Effect of pressure on magnetic phase transitions, and bulk magnetostriction in the vicinity of the Curie point in a terbium–gadolinium alloy

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The magnetization of the single-crystal ferromagnetic alloy $Tb_{0.1}Gd_{0.9}$ was measured at temperatures from 80 to 310 K, at atmospheric pressure, and at hydrostatic pressures up to 10^{10} dyn/cm^2. Measurements in a magnetic field up to 15 kOe were made both in the basal plane of a single crystal of hexagonal structure and along the difficult-magnetization axis **C**. The influence of the pressure on the spin-flip transition was analyzed on the basis of the Landau thermodynamic theory. A field-induced spin-flip transition changes strongly the volume of the sample via a transition from a high- to a low-symmetry phase. It was observed that the bulk magnetostriction of $Tb_{0.1}Gd_{0.9}$ reaches near the Curie point gigantic values of order $5\cdot10^{-5}$. It is concluded that the anisotropic-exchange energy has no noticeable influence on the bulk magnetostriction near the Curie point.

The pressure-induced shift of the Curie point was determined for many ferro- and antiferromagnets, including a number of rare earth metals (REM) and their alloys.[1–3] Magnetic phase transitions due to simultaneous action of pressure and a magnetic field in the vicinity of the Curie point in anisotropic ferromagnetic REM and their alloys have, however, not been investigated so far. This is due to certain experimental difficulties including the need for measuring the magnetization curves of single crystals along various crystallographic directions under hydrostatic pressure. What was actually measured therefore in the reported studies[1–3] was the variation of the magnetic susceptibility with pressure near the Curie temperature Θ.

At the same time, the magnetic phase transitions in a strongly anisotropic ferromagnet in the presence of a magnetic field differ substantially in character near the Curie temperature, depending on the orientation of the easy magnetization axis. In this case a theoretical description of the magnetic phase transitions must take into account the fact that the order parameter has many components, in contrast to the isotropic case, and spin-flip phenomena take place at $T<\Theta$ in a magnetic field applied along the difficult magnetization axis.[4]

We report here a study of the effect of pressure on magnetic phase transitions in the region of the Curie point of the uniaxial ferromagnetic alloy $Tb_{01}Gd_{0.9}$. Single crystal of this alloy have an hexagonal structure. The hexagonal axis *C* is a difficult-magnetization axis. This alloy was chosen to study the magnetic properties under hydrostatic pressure because its magnetic anisotropy is much lower than that of terbium because of the added gadolinium. The spin-flip transitions near the Curie temperature are therefore manifested in a magnetic-field range favorable for experimentation (1–10 kOe).

The technology of growing terbium–gadolinium single crystals and investigations of their structure were reported earlier.[5] It was established that these alloys are solid solutions.[5]

The procedure of measuring the magnetization curves of samples under pressure was the following. A sample in the form of a rod of length on the order of 8 mm and a cross section close to 1 mm^2 was placed in a central measuring coil, to which two symmetrically placed compensation coils were connected. The sample and the coils were placed in a beryllium-bronze high-pressure chamber. The chamber was connected to a high-pressure booster actuated by a compressor. The compressor produced also a priming pressure up to $2.5\cdot10^9$ dyn/cm^2 in the low-pressure system. A magnetic field of up to 15 kOe was produced by an iron-clad electromagnet. The high-pressure chamber was placed between permendur polepieces magnetized with a solenoid, and electric current up to 60 A was passed through the electromagnet solenoid for approximately 10 s. The magnetic field acting on the sample had then a maximum strength 15 kOe.

A change in the sample magnetization induced in the measuring coil an emf proportional to the time derivative of the sample magnetization. The compensating coils cancelled out the emf due to the change of the magnetic field. After integration, the signal was applied to the Y input of an X–Y potentiometer. The X input was the integrated signal induced in the coil intended for the measurement of the magnetic field. A potentiometer plotted the dependence of the magnetization on the magnetic field. The error in the measurement of the magnetic field was 2%. The absolute specific magnetization σ was measured at atmospheric pressure with a 3% error. At high pressure, in view of the displacement of the investigated sample by the deformation of the coils, this error increased to 5%. The error of $\partial\sigma/\partial P$ near the Curie temperature was $\sim$10%.

