Magnetostriction and phase transitions in terbium-yttrium alloys

V. S. Belovol, V. A. Finkel', and V. E. Sivokon'

Physico-technical Institute, Ukrainian Academy of Sciences

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The crystal structure of alloys containing Tb and 5, 10, 20 and 50 wt.% of Y is studied in the 77–300 K temperature range and in magnetic fields up to 16 kOe. It is shown that the effects observed (magnetostriction of the crystal lattice and "helicoidal antiferromagnetism-collinear ferromagnetism" phase transitions) are mainly due to deformation of the magnetic structure on variation of the temperature and of the magnetic field strength. It is found that dilution of Tb by paramagnetic Y results in an appreciable decrease of all magnetostrictive effects.

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1. INTRODUCTION

Terbium and yttrium form a continuous series of solid solutions with hexagonal structure (hcp).[1,2] As the temperature is lowered, the following magnetic states are realized in their alloys: paramagnetism at $T > T_N$, helicoidal antiferromagnetism at $T_C < T < T_N$ (the helicoid axis is the ⟨0001⟩ hexagonal axis), and collinear ferromagnetism at $T < T_C$ (the magnetic moment **M** is parallel to the axis b ⟨01$\bar{1}$0⟩).[3] The temperatures T_N and T_C are lowered when the terbium is diluted with yttrium; no ferromagnetic ordering is observed in alloys containing more than 25 at.% Y.[4] In the alloys, these temperatures are lowered under the influence of hydrostatic compression.[5] The helicoidal structure in Tb-Y alloys is destroyed when an external magnetic field is applied, and the magnetic field intensities that lead to the transition to the ferromagnetic state (H_{cr}) increase as a result of magnetic dilution.[6,7]

Inasmuch as the magnetic properties of Tb-Y alloys are regularly altered by dilution, they can be regarded as model objects for the study of the relation between the crystal structure and the magnetism of metals. Usually the change of the magnetic properties or of the magnetic structure of rare-earth metals (REM) following introduction of paramagnetic impurities into the lattice or following a change of temperature or pressure is regarded as a result of the change of the crystal-lattice parameters (or of their ratio).[8-10] The REM crystal-lattice parameters themselves, however, are also strongly dependent on the magnetic state of the system; considerable information can therefore be extracted from experiments in which it is possible to study the change produced in the crystal structure by direct action on the spin system. The method of x-ray diffraction in a magnetic field, previously developed[11-15] for pure REM (Gd, Tb, Dy), makes it possible to study the magnetic deformation of the crystal lattice (i.e., the induced magnetostriction), phase transitions "in terms of the magnetic field," and also processes connected with domain motion. A joint analysis of the influence of magnetic dilution, temperature, and external magnetic field on the crystal structure is obviously the optimal way of constructing the overall picture of the relation between the crystal structure and the magnetism of a metal.

The main content of the present article is therefore devoted to an x-ray diffraction study of the spontaneous and induced magnetostriction of the crystal lattices of Tb-Y alloys, and also of the magnetic phase transitions with respect to the temperature and the magnetic field. The objects of the investigations were alloys of Tb with 5, 10, 20, and 50 wt.% Y (8.6, 16.3, 30.9, and 61.1 at.%, respectively), in which are realized all the qualitatively possible types of temperature dependences of the parameters of the helicoidal and collinear magnetic structures.

2. PROCEDURE

The Tb-Y alloys were fused in an arc furnace with nonconsumable electrode in an argon atmosphere.1) The alloy samples were mechanically heat treated to obtain a strong texture of the basal plane (0001) of the hcp lattice or of a prism of the first kind (10$\bar{1}$0). The use of textured samples extends greatly the possibilities of the magnetic neutron-diffraction method, making it possible to determine quite correctly the change of the crystal-lattice parameters in the magnetic field.

The temperature dependences of the Tb-Y alloy lattice parameters were measured in the 77–300°K range with a low-temperature attachment to the URS-50I diffractometer.[16] Reflections of the type (h0$\bar{\mathrm{h}}$0) and (000l) from the hcp lattice were recorded. The relative accuracy with which the lattice parameters were measured ($\Delta a_i/a_i$) was $\sim 3 \times 10^{-5}$.

The x-ray diffraction patterns of the samples in magnetic fields of intensity $0 < H < 16$ kOe were obtained by a photographic procedure[11] in the temperature interval 77–300°K. The measurement accuracy was $\Delta a_i/a_i \sim 1 \times 10^{-4}$.

The criterion of the alloy transition from the antiferromagnetic to the ferromagnetic state was the lowering of the crystal-lattice symmetry from hexagonal to rhombic, accompanied by line splitting in accord with the scheme

$$(hkil)_{\mathrm{r}} \rightarrow \begin{matrix} (h, & 2k+h, & l)_{\mathrm{p}} \\ (k, & 2h+k, & l)_{\mathrm{p}}, \\ (\bar{h}+\bar{k}, & \bar{h}+k, & l)_{\mathrm{p}} \end{matrix} \qquad (1)$$

with

$$2\theta(k, 2h+k, l)_{\mathrm{p}} < 2\theta(h, 2k+h, l)_{\mathrm{p}} < 2\theta(\bar{h}+\bar{k}, \bar{h}+k, l)_{\mathrm{p}}, \qquad (2)$$

where 2θ is the diffraction angle. The inequalities (2) are characteristic of a rhombic lattice with an axis ratio $b/a > \sqrt{3}$.

3. RESULTS