DETERMINATION OF THE MAGNETIC UNIAXIAL ANISOTROPY CONSTANTS OF HOLMIUM FROM MAGNETIZATION MEASUREMENTS IN FIELDS UP TO 240 kOe

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The magnetization of a holmium single crystal in the basal plane and along the hexagonal axis is measured at temperatures between 80 and 300°K in pulsed magnetic fields up to 240 kOe. The uniaxial anisotropy constants of holmium are calculated from the magnetization data by taking into account the paraprocess and the interaction responsible for the helicoidal structure of the metal. Between 80 and 122.5°K the temperature dependence of the first uniaxial anisotropy constant of holmium is satisfactorily described by the theoretical formula. The value of the first anisotropy constant at 0°K, obtained by extrapolation from the temperature region above 80°K, is $(2.5 \pm 0.25) \times 10^7$ erg/g.

As is well known, the energy of magnetic uniaxial anisotropy of ferromagnetic rare-earth metals with nonzero orbital angular momentum (terbium, dysprosium, holmium, erbium, thulium) is so large that in the magnetically-ordered state none of these metals could be magnetized to saturation along the direction of the difficult magnetization in fields on the order of 100 kOe[1-3]. Yet the behavior of such strongly anisotropic ferromagnets in fields exceeding the saturation field is of considerable interest, since such measurements make it possible to determine the magnetic anisotropy constants, and also to estimate the magnetization anisotropy, the existence of which follows from the most general considerations in the case when the energy of the anisotropy is comparable in magnitude with the energy of the change interaction[4-6].

Among the foregoing rare-earth ferromagnets, holmium is the most convenient for the investigation of the magnetization along the difficult direction, since it has the lowest magnetic-anisotropy energy. This is seen from the comparison of the anisotropy of the paramagnetic Curie point, which for terbium, dysprosium, holmium, and erbium amounts to 44, 48, 15, and 29°K, respectively[7].

We present below the results of measurements of the magnetization of single-crystal holmium grown by the method of recrystallization annealing. The measurements were performed in the temperature interval 8–300°K in pulsed magnetic fields up 240 kOe along the hexagonal axis of the crystal (the difficult-magnetization direction) and in the basal plane (the easy-magnetization plane), using the setup described in[8,9].

Figure 1 shows the isotherms of the magnetization in the basal plane, while Fig. 2 shows the isothermal of the magnetization along the hexagonal axis of the crystal.

In the paramagnetic temperature region ($T > \Theta_2 = 133°K$), the magnetization in both directions depends linearly on the field, with the exception of the strong-field interval near Θ_2.

In the temperature interval 20–133°K, holmium has an antiferromagnetic helicoidal structure with a heli-

coid axis parallel to the hexagonal axis of the crystal[10,11]. As shown in[12,13], when the helicoid in the basal plane is magnetized in fields smaller than the critical field H_C, the magnetization increases relatively slowly. In the field H_C, the helicoid becomes destroyed, causing a magnetization jump, and when $H_C \leq H \leq H_0$ the growth of the magnetization is due to the gradual transformation of the resultant sinusoidal structure into a collinear ferromagnetic structure. When $H \geq H_0$, the growth of the magnetization is connected with the paraprocess. The experimental isotherms of the magnetization of holmium in the basal plane (Fig. 1) agree qualitatively with the theoretical curves, and the values of H_C determined from our measurements are close to the data given by Flippen[14].