The temperature was measured with a copper-constantan thermocouple. The correction for the pressure dependence of the thermoelectric power was calculated on the basis of Ref. 6. The magnetization curve were measured while the chamber with the sample was slowly cooled with liquid nitrogen and its vapor. A thermal stabilization system permitted measurements at a fixed temperature maintained accurate to 0.1 K. The measurements were made at atmospheric pressure and at pressures up to 10^{10} dyn/cm^2.

Figures 1 and 2 show the temperature dependence of the specific magnetization of a $Tb_{0.1}Gd_{01}$ alloy in various magnetic fields. The magnetic field was directed along the *B* axis (Fig. 1) and along the **C** axis (Fig. 2). When the magnetic field was applied along the easy-magnetization axis (**H**$\|$**B**) the magnetization decreased monotonically with rise of temperature and dropped steeply in the region of the Curie temperature (Fig. 1), as is usually observed for classi-

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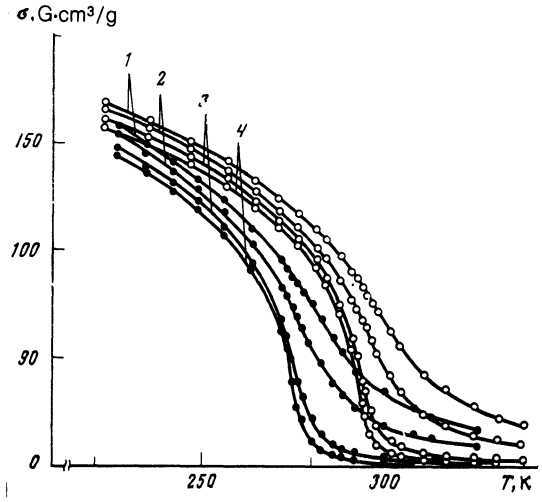

FIG. 1. Temperature dependence of the specific magnetization of a $Tb_{0.1}Gd_{0.9}$ single crystal at atmospheric pressure and under hydrostatic compression, in a magnetic field directed along the **B** axis: ○—$P = 10^6$ dyn/cm²; ●—10^{10} dyn/cm²; 1—$H = 10$ kOe; 2—5 kOe; 3—1 kOe; 4—0.5 kOe.

cal ferromagnets having low magnetic anisotropy. Pressure shifts the temperature of the maximum of $-\partial\sigma/\partial T$ towards lower temperatures.

In a magnetic field applied along the difficult-magnetization axis (**H**||**C**), the temperature dependence of the specific magnetization $\sigma(T)$ has a different character. The $\sigma(T)$ curve shows near the Curie temperature in a weak magnetic field a maximum that shifts towards lower temperatures with increase of the magnetic field. As seen from Fig. 2, pressure lowers noticeably the temperatures of the maxima.

It was shown in Refs. 4 and 7 that so different a behavior of $\sigma(T)$ in magnetic fields **H**||**B** and **H**||**C** in an anisotropic ferromagnet near the Curie fact is due to the fact that at **H**||**B** the magnetic field produces only an intense paraproceses, while at **H**||**C** it produces also a spin flip, i.e., rotation of the magnetic moment of the crystal on the basal plane towards the hexagonal axis **C**.

Below the temperature $\Theta_n(H)$ of the maximum on the $\sigma(T)$ curve (Fig. 2), measured at a definite value of the magnetic field, there exists a (low-symmetry) phase with specific-magnetization components along the **C** axis ($\sigma_\parallel \neq 0$ and on the basal plane ($\sigma_\perp \neq 0$).

At $T > \Theta_n(H)$ there exists a (high-symmetry) phase with $\sigma_\perp = 0$. The temperature Θ_n as a function of the applied magnetic field is shown in Fig. 2 by a dashed line joining the maxima of the $\sigma(T)$ curves. Hydrostatic pressure lowers strongly the temperature $\Theta_n(H)$.

