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ANISOTROPY OF THE MAGNETIC PROPERTIES OF GADOLINIUM NEAR THE CURIE POINT

K. P. BELOV, Yu. V. ERGIN, R. Z. LEVITIN, and A. V. PED'KO

Moscow State University

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The temperature dependence of the magnetic anisotropy energy is calculated on the basis of the magnetization curves of gadolinium single crystals, measured near the Curie point along the a and c axes. It is shown that the anomalous increase of the anisotropy constant upon approach to the Curie point and its strong dependence on the magnetic field can be attributed to the effect of the paraprocess. A noticeable anisotropy of the Curie point is observed in gadolinium single crystals.

1. Complicated anomalies were observed in the temperature variation of the electric resistivity, thermal expansion, magnetostriction, and other properties of gadolinium near the Curie point. These anomalies differ strongly in their character from those measured in "normal" ferromagnets (Ni and Fe), and are strikingly reminiscent of those observed in dysprosium and terbium in the region of the point of transition from "helicoidal" antiferromagnetism to paramagnetism[1]. Detailed investigations of the magnetization and concomitant phenomena near the Curie point can provide information on the antiferromagnetic ordering in gadolinium. The question of the existence of antiferromagnetic ordering in gadolinium has not yet been decided[1]. The energy of magnetic anisotropy must be taken into account in studies of magnetic phenomena near the Curie point of uniaxial ferromagnets[2]. Graham[3] and Corner et al[4] have shown that the energy of uniaxial magnetic anisotropy of gadolinium (the axis of easy magnetization coincides with the hexagonal c axis) has a complicated temperature variation in the temperature interval near the Curie point: it increases on approaching the Curie point, reaches a maximum value, and then decreases slowly. In order to study the influence of magnetic anisotropy on the magnetic phenomena near the Curie point, we have undertaken detailed measurements of the magnetization curves of single-crystal gadolinium (in the temperature interval 280—300°K).

2. The magnetization measurements were made with a Domenicali pendulum magnetometer by a null method, in fields up to 15,000 Oe. Samples in the form of rods 5 mm long and 0.2 × 0.4 mm in cross section were cut from single-crystal gadolinium 1) along the a and c axes. To eliminate the effect of work hardening, the surface of the samples was etched in a solution of nitric acid and alcohol to a depth 0.2 mm. To exclude the influence of the magnetocaloric effect, the magnetization measurements were made in the isothermal mode (slow increase and decrease of the field). An estimate of the measurement error and control experiments with polycrystalline samples of the same dimensions as the investigated single crystals have shown that the error in determination of the Curie point by the method described below does not exceed 0.1°.

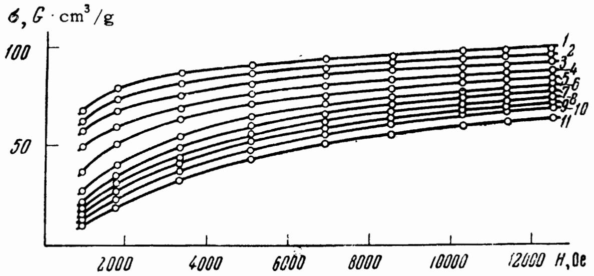

FIG. 1. Isotherms of magnetization of single-crystal gadolinium near the Curie point along the a axis. Curve 1 – 281.7, 2 – 283.5, 3 – 285.2, 4 – 286.8, 5 – 288.5, 6 – 290.2, 7 – 291.5, 8 – 293.0, 9 – 294.0, 10 – 295.3, 11 – 297.0°K.

3. Figures 1 and 2 show isotherms of the magnetization of the crystal of gadolinium along the a and c axes in the temperature interval 280—300°K. Because of the strong influence of the paraprocess, there is no saturation on these curves. These iso-

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1) The single crystal was grown in the laboratory of Professor E. M. Savitskii by the method of recrystallization annealing of distilled gadolinium.

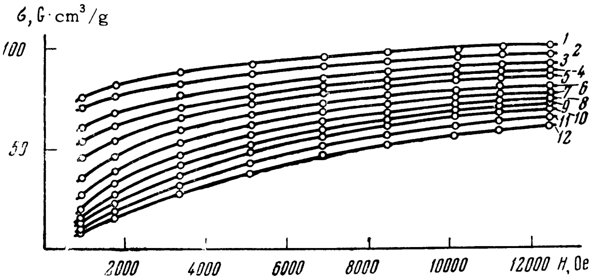

FIG. 2. Isotherms of magnetization of single-crystal gadolinium near the Curie point along the c axis. Curve 1 – 281.3, 2 – 283.1, 3 – 285.1, 4 – 287.0, 5 – 288.4, 6 – 290.3, 7 – 291.9, 8 – 293.2, 9 – 294.3, 10 – 295.8, 11 – 297.7, 12 – 299.3°K.