At $T < \Theta_2$, the isotherms of magnetization along the hexagonal axis (Fig. 2) show clearly two sections, a relatively rapid increase in fields weaker than the
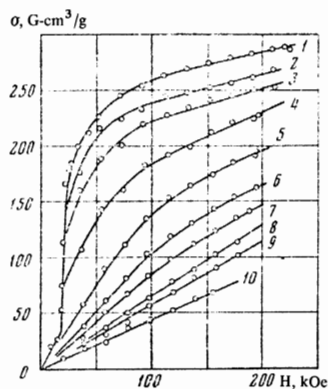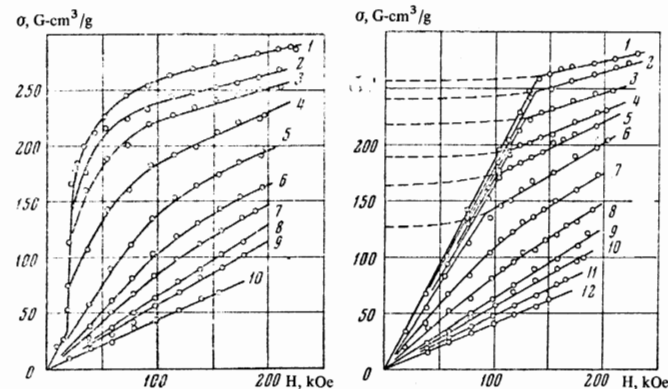

FIG. 1.

FIG. 2.

FIG. 1. Dependence of the magnetization of holmium in the basal plane on the field. Curve 1–80; 2–89; 3–100; 4–116; 5–133; 6–155; 7–173; 8–203; 9–218; 10–292°K.

FIG. 2. Dependence of the magnetization of holmium along the hexagonal axis on the field. Curve 1–80; 2–85; 3–97; 4–107; 5–116; 6–123; 7–141; 8–173; 9–198; 10–227; 11–240; 12–294°K; dashed-dependence of the absolute value of the magnetization on the field.

saturation field H_S, due to rotation processes, and a slower growth at $H > H_S$, due to the paraprocess.

We note that in the investigated temperature interval, the susceptibility of the paraprocess is large and amounts to 0.15—0.3 of the susceptibility due to the rotation processes, i.e., it is comparable with the latter in order of magnitude. The anisotropy of the magnetization of holmium in the magnetically ordered state at $H > H_S$ does not exceed the errors in the measurements of the absolute value of the magnetization (~10%).

In the calculation of the anisotropy constants, it is usually assumed that the magnetic moment remains constant in the process of rotation. This assumption is justified in the case of ferromagnets of the iron group, in which the anisotropy energy is smaller by several orders of magnitude than the energy of the isotropic exchange interaction. In heavy rare-earth metals, the energy of the uniaxial anisotropy is comparable in magnitude with the energy of the exchange interaction, and the magnetic moment changes, in general, whenever it deviates from the basal plane[4]. Therefore to calculate the constants of the uniaxial anisotropy of heavy rare-earth metals it is necessary to know the dependence of the absolute value of the magnetic moment of the crystal on the field when the crystal is magnetized along the difficult direction below the saturation field.

We describe below briefly the method used by us to calculate the constants of the uniaxial anisotropy of holmium with allowance for the paraprocess and the energy of the helicoid.

The energy of the helicoid can be written in the form[12,13]

$$E_h = -I_1(\sigma_n\sigma_{n+1}) - I_2(\sigma_n\sigma_{n+2}) - \cdots. \quad (1)$$

Here σ_n, σ_{n+1}, and σ_{n+2} are the magnetizations of the n-th, (n + 1)-st etc. layers, and in the case of magnetization along the axis of the helicoid we have $|\sigma_n|$ = $|\sigma_{n+1}|$ = $|\sigma_{n+2}|$ = σ, I_1 and I_2 are the integrals of exchange interaction respectively between the nearest layers and the layers that are separated from one another by one layer. With allowance for the helicoidal structure, the energy of the holmium in a field parallel to the hexagonal axis is

$$E = E_0(\sigma) - \sigma^2[I_1(\sin^2\psi + \cos^2\psi\cos\alpha) + I_2(\sin^2\psi + \cos^2\psi\cos 2\alpha)] + K_1\sin^2\psi + K_2\sin^4\psi - H\sigma\sin\psi. \quad (2)$$

Here $E_0(\sigma)$ is the exchange energy inside the layer; $K_1(\sigma)$ and $K_2(\sigma)$ are the first and second constants of uniaxial anisotropy, and in accordance with the theoretical papers[4,5,15], we propose that the constants of the constants of the anisotropy depend on the field and the temperature only via the magnetization; ψ is the angle between the direction of the magnetic moment of the layer and the basal plane; α is the angle between the projections of the magnetic moments of neighboring layers on the basal plane.