At a fixed temperature, an increase of the magnetic field leads at $H = H_n$ to a transition from the low-symmetry phase with $\sigma_\perp \neq 0$ and $\sigma_\parallel \neq 0$ into a high symmetry phase with $\sigma_\perp = 0$ and $\sigma_\parallel \neq 0$. Hydrostatic pressure shifts noticeably the phase-equilibrium curve $H_n(T)$ (inset of Fig. 2).

The experimental data can be interpreted on the basis of the Landau thermodynamic theory of second-order phase transitions.[8] To this end it must be recognized that the order parameter has two components: magnetization-vector projections along the **C** axis ($I_\parallel$) and on the basal plane ($I_\perp$). The thermodynamic potential of a uniaxial ferromagnet in a magnetic field under pressure can be expressed in the form

$$\Phi = \frac{\alpha_1}{2} I_\perp^2 + \frac{\varkappa_1}{2} I_\perp^2 P + \frac{\alpha_2}{2} I_\parallel^2 + \frac{\varkappa_2}{2} I_\parallel^2 P + \frac{\beta_1}{4} I_\perp^4 + \frac{\gamma}{2} I_\perp^2 I_\parallel^2 + \frac{\beta_2}{4} I_\parallel^4 - \mathbf{IH} + \frac{1}{2} g P^2, \quad (1)$$

where $\alpha_1, \varkappa_1, \alpha_2, \varkappa_2, \beta_1, \beta_2, \gamma$, and g are the thermodynamic coefficients, P the pressure and **H** the external-magnetic-field strength.

Stable phases and the limits of their existence can be obtained from the condition that the thermodynamic potential be a minimum.[4,7] The relevant analysis was carried out in Refs. 4 and 7 on the basis of the thermodynamic potential (1) at $P = 0$. Allowance for the pressure leads to a renormalization of the thermodynamic coefficients: $\alpha_1 \to \alpha_1 + \varkappa_1 P$, $\alpha_2 \to \alpha_2 + \varkappa_2 P$. We present here therefore only the equations that describe the pressure effects observed by us in experiment.

In the case of a uniaxial ferromagnet with **C** the difficult magnetization axis we have $\alpha_2 > \alpha_1$. The magnetic phase transition at $P = 0$ can be described[4,7] by assuming that the thermodynamic coefficients α_1 and α_2 of the squared magnetization components are linear in temperature and reverse sign at the Curie point:

$$\alpha_1 = a_1(T - \Theta^{(1)}), \quad \alpha_2 = a_2(T - \Theta^{(2)}), \quad \Theta^{(1)} > \Theta^{(2)}, \quad (2)$$

where $a_1 = \partial\alpha_1/\partial T$, $a_2 = \partial\alpha_2/\partial T$.

Under the action of the pressure, the sums of the thermodynamic coefficients $\alpha_1 + \varkappa_1 P$ and $\alpha_2 + \varkappa_2 P$ of the squares of the magnetization components vanish at the respective temperatures $\Theta^{(1)}(P)$ and $\Theta^{(2)}(P)$:

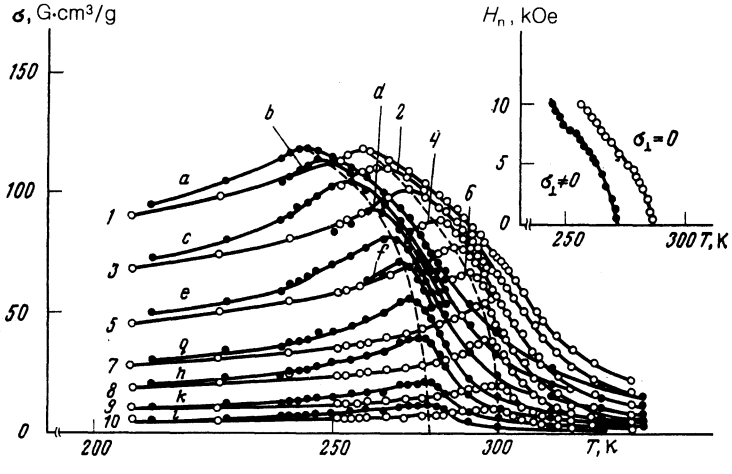

FIG. 2. Temperature dependence of the specific magnetization of a $Tb_{0.1}Gd_{0.9}$ single crystal at atmospheric pressure and under hydrostatic compression, in a magnetic field directed along the **C** axis, and the phase diagram: ○—$P = 10^6$ dyn/cm²; ●—10^{10} dyn/cm²; 1, *a*—$H = 10$ kOe; 2, *b*—9 kOe; 3, *c*—7.5 kOe; 4, *d*—6 kOe; 5, *e*—5 kOe; 6, *f*—4 kOe; 7, *g*—3 kOe; 8, *h*—2 kOe; 9, *k*—1 kOe; 10, *l*—0.5 kOe.

$$\alpha_1+\varkappa_1 P=a_1(T-\Theta^{(1)}(P)), \tag{3}$$

where

$$\Theta^{(1)}(P)=\Theta^{(1)}-\varkappa_1 P/a_1,$$

and

$$\alpha_2+\varkappa_2 P=a_2(T-\Theta^{(2)}(P)), \tag{4}$$

where

$$\Theta^{(2)}(P)=\Theta^{(2)}-\varkappa_2 P/a_2.$$

At $\mathbf{H}\perp\mathbf{C}$ and $I_\parallel = 0$, minimization of the thermodynamic potential leads to the equation

$$\alpha_1+\varkappa_1 P+\beta_1 I_\perp^2=H/I_\perp. \tag{5}$$

At $\mathbf{H}\parallel\mathbf{C}$ in the high-symmetry phase with $I_\perp = 0$ we get from the minimum condition

$$\alpha_2+\varkappa_2 P+\beta_2 I_\parallel^2=H/I_\parallel. \tag{6}$$

In the low-symmetry pase with $I_\perp \neq 0$ we get from the minimum condition

$$(\alpha_2+\varkappa_2 P)-(\alpha_1+\varkappa_1 P)\gamma/\beta_1+(\beta_2-\gamma^2/\beta_1)I_\parallel^2=H/I_\parallel. \tag{7}$$

Equations (5)–(7) describe well the experimental data in the vicinity of the Curie point at $\mathbf{H}\parallel\mathbf{C}$ and $\mathbf{H}\perp\mathbf{C}$ and $P\neq 0$: a linear dependence of H/I on I^2 is observed at $\mathbf{H}\parallel\mathbf{C}$ and $\mathbf{H}\perp\mathbf{C}$.

Figure 3 shows plots of the thermodynamic coefficients α_1, $\alpha'_1=\alpha_1+\varkappa_1 P$, α_2 and $\alpha'_2=\alpha_2+\varkappa_2 P$ vs temperature, obtained by reducing the magnetization isotherms using Eqs. (5)–(7). It can be seen that all these coefficients reverse sign and have a linear temperature dependence in the vicinity of the Curie point, as predicted by the thermodynamic theory. The pressure $P=10^{10}$ dyn/cm^2 lowers noticeably the temperatures $\Theta^{(1)}(P)$ and $\Theta^{(2)}(P)$ where α_1 and α_2 reverse sign (by 13.3 K in the case of $\alpha_1$and by 15.1 K in the case of α_2). Using the experimental data (Fig. 3), and also Eqs. (3) and (4), we found the values of the thermodynamic coefficients: $a_1=1.5\ \mathrm{K}^{-1}$, $a_2=1.7\ \mathrm{K}^{-1}$, $\varkappa_1=2.2\cdot10^{-9}$ cm·s^2/g, $\varkappa_2=2.2\cdot10^{-9}$ cm·s^2/g.

