Magnetic phase transformations and the magnetocaloric effect in single crystals of Tb-Y alloys

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The magnetic phase transitions in single crystals of Tb and Tb-Y alloys are investigated with the aid of the magnetocaloric effect, using the results of the magnetization and magnetostriction measurements. The energy contributions to the entropy change that occurs in the helical antiferromagnetic-ferromagnetic transition are found on the basis of a thermodynamic analysis of the experimental data. It is established that the destruction of the helical structure in this transition occurs largely as a result of gigantic magnetostrictive deformations.

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The magnetic phase transformations occurring in the rare-earth metals and alloys have been studied through the measurement of the magnetic, galvanomagnetic, and magnetostriction properties. [1] However, these investigations do not yield detailed information about the changes in energy and entropy that occur during the magnetic transitions. This information can be obtained, in particular, from measurements of the magnetocaloric effect. [2] The object of the present work was to investigate the magnetic phase transitions occurring in single crystals of terbium-yttrium alloys with the aid of the magnetocaloric effect (the ΔT-effect), using the data on the magnetic and magnetostriction properties. Up to the present the magnetocaloric effect in the rare-earth metals (REM) has been measured only on polycrystalline Gd and Dy samples. [1,3] However, owing to the huge magnetic anisotropy of the REM and their alloys, [1] the behavior of the ΔT-effect and other properties along the hexagonal axis differs significantly from the behavior in the basal plane, and therefore the results of measurements on polycrystalline samples do not give sufficiently detailed information for the interpretation of the magnetic phase transformations in these substances.

EXPERIMENTAL RESULTS

The method of growing single crystals of the Tb-Y alloys and their analysis have been described earlier. [4] The magnetocaloric-effect measurements were carried out in an evacuated casing (10^{-5}-Torr vacuum) with the aid of a differential thermocouple. The temperature-stabilization system guaranteed a constancy of the temperature in the active volume to within 0.005 K. The magnetization was measured with a vibrating magnetometer with an oscillating sample.

In Fig. 1 we show the temperature dependences of the ΔT-effect for terbium and the alloys Tb-9 at .% Y and Tb-16.5 at .% Y in a magnetic field applied in the basal plane along the b axis (the axis of easy magnetization) and along the hexagonal axis c (the axis of difficult magnetization). The curves exhibit maxima in the temperature behavior of the ΔT-effect at temperatures that coincide with the magnetic-phase-transition tempera-

tures determined from the magnetic measurements. According to the neutron-diffraction data, [5] the ΔT-effect maximum occurring at the higher temperature at the point Θ_2 corresponds to the paramagnetic-helical antiferromagnetic phase transition. The temperature dependence of the magnetization has here a maximum similar to the maximum at the Neel point of antiferromagnetic materials. The ΔT-effect maximum at the lower temperature is due to the helical antiferromagnetic-ferromagnetic transition, which in the absence of a magnetic field occurs at the point Θ_1. In the case of terbium, this low-temperature maximum in the vicinity of the point Θ_1 is observed only in weak fields (see the inset in Fig. 1a). The values of Θ_1 and Θ_2 determined from the measurements along the b and c axes coincide, except for terbium. The magnetic-phase-transition temperatures for the Tb-Y alloys are given in Table I.

According to our measurements, the magnetization in the Tb-Y alloys exhibits a stepwise variation in its magnitude in definite critical fields $H = H_{cr}$ (see Fig. 2). In these fields the helical magnetic structure is destroyed. The temperature dependence of H_{cr} has a maximum in the temperature range $\Theta_1 - \Theta_2$, and, as the points Θ_1 and Θ_2 are approached, the magnitude of H_{cr} decreases.

In a magnetic field (Fig. 3) applied along the b axis, the magnetocaloric effect undergoes in the temperature range $\Theta_1 - \Theta_2$ a stepwise change in its magnitude at $H = H_{cr}$, which, as in the case of the magnetization, can clearly be explained by the destruction of the helical magnetic structure by the external field. Above a definite temperature (207 K for Tb-9 at .% Y and 190 K for Tb-16.5 at .% Y) there occurs a change in the sign of

TABLE I. The magnetic phase transition temperatures Θ_1 and Θ_2 in single crystals of Tb-Y alloys.