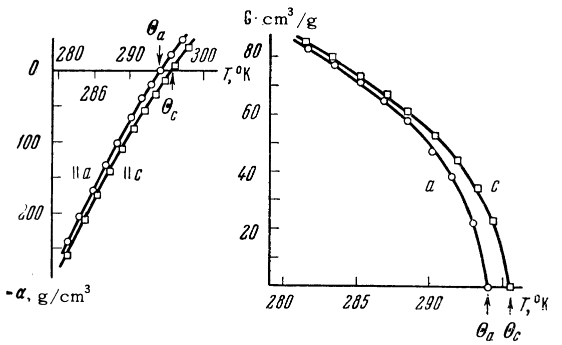

FIG. 4. Temperature dependence of the coefficients α and of the spontaneous magnetizations σ_S of single-crystal gadolinium along the a and c axes.

therms can be described by the thermodynamic equation[5]

$$\alpha\sigma + \beta\sigma^3 = H, \qquad (1)$$

where σ—specific magnetization and α and β are the thermodynamic coefficients. Figure 3 shows by way of an example a plot of H/σ against σ^2 for the a axis. We see that Eq. (1) is fairly accurate at large magnetizations (region of the paraprocess). These curves were used to determine the temperature variation of α and of the spontaneous magnetization $\sigma_S = -(\alpha/\beta)^{1/2}$. Figure 4 shows the temperature variation of σ_S and of the coefficient α. We see that the Curie temperature, determined from the condition $\alpha = 0$, is somewhat higher along the c axis ($\Theta_c = 295.5$°K) than in the difficult a-axis direction ($\Theta_a = 294$°K). Accordingly, the "slope" of the magnetic transformation ξ, as follows from Fig. 5, which shows the lines described by the thermodynamic equation

$$\left(\frac{\sigma_S}{\sigma_0}\right)^2 = \xi\left(1 - \frac{T}{\Theta}\right), \qquad (2)$$

is smaller in the c-axis direction ($\xi_c = 2.29$) than in the a-axis direction ($\xi_a = 2.54$).

The differences between Θ_c and Θ_a or ξ_c and ξ_a are explained by the fact that an effective magnetic-anisotropy field acts along the easy magnetization axis (c axis). In analogy with the apparent increase in the Curie temperature and decrease in the slope of the $\sigma(T)$ curve in the region of the Curie point, which is brought about by the external field as a result of the paraprocess, the effective anisotropy field also contributes to the ordering of the magnetic spins, as a result of which the Curie point increases somewhat in the direction of easy magnetization, and ξ_c decreases. The effect of apparent anisotropy of the Curie point in crystals of uniaxial ferromagnets was predicted theoretically before[6].

4. The anisotropy of the Curie point and the

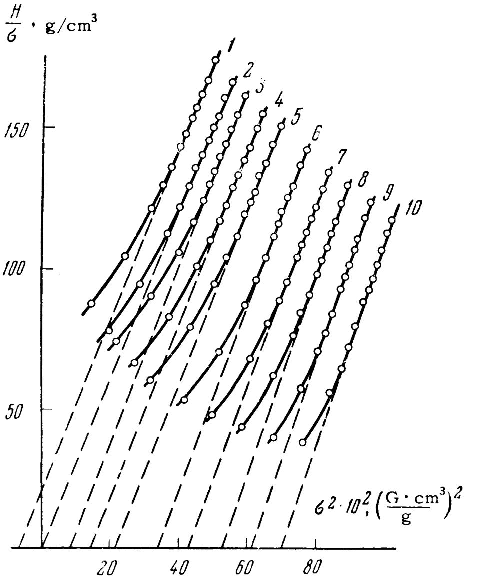

FIG. 3. Plots of H/σ (σ^2) for single-crystal gadolinium along the a axis. 1 – 285.3°K, 2 – 294.0, 3 – 293.0, 4 – 291.5, 5 – 290.2, 6 – 288.5, 7 – 286.8, 8 – 285.2, 9 – 283.5, 10 – 281.7°K.