Pressure alters substantially the character of the magnetization isotherms in the vicinity of the Curie temperature (Fig. 4). For example, at $T=285$ K and atmospheric pressure the dependence of the specific magnetization (H) at $\mathbf{H}\parallel\mathbf{C}$ is nonlinear, since magnetization takes place here in the low-symmetry (ferromagnetic phase (curve 2 of Fig. 4). A pressure $P=10^{10}$ dyn/cm^2 transforms the sample into a high-symmetry (paramagnetic) phase, where $\sigma_\perp = 0$. The magnetization processes are characterized here by a linear dependence of the magnetization on the magnetic field (curve 4).

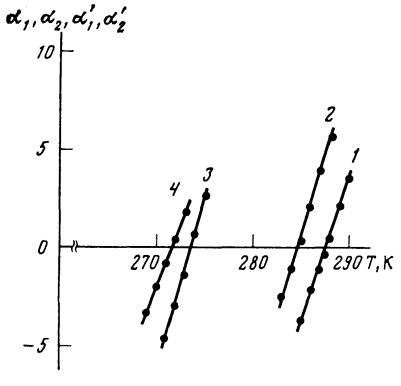

FIG. 3. Temperature dependences of the thermodynamic coefficients: 1—$\alpha'_2=\alpha_2+\varkappa_2 P$, 2—$\alpha'_1=\alpha_1+\varkappa_1 P$, 3—$\alpha_2$, 4—$\alpha_1$.

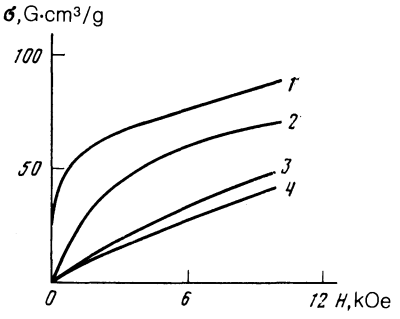

FIG. 4. Isotherms of specific magnetization of a single crystal of the alloy $Tb_{0.1}Gd_{0.9}$ at $T=285$ K: 1, 3—$\mathbf{H}\parallel\mathbf{B}$; 2, 4—$\mathbf{H}\parallel\mathbf{C}$; 1, 2—$P=10^6$ dyn/cm^3; 3, 4—$P=10^{10}$ dyn/cm^{-3}

At $\mathbf{H}\perp\mathbf{C}$ a pressure $P=10^{10}$ dyn/cm^2 transforms the sample at $T=283$ K from a high-symmetry ferromagnetic phase into a paramagnetic one, where the magnetization is also linear in the magnetic field (curves 1 and 3 in Fig. 4).

The data obtained on the pressure dependence of the magnetization permit calculation of the magnetostriction of single-crystal $Tb_{0.1}Gd_{0.9}$ from the thermodynamic relation

$$(\partial\omega/\partial H)_{P,T}=-(\partial I/\partial P)_{H,T}, \tag{8}$$

where $\omega=(V-V_0)/V_0$ is the relative change of the sample volume.

Integrating Eq. (8), we obtain the change of the volume upon magnetization:

$$\omega(P,H)=-\int_0^H(\partial I/\partial P)\,dH. \tag{9}$$

The calculation results are shown in Figs. 5 and 6. It can be seen that the bulk magnetostriction reaches near the Curie temperature Θ rather high values, of the order of $5\cdot10^{-4}$ at $\mathbf{H}\parallel\mathbf{B}$ and $3\cdot10^{-4}$ at $\mathbf{H}\parallel\mathbf{C}$. Threshold fields H_{th} are observed on the $\omega(H)$ isotherms: at $H<H_{th}$ we have $\omega<0$ and $\partial\omega/\partial H<0$, and at $H>H_{th}$ we have $\partial\omega/\partial H>0$ (see Fig. 6). This variation of $\omega(H)$ in a field $\mathbf{H}\parallel\mathbf{C}$ can be attributed to a transition from the low-symmetry phase with $\sigma_\perp\neq0$ to a high-symmetry one with $\sigma_\perp=0$.

The negative sections on the plots of Figs. 5 and 6 are due to rotation of the magnetic moment on the basal plane towards the C axis. The positive sections are due to the increase of the absolute value of the magnetic moment. With increase of the magnetic field strength in the extremum region, the second effect begins to overlap the first. This behavior can be illustrated with the aid of the phase diagram in the inset in Fig.2. To the right of the phase boundary the magnetic moment coincides with the direction of the magnetic field, and on the left there is a small angle between them.