Minimizing (2) with respect to α, ψ, and σ, we arrive at the following conclusions:

a) When the helicoid is magnetized along the axis, the angle between the projections of the magnetic moments of the layers on the basal plane in fields $H < H_S$ is constant and is equal to the angle of the helicoid α_0 in the absence of a field.

b) At $H < H_S$ the magnetization σ_c of the helicoidal ferromagnet in a field parallel to the hexagonal axis is described by the same relation as for an ordinary uniaxial ferromagnet:

$$\sigma^2H / \sigma_c = 2K_{1\,\mathrm{eff}} + 4K_2(\sigma_c / \sigma)^2. \quad (3)$$

For a helicoidal ferromagnet however, the first uniaxial anisotropy constant K_1 in (3) is replaced by the effective first anisotropy constant $K_{1\mathrm{eff}}$, which includes the contribution due to the helicoidal interaction:

$$K_{1\,\mathrm{eff}} = K_1 + \Delta K = K_1 + {}^1/_2\sigma H_0. \quad (4)$$

The addition ΔK characterizes the energy of destruction of the helicoid upon magnetization in the basal plane, and can be calculated as the work necessary to destroy the helicoid from the isotherms of Fig. 2:

$$\Delta K = \frac{1}{2}\sigma H_0 = \int_0^{\sigma_s} H\,d\sigma. \quad (5)$$

c) The absolute magnitude of the magnetic moment σ in a field parallel to the hexagonal axis equals, accurate to terms of first order of smallness in $(\sigma - \sigma_S)/\sigma_S$,

$$\sigma = \sigma_s - \chi\left\{H_s - H\frac{\sigma_c}{\sigma_s} - \left(\frac{dK_{1\mathrm{eff}}}{d\sigma}\right)_{\sigma=\sigma_s}\left[1 - \left(\frac{\sigma_c}{\sigma_s}\right)^2\right]\right.$$
$$\left. - \left(\frac{dK_2}{d\sigma}\right)_{\sigma=\sigma_s}\left[1 - \left(\frac{\sigma_c}{\sigma_s}\right)^4\right]\right\}. \quad (6)$$

Here σ_S is the magnetization in the saturation field along the hexagonal axis, χ is the susceptibility of the paraprocess (in calculating the value of χ, accurate to terms of first order of smallness in $(\sigma - \sigma_S)/\sigma_S$, the susceptibility of the paraprocess can be assumed to be isotropic and independent of the field).

According to our experimental data, with the aid of relations (3)—(6) we calculated by the method of successive approximation the dependences of the absolute value of the magnetization σ of holmium in the case of magnetization along the hexagonal axis with $H \leq H_S$, and the dependence of the anisotropy constants of this metal on the magnetization.

In the zeroth approximation, it is assumed that the magnetic moment of the layer at $H < H_S$ is constant and equals σ_S; the anisotropy constants are calculated from the isotherms of the magnetization with the aid of relation (3). From the calculated functions $K_{1\mathrm{eff}}(\sigma)$ and $K_2(\sigma)$ one determines the first derivatives of the anisotropy constants, and this makes it possible to find, with the aid of relations (6) and (3), the values of $\sigma(H)$ when $H \leq H_S$, the anisotropy constants in the first approximation, etc. The number of approximations was determined by starting from the requirement that the error due to the approximate nature of the calculation be much smaller than the experimental error. The dashed curves in Fig. 2 are the plots of $\sigma(H)$ determined by us in this manner for $H < H_S$.