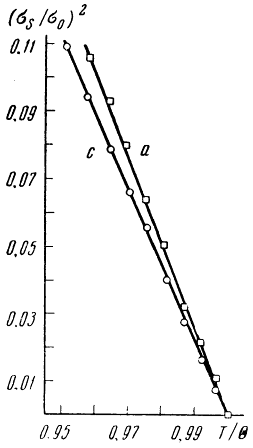

FIG. 5. Plot of $(\sigma_S/\sigma_0)^2$ against T/Θ for single-crystal gadolinium along the a and c axes.

slope of the magnetic transformation ξ can be calculated from the thermodynamic theory of second-order phase transitions[2]. For a hexagonal crystal, the expansion of the thermodynamic potential near the Curie point with account of the energy of uniaxial anisotropy, is of the form

$$\Phi = \Phi_0(T) + \frac{\alpha}{2}\sigma^2 + \frac{\beta}{4}\sigma^4 + k'(\sigma_x^2 + \sigma_y^2) - \sigma\mathbf{H}, \qquad (3)$$

where k′—thermodynamic anisotropy coefficient.

Minimization of this potential leads to two cubic equations of the form (1), describing the magnetization of the paraprocess along the c axis ($H = H_z = H_c$), and perpendicular to it along the a axis ($H = H_x = H_a$). We neglect here the anisotropy in the basal plane. These equations differ from each other only in that the coefficient α_c is smaller than α_a by an amount $2k'$, proportional to the energy of the magnetic anisotropy (the coefficient α is negative below the Curie point):

$$\alpha_a = \alpha_c + 2k'. \qquad (4)$$

The difference between α_c and α_a was determined by the magnetic anisotropy and is the cause of the anisotropy of the Curie point and of the anisotropy of the slope ξ in a hexagonal crystal.

5. By determining α_c and α_a experimentally, we can calculate the temperature variation of the anisotropy energy near the Curie point. The anisotropy energy per cubic centimeter of the crystal can be represented in the following form:

$$K = \rho k'\sigma^2 = \rho k'(\sigma_S + \sigma_i)^2, \qquad (5)$$

where σ_S—per-unit spontaneous magnetization, σ_i—per-unit magnetization of the paraprocess, and ρ—density. It is seen from the latter expression that the energy K can be broken up into two parts:

$$K = K_S + K_H, \qquad (6)$$

where K_S—anisotropy energy, which does not depend on the field (connected only with the quantity σ_S), and K_H is field dependent as a result of the influence of the paraprocess (σ_i).

The coefficient k′ can be easily obtained from Fig. 3 for each temperature, being the difference between the coefficients α_c and α_a.

The temperature dependence of k′ is shown in Fig. 6. We see that k′ decreases upon cooling. The same figure shows the temperature dependence of K, K_S, and K_H (in a field of 12,500 Oe). We see that K_S decreases monotonically on approaching the Curie point, where it vanishes. K_H rises and reaches a maximum value at Θ, for here the paraprocess is maximal. The magnitude and character of the temperature dependence of the constant $K = K_S + K_H$, calculated from the observed anisotropy of the Curie point, coincides with the magnitude and character of the temperature dependence of the anisotropy energy, measured directly in the region of the Curie point[3,4]. The presence of the component K_H explains the experimental fact, which seems like a paradox, that the energy of the magnetic anisotropy increases anomalously near the Curie point in single-crystal gadolinium and depends strongly on the external magnetic field.

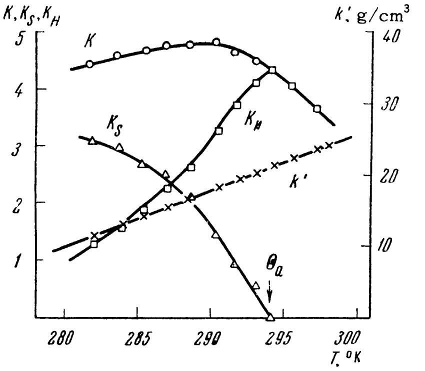

FIG. 6. Temperature dependence of the coefficient k′ and of the constants K, K_S, and K_H (in units of 10^5 erg/cm³), for single-crystal gadolinium near the Curie point.

In conclusion we note that all the phenomena considered above will be more strongly manifest in single-crystal Tb, Dy, Ho, Er, and Tu, inasmuch as the uniaxial anisotropy in these crystals is very large.

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