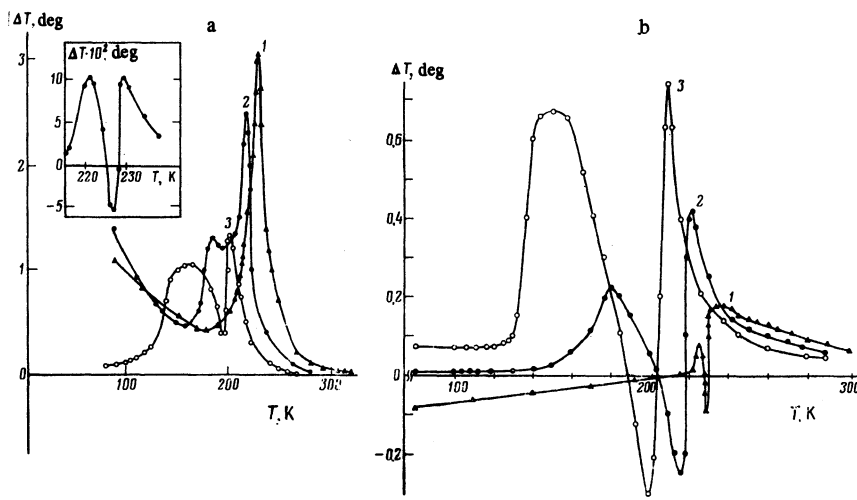| Alloy;	Θ_1, K	Θ_2, K
Tb	221	{229 along the b axis; {235 along the c axis
Tb—9 at.% Y	175	217
Tb – 16.5 at.% Y	133	207

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FIG. 1. Temperature dependence of the
magnetocaloric effect in single crystals of
terbium (the curve 1) and Tb-9 at.% Y and
Tb-16.5 at.% Y alloys (the curves 2 and 3):
a) in an 8-kOe magnetic field applied in the
basal plane along the b axis; b) in a 12-kOe
magnetic field applied along the hexagonal
axis c. The inset in Fig. 1a shows the de-
pendence $\Delta T(T)$ for terbium in a 200-Oe field
parallel to the b axis.

the jump in the magnetocaloric effect at $H = H_{cr}$ from
positive to negative.

The helical antiferromagnetic-ferromagnetic transi-
tion, which is accompanied by a maximum in the tem-
perature-versus-ΔT-effect curve and a sharp increase
in the magnetization, shifts, as the field strength is in-
creased, toward the region of higher temperatures in
accordance with the dependence $H_{cr}(T)$. The minimum
of the ΔT-effect in the $\Theta_1 - \Theta_2$ temperature range be-
comes less pronounced in a strong field.