We note one more detail in the processing of the experimental data. The presence of an appreciable paraprocess makes it impossible for us to regard the anisotropy constants and independent of the field. Therefore the anisotropy constants in the first and succeeding approximations were calculated by means of formula (3) at a constant magnetization, using dif-
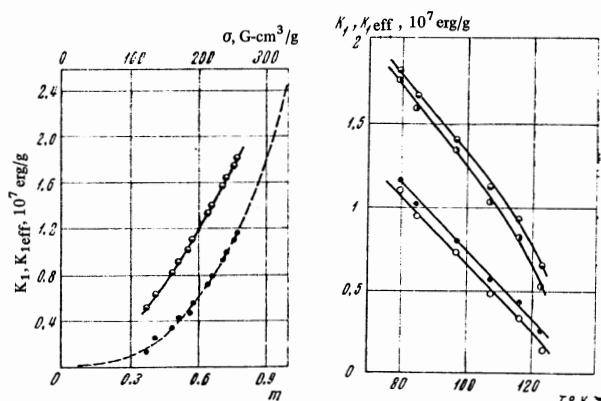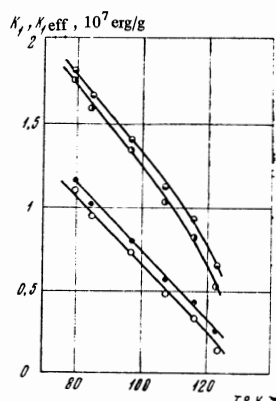
FIG. 3

FIG. 4

FIG. 3. Dependence of the anisotropy constants of holmium K_1 eff and K_1 on the magnetization σ and on the reduced magnetization $m = \sigma/\sigma_0$ (σ_0—magnetization at $0°$). ●—for K_1, ◐—for K_1 eff, dashed curve—for $K_1(m) = (3/2) k_2^0 I_{5/2} [\mathscr{L}^{-1}(m)] : 2.5 \times 10^7 I_{5/2} [\mathscr{L}^{-1}(m)]$ [erg/g].

FIG. 4. Dependence of the anisotropy constants of holmium K_1 eff and K_1 on the temperature. For K_1: ○—H = 0, ●—H = H_S; for K_1 eff: ◐— H = 0, ◑—H = H_S.

ferent isotherms $\sigma_c(H)$, and not only one isotherm as is customary.

Figure 3 shows the plots of K_1 eff and K_1 against the magnetization, calculated by this method, and Fig. 4 shows plots of K_1 eff and K_1 against the temperature. The second constant of uniaxial anisotropy of holmium in the investigated temperature interval ($80-122.5°K$), according to our measurements, is negligibly small compared with the first ($K_2 < 3 \times 10^5$ erg/g).

It is seen from Figs. 3 and 4 that in holmium, at nitrogen temperature, K_1 reaches 10^7 erg/g, which, while somewhat smaller, is comparable with the anisotropy energy of dysprosium and terbium[2]. It follows also from our results that in holmium the interaction giving rise to the helicoid makes an appreciable contribution to the effective first constants of the uniaxial anisotropy K_1 eff.

In the interpretation of the experimental results and in their comparison with the theory, it is more convenient to use not the anisotropy constants K_1, K_2, etc., but the coefficient of expansion of the anisotropy energy is spherical harmonics k_2, $k_4 \ldots k_l$)[15]. In the case $K_2 = 0$, the values of K_1 and k_2 are connected by the relation $K_1 = 3k_2/2$.

It is shown in[16] that the temperature dependence of the anisotropy coefficient k_2 of terbium and dysprosium is satisfactorily described by a relation that follows from the theory of single-ion anisotropy[15]

$$k_2[\sigma(T, H)] = k_2^0 I_{5/2}\{\mathscr{L}^{-1}[m(T, H)]\}. \tag{7}$$

Here k_2^0 is the value of the coefficient k_2 at $0°K$, $\hat{I}_{5/2}$ is the reduced hyperbolic Bessel function, $\mathscr{L}^{-1}$ is the reciprocal Langevin function, $m = \sigma/\sigma_0$ is the reduced magnetization, and σ_0 is the magnetization at $0°K$.