A thermodynamic description of the behavior of the bulk magnetostriction in the Curie-temperature region can be based on an analysis of the thermodynamic potential (1).

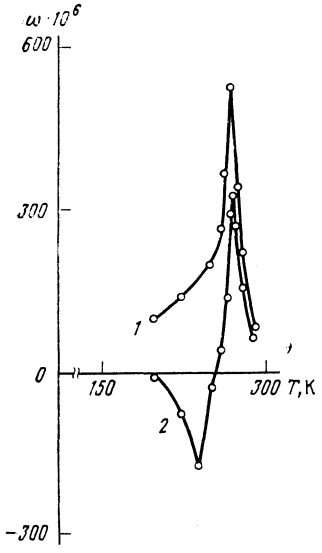

FIG. 5. Temperature dependence of the bulk magnetostriction of a $Tb_{0.1}Gd_{0.9}$ single crystal in a magnetic field $H = 10$ kOe at a pressure $P = 10^{10}$ dyn/cm^2: 1—**H**||**B**; 2—**H**⊥**C**.

The volume of the ferromagnet sample can be calculated from the equation

$$\omega = \partial\Phi/\partial P = gP + (\varkappa_1 I_\perp^2/2 + \varkappa_2 I_\parallel^2/2). \quad (9)$$

At **H**⊥**C** we have $I_\parallel = 0$ and $I_\perp \neq 0$. Consequently,

$$\omega = \varkappa_1 I_\perp^2/2 + gP. \quad (11)$$

If the sample is magnetized in a field **H**⊥**C** the bulk magnetization $\omega(H) - \omega(0)$ is

$$\omega(H) - \omega(0) = \varkappa_1 (I_\perp^2 - I_s^2)/2, \quad (12)$$

where I_s is the spontaneous magnetization.

At **H**||**C** in the low-symmetry phase ($I_\parallel \neq 0, I_\perp \neq 0$) we obtain the bulk magnetostriction by subtracting from ω [Eq. (10)] the spontaneous bulk magnetostriction:

$$\omega(H) - \omega(0) = \varkappa_1 I_\perp^2/2 + \varkappa_2 I_\parallel^2/2 - \varkappa_1 I_s^2/2. \quad (13)$$

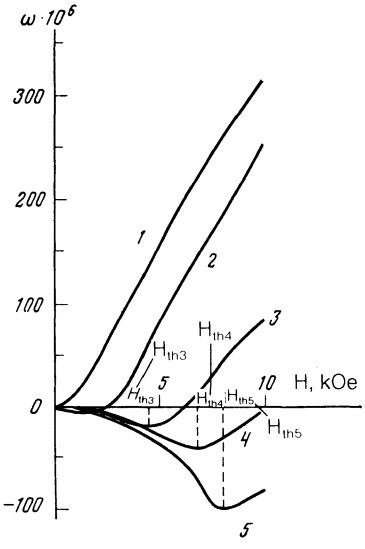

FIG. 6. Isotherms of bulk magnetization of single-crystal $Tb_{0.1}Gd_{0.9}$ at a pressure $P = 10^{10}$ dyn/cm^2 and **H**||**C**: 1—$T = 272.5$ K; 2—267.5 K; 3—262.5 K; 4—255 K; 5—250 K.

At **H**||**C** we obtain similarly in the high-symmetry phase with $I = 0$ at $H > H_{th}$

$$\omega(H) - \omega(0) = \varkappa_2 I_\parallel^2/2 - \varkappa_1 I_s^2/2. \quad (14)$$

We used the thermodynamic equations (12) and (14) to calculate the bulk magnetostriction from the experimental values of the specific magnetization $\sigma_\parallel$ and $\sigma_\perp$ and the coefficients $\varkappa_1$ and $\varkappa_2$ given above. For the high-symmetry phase at **H**||**B** and **H**||**C** these data are shown in Fig. 7 as functions of the square of the specific magnetization. It can be seen that, in agreement with the predictions of the thermodynamic theory, the bulk magnetostriction is indeed proportional to the squared specific magnetizations, and the intercepts of the straight lines $\omega = \omega(\sigma^2)$ with the ordinate axis should be treated as the spontaneous bulk magnetostriction ω_s.