From the isotherms of the magnetocaloric effect in a
field applied along the c axis it can be seen (Fig. 4) that,
as the temperature is raised in the $\Theta_1 - \Theta_2$ temperature
region, the positive ΔT-effect gradually decreases to
zero, and then the ΔT-effect becomes negative. As the
temperature is raised further and the point Θ_2 is ap-
proached, kinks develop in the isotherms, and in the im-
mediate vicinity of the point Θ_2 in the paramagnetic re-
gion the magnetocaloric effect becomes positive in any
external field.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The destruction of the helical magnetic structure by
a field $H \geqslant H_{cr}$ is manifested in a stepwise increase in
the magnetization and in a sudden evolution or absorp-
tion of heat, which is characteristic of first-order phase
transitions. The data obtained in the magnetization and
magnetocaloric-effect measurements allowed the deter-
mination of the dependence $H_{cr}(T)$ (see the inset in Fig.
2). There occur in the magnetocaloric-effect curves
$\Delta T(H)$ in the region of increase of H_{cr} positive jumps
at $H = H_{cr}$ (see Fig. 3). At temperatures at which H_{cr}
attains its maximum, there occurs a change in the sign
of the jump in the isotherms $\Delta T(H)$. The jump in the
magnetocaloric effect becomes negative in the tempera-
ture region where H_{cr} decreases with increasing tem-
perature. The shift of the transition temperatures
under the action of magnetic fields is connected, ac-
cording to thermodynamics, with the heat of transi-
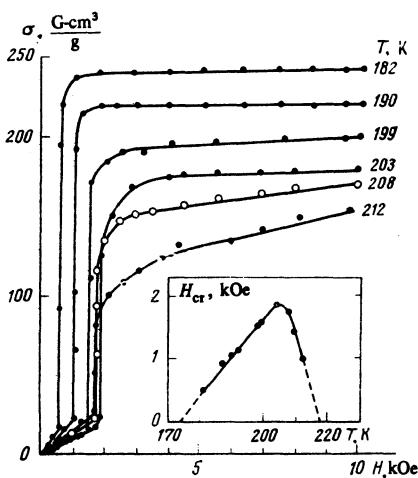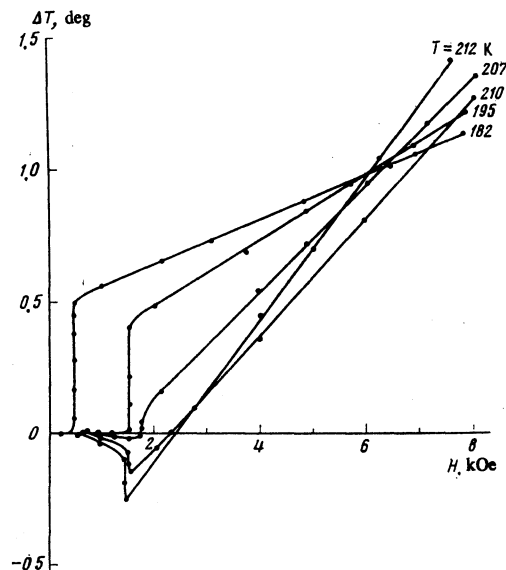tion.[6] On the basis of the thermodynamic relations

FIG. 2. Dependence of the magnetization of a single crystal of
the alloy Tb-9 at.% Y on the strength of a magnetic field ap-
plied along the b axis. The inset shows the temperature depen-
dence of the critical field.

FIG. 3. Isotherms of the magnetocaloric effect in a Tb-9 at.%
Y single crystal in the $\Theta_1-\Theta_2$ temperature region ($H \| b$).

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FIG. 4. Isotherms of the magnetocaloric effect in a Tb-16.5 at.% Y single crystal in the $\Theta_1-\Theta_2$ temperature region $(H \| c)$.
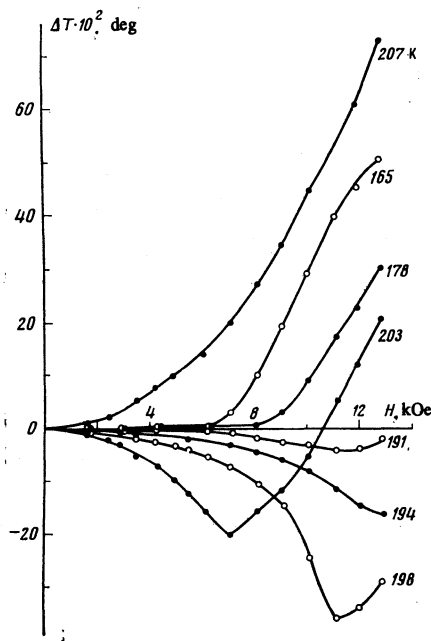
that are valid for first-order phase transitions, we can derive an equation similar to the Clapeyron-Clausius equation:

$$dH_{cr}/dT = -\Delta S/\Delta I. \tag{1}$$

On the other hand, the magnitude of the ΔT-effect is connected with the change, ΔS, in the entropy by the formula

$$\Delta T = -\frac{1}{C_p} T \Delta S. \tag{2}$$

Here C_p is the specific heat at constant pressure. The quantity ΔI in the formula (1) is the jump in the magnetization occurring in the transition from the helical-antiferromagnetic to the ferromagnetic state and ΔS is the jump in the entropy occurring in the transition.

