A. Figueroa, J. Blasco, A. Arauzo, M. S. Platunov, V. V. Rudenko, and N. V. Kazak, Solid State Phenom. **168–169**, 501 (2011).
10. Y. Tokura, Y. Okimoto, S. Yamaguchi, H. Taniguchi, T. Kimura, and H. Takagi, Phys. Rev. B: Condens. Matter: Condens. Matter **58**, 1699 (1998).
11. G. Demazeau, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **9**, 202 (1974).
12. C. V. Vonsovskii, *Magnetism* (Nauka, Moscow, 1971; Wiley, New York, 1974).
13. J. D. Cashion, A. H. Cooke, T. L. Thorp, and M. R. Wells, Proc. R. Soc. London, Ser. A **318**, 473 (1970).
14. K. Knizek, Z. Jirak, J. Hejtmanek, M. Veverka, M. Marysko, and G. Maris, Phys. Rev. B: Condens. Matter **71**, 054420 (2005).
15. M. Itoh, M. Mori, S. Yamaguchi, and Y. Tokura, Physica B (Amsterdam) **259–261**, 902 (1999).
16. M. Itoh, J. Mashimoto, S. Yamaguchi, and Y. Tokura, Physica B (Amsterdam) **281–282**, 510 (2000).

Translated by Yu. Ryzhkov