The experimental dependence of the coefficient of uniaxial anisotropy of holmium k_2 on the magnetization, obtained by us, is also well described by relation (7) (see Fig. 3), and the value of the coefficient k_2^0 at absolute zero, obtained by extrapolation of the experi-

mental data to the value $m = 1$, is $k_2^0 = (1.65 \pm 0.17) \times 10^7$ erg/g. This corresponds to the value of the first anisotropy constant at $0°K$, $K_1^0 = 3k_2^0/2 = (2.5 \pm 0.25) \times 10^7$ erg/g (under the condition that the second anisotropy constant at $0°K$ is equal to zero).

A comparison of the values obtained in our investigation for the anisotropy constants with the data for terbium and dysprosium[9,15] shows that in holmium the energy of the uniaxial anisotropy is smaller by a factor $2-3$ than in terbium and dysprosium. This fact is attributed to the dependence of the symmetry of the spatial distribution of the charges of the electrons of the unfilled f shell in the atoms of the metals under consideration on their atomic number[17]. The cloud of charges of the electrons of the f shell in terbium, dysprosium, and holmium is oblate in the direction of the magnetic moment of the ion, while in the case of erbium it is prolate, the minimum spatial anisotropy being possessed by the holmium ion, leading to a smaller uniaxial anisotropy energy compared with the other heavy rare-earth metals.

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[1]R. Z. Levitin, and B. K. Ponomarev, Zh. Eksp. Teor. Fiz. 53, 1978 (1967) [Sov. Phys.-JETP 26, 1121 (1968)].

[2]K. P. Belov, R. Z. Levitin, and B. K. Ponomarev, J. Appl. Phys. 39, 3285 (1968).

[3]J. Rhyne, S. Foner, E. McNiff, and R. Doclo, J. Appl. Phys. 39, 892 (1968).

[4]E. Callen and H. Callen, J. Phys. Chem. Sol. 16, 310 (1960).

[5]E. Callen, Phys. Rev. 124, 1374 (1961).

[6]K. P. Belov, Yu. V. Ergin, L. I. Koroleva, R. Z. Levitin, and A. B. Ped'ko, Phys. Stat. Sol. 12, 219 (1965).

[7]K. P. Belov, M. A. Belyanchikova, and R. Z. Levitin, Redkozemel'nye ferro- i antiferromagnetiki (Rare-earth Ferro- and Antiferromagnets), Nauka, 1965.

[8]K. P. Belov, R. Z. Levitin, and B. K. Ponomarev, Zh. Eksp. Teor. Fiz. 51, 1634 (1966) [Sov. Phys.-JETP 24, 1101 (1967)].

[9]B. K. Ponomarev, Dissertation, Moscow, 1967.

[10]D. Standburg, S. Legvold, and F. Spedding, Phys. Rev. 127, 2046 (1962).

[11]W. Koehler, J. Cable, M. Wilkinson, and E. Wollan, Phys. Rev. 151, 414 (1966).

[12]A. Herpin and P. Meriel, J. Phys. Radium 22, 337 (1961).

[13]Y. Kitano and T. Nagamiya, Progr. Theor. Phys. 31, 1 (1964).

[14]R. Flippen, J. Appl. Phys. 35, 1047 (1964).

[15]H. Callen and E. Callen, J. Phys. Chem. Sol. 27, 1271 (1966).

[16]J. Rhyne and A. Clark, J. Appl. Phys. 38, 1379 (1967).

[17]N. Tsuya, A. Clark, and R. Bozorth, Proc. Intern. Conf. on Magnetism, Nottingham, (1964), p. 250.