As the Curie point Θ is approached, ω_s decreases like $\omega_s \sim (\Theta - T)^{1/2}$. At $T = \Theta$ and **H**||**B** the line $\omega = \omega(\sigma^2)$ passes through the origin. This means that the bulk magnetostriction ω_s is zero at $T = \Theta$.

A sharp kink of the $\omega_s(T)$ curve is observed at the Curie point at **H**||**C**, with ω_s remaining finite at $T > \Theta$. The presence of negative bulk magnetostriction in fields weaker than the threshold field H_{th}, i.e., at $H < H_{th}$, cannot be explained by the employed thermodynamic theory. The apparent reason is that in this variant of the theory no account is taken of the formation of noncollinear configuration of the magnetic moments of the ions of terbium and gadolinium, which have unequal on-ion-anisotropy constants. Canted structures can exist in weak fields $H < H_{th}$, whereas at $H > H_{th}$ the magnetic moments of the terbium and gadolinium ions are parallel.

An important result of the investigation of bulk magnetostriction is the experimentally established law that bulk magnetostruction varies linearly with the square of the specific magnetization, with a proportionality coefficient that remains practically constant regardless of the direction of the applied magnetic field. This conclusion is not obvious for anisotropic crystals. It is known[9] that the bulk magnetostriction in the region of the Curie point is proportional to the derivative of the exchange integral with respect to volume, i.e., $\omega \sim \partial A/\partial\omega$. The result indicates thus that in the investigated rare-earth alloy the derivative of the exchange integral

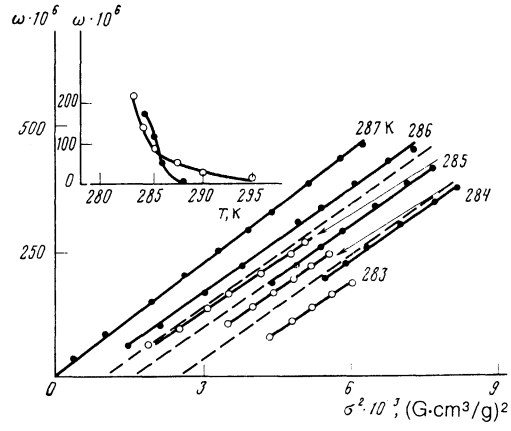

FIG. 7. Dependence of the bulk magnetostriction on the square of the specific magnetization near the Curie temperature: ○—at **H**||**B**; ●—at **H**||**C**; dashed line—theoretical dependence.

with respect to volume is practically independent of the angles between the magnetization and the crystal axes. In present developments of a theory of the magnetically ordered state of rare-earth metals account is taken of the isotropic indirect exchange, the anisotropic exchange, and of the magnetic anisotropy due to the interaction of the orbital momentum with the crystal field.[10] Our data point to a weak dependence of the exchange-interaction energy on the angle θ between the magnetic moment of the crystal and the crystal axes. In fact, the bulk magnetostriction of the paraprocess can be represented in the general case as proportional to the quantity

$$\omega \sim \frac{\partial A_0}{\partial \omega}\sigma^2 + \frac{\partial A_{an}}{\partial \omega}(\theta)\sigma^2, \qquad (15)$$

where A_0 is the integral of the isotropic exchange interaction (is independent of the angle θ), and A_{an} is the integral of the anisotropic exchange integral (depends on the angle θ).

Our data indicate that $\partial A_{an}/\partial\omega \approx 0$. It can therefore be concluded that the anisotropic-exchange energy (the dependence of the exchange integral on the angle θ) exerts no noticeable influence on the behavior of the bulk magnetostriction near the Curie point in the terbium–gadolinium rare-earth alloy.

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