The change of sign of the jump in the ΔT-effect at $H = H_{cr}$ in the $\Theta_1 - \Theta_2$ temperature range is in accord with the theoretical formulas (1) and (2). It can be seen from these formulas that at temperatures where $dH_{cr}/dT > 0$, the theory predicts that $\Delta T > 0$ and $\Delta S < 0$; if $dH_{cr}/dT < 0$, then $\Delta T < 0$ and $\Delta S > 0$, which agrees with the experimental data. At the temperature at which the $H_{cr}(T)$ curve has a maximum (here $dH_{cr}/dT = 0$), there is virtually no jump in the ΔT-effect, whereas quite a noticeable jump in the magnetization is exhibited in the isotherms $\sigma(H)$ (Figs. 2 and 3).

In terbium, at temperatures in the range $\Theta_1 - \Theta_2$ and in fields ~ 200 Oe, the temperature dependence of the ΔT-effect is similar in character to the dependence that we observed in the alloys. However, the low critical fields make the observation of the jumps in $\sigma(H)$ and $\Delta T(H)$ at $H = H_{cr}$ difficult.

According to thermodynamics, the jump in the entropy occurring in the transition is given by $\Delta S = -\Delta(\partial \Phi/\partial T)_p$. If we take into consideration the formula (2) and the previously-calculated[7-9] change occurring in the thermodynamic potential in the helical antiferromagnetic-ferromagnetic transition, then for the magnetocaloric effect due to the transition at $H = H_{cr}$ we can derive the relation

$$\Delta T_t = -\frac{T}{C_p} \Delta S = \frac{T}{C_p} \left[\Delta \left(\frac{\partial F^0}{\partial T} \right)_p - c_{33} \frac{\partial}{\partial T}[(\lambda_f^c)^2 - (\lambda_h^c)^2] \right.$$

$$\left. - \frac{1}{4}(c_{11}-c_{12})\frac{\partial(\lambda^{r,2})^2}{\partial T} - \frac{\partial K_6}{\partial T} - \frac{H\partial(\Delta I)}{\partial T} \right]. \tag{3}$$

Here ΔF^0 is the change occurring in the free energy of the exchange interaction in the transition; λ_h^c and λ_f^c are the spontaneous strictions along the hexagonal axis c in the helical-antiferromagnetic and ferromagnetic phases, respectively; $\lambda^{r,2}$ is the difference, measured in the basal plane in the ferromagnetic state, between the longitudinal and transverse saturation strictions; K_6 is the anisotropy constant in the basal plane; c_{11}, c_{12}, and c_{33} are elastic moduli; and H is a magnetic field applied in the basal plane.

The heat of transition ΔQ is connected with the quantity ΔT_t in the following manner

$$\Delta Q = C_p \Delta T_t. \tag{4}$$

Thus, it can be seen from (3) that the magnetocaloric effect resulting from the destruction of the helical structure contains contributions due to different processes. The first term in the square brackets in the formula (3) is a consequence of the change that occurs during the phase transition in the free energy (without its magnetoelastic part) of the exchange interaction between the layers; the second arises owing to the decrease in the magnetoelastic energy of the exchange interaction as a result of the magnetostrictive deformation along the hexagonal axis c; the third is due to a decrease in the magnetoelastic energy in the basal plane; the fourth, to a decrease in the energy of the magnetic anisotropy in the basal plane; and the fifth, to a change in the magnetization-magnetic field interaction energy.

The magnitudes of the contributions to the heat of transition ΔQ and the magntiude of the magnetocaloric effect ΔT_t were found by us for different temperatures with the aid of the data on the magnetization, the magnetostriction, and the thermal expansion.[10] The specific heat was determined from the measurements of the magnetocaloric effect and the magnetic susceptibility in the paramagnetic region, using the formula

$$C_p = \frac{CH^2}{2\Delta T} \frac{T}{(T-\Theta_\parallel)^2}. \tag{5}$$

(where $\Theta_\parallel$ is the paramagnetic Curie temperature for a magnetic field directed along the hexagonal axis and C is the Curie-Weiss constant), which follows from the Curie-Weiss law and the thermodynamic relations. A similar formula can be derived for the basal plane. The
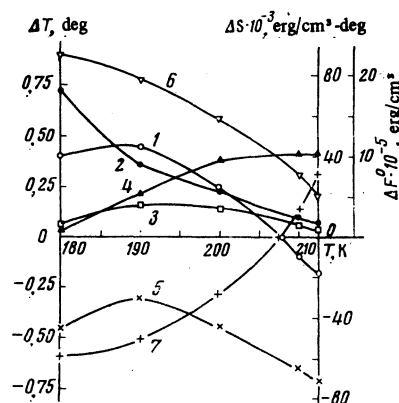
FIG. 5. Temperature dependence of the energy contributions to the magnetocaloric effect ΔT_t induced by the transition in $H = H_{cr}$ for the alloy Tb-9 at.% Y (the computations were carried out, using the formula (3)). Curve 1: ΔT_t jump measured experimentally; curve 2:

$$- \frac{T}{C_p} c_{33} \frac{\partial}{\partial T} [(\lambda_f{}^c)^2 - (\lambda_h{}^c)^2];$$

curve 3:

$$- \frac{T}{C_p} \frac{c_{11} - c_{12}}{4} \frac{\partial (\lambda^{\gamma,2})^2}{\partial T};$$

curve 4: $- (T/C_p) H \partial \Delta I/\partial T$; curve 5: $(T/C_p)\Delta(\partial F_0^0/\partial T)_p$; curve 6: jump in the free energy of the interlayer exchange interaction for $H = H_{cr}$, $\Delta F_0^0 = F_f^0 - F_h^0$; curve 7: the entropy jump ΔS for $H = H_{cr}$.

obtained specific-heat values for terbium ($C_p = 0.24$ J/g-deg) are in satisfactory agreement with the data of Ref. 11. For the two remaining samples, the specific-heat value was equal to ~ 0.25 J/g-deg.

The values of the various contributions to the magnetocaloric effect are shown in Fig. 5. As can be seen, the dominant role is played by the contribution due to the change in the free energy of the exchange interaction between the layers for $H = H_{cr}$ and the contribution due to the change in the magnetoelastic part of the exchange interaction as a result of the magnetostrictive deformation along the c axis. This latter contribution is extremely high in the REM and in Tb-Y alloys, as a result of which the magnetostriction in them attains huge values $(\lambda_f^c - \lambda_h^c) \sim 10^{-3}$. [10,12] The heat of transition near Θ_1 is due largely to the conversion of the magnetoelastic energy into heat in the case when $H = H_{cr}$ ($\Delta T > 0$). This agrees with the inference[9] that the huge magnetostriction exerts considerable influence on the phase transition at the point Θ_1. The helical antiferromagnetic-ferromagnetic phase transition can be explained on the basis of the temperature dependence of the exchange parameters, [13] which, in the terbium-yttrium alloys, decrease sharply upon cooling owing to the gigantic magnetostriction. [9,10,12]

As the temperature is increased, the contributions to ΔT_t due to the magnetoelastic energy and the magnetic anisotropy in the basal plane decrease appreciably. On the other hand, as the temperature is raised and the point Θ_2 is approached, the negative contribution

$$\left(\Delta T_\pi{}^0 = \frac{T}{C_p} \Delta \frac{\partial F^0}{\partial T} \right)_p$$

increases sharply in absolute value (the curve 5 in Fig. 5), exceeding the positive contributions, as a result of which, above the temperature at which $dH_{cr}/dT = 0$, the magnetocaloric effect becomes negative. This negative contribution can be explained by the decrease in the interlayer exchange interaction $F^0 = F^0(I_s, \omega)$ (as well as the decrease in the change, ΔF^0, occurring in it during the phase transition), as a result of a decrease in the spontaneous magnetization and an increase in the interlayer turn angle ω [1,5] as the temperature is raised (see the curve 6 in Fig. 5).

The temperature dependence of the $\Delta T_{\parallel}$-effect along the hexagonal axis exhibits, besides the maxima at the points Θ_1 and Θ_2 connected with the above-described transitions, a deep negative minimum in the middle of the temperature interval $\Theta_1 - \Theta_2$ (see Fig. 1b). A number of the $\Delta T_{\parallel}$-effect isotherms have a negative sign in the entire region of fields (the 191-, 194-, and 198-K isotherms in Fig. 4). Since the magnitude of the ΔT-effect is proportional to $- \partial\sigma/\partial T$, the steep negative minimum in the temperature-versus-ΔT-effect curves in Fig. 1b indicates that there occurs at the temperature corresponding to this minimum a rapid increase in the magnetization along the c axis in an external field applied along the hexagonal axis. Such an explanation is in accord with the results of the theoretical computations of the behavior of the magnetization of a REM located in a field parallel to the hexagonal axis[14] and with the computations of the magnetic susceptibility of a ferromagnetic material in a magnetic field applied along the axis of difficult magnetization. [15]

As a result of the process of spin orientation along the field, the helical magnetic structure (the antiferromagnetic spiral) gets transformed into a ferromagnetic spiral with the resultant magnetic moment along the c axis. Such a structure was observed earlier in a dysprosium single crystal. [16] The process of spin orientation in a field directed along the hexagonal axis occurs more intensely in yttrium-rich Tb-Y alloys, owing to the decrease of the magnetic-anisotropy constant as terbium is diluted with yttrium. [13] This is indicated by the growth of the maximum of the $\Delta T_{\parallel}$-effect at the point Θ_2 as the yttrium content is increased (Fig. 1b).

It is noteworthy that, in contrast to the measurements in the basal plane, when the field is applied along the c axis, no jump is observed in the $\Delta T_{\parallel}$-effect as the field is increased (Fig. 4). This indicates a gradual transformation of the helical magnetic structure into a ferromagnetic spiral without a jump in the magnetization, which is in accord with theory. [14,15]

CONCLUSION AND DEDUCTIONS

Thus, the study of the magnetic phase transitions by means of magnetocaloric-effect and magnetization mea-

surements on single crystals of terbium and the Tb-Y alloys and the thermodynamic analysis of the experimental data have shown that, in a magnetic field applied in the basal plane, the helical antiferromagnetic-ferromagnetic transition is a first-order phase transition. In this transition, the abrupt liberation or absorption of heat occurs mainly as a result of changes in the interlayer exchange interaction and the magnetoelastic energy.

In the case when the magnetic field is applied along the hexagonal axis c, the character of the magnetic phase transformations changes significantly. To wit, a helical antiferromagnetic-helical ferromagnetic transition occurs. This transition is accomplished without stepwise increases in the entropy and the magnetization.

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Resistivity of shock-compressed ytterbium

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Results are reported of an experimental investigation of the electric conductivity of shock-compressed ytterbium in the pressure range up to 220 kbar. It is shown that up to ~30 kbar the resistivity of ytterbium increases with pressure, and the ytterbium acquires semiconducting properties. At pressures on the order of 20 to 30 kbar the ytterbium undergoes a phase transition and becomes metallic again. Further increase of the shock-loading amplitude leads, at 80–150 kbar, to a sharp increase of the ytterbium resistivity, thus attesting to still another transition due to a realignment of the electron structure, a transition not heretofore observed under static compression conditions. The temporal characteristics of the aforementioned transitions were measured under actual shock-loading conditions. It is shown that raising the temperature and increasing the intensity of the shear deformations accelerates the transitions and decreases the values of the corresponding critical pressures.

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The investigated shock-compressed ytterbium was 99.9% pure, had an initial resistivity $\sim 2.8 \times 10^{-5}$ Ω-cm at room temperature and atmospheric pressure, and a density 6.97 g/cm^3. The dependence of the relative change of the resistance of the ytterbium on the shock-loading pressure, $R/R_0 = f(P)$, where R_0 and R are the ytterbium resistances prior to and during the compression and P is the shock-loading pressure, was obtained by performing a series of experiments (see Fig. 1) in which the loading pressure of a standard material with an inlayed ytterbium sample was known beforehand.

The ytterbium sample was a sinusoid of ytterbium foil 0.05 mm thick glued with epoxy resin between the layers of the standard material. The leads for the ytterbium sample were strips of copper foil. When necessary, the ytterbium sample was insulated from (metallic) the standard material with a film of ftoroplast-4 (Teflon) 0.02 mm thick. The sample was compressed by a plane shock wave produced by exploding a cylindrical explosive whose strength was varied. Shock waves of different intensity were applied to the standard substances with the inserted ytterbium samples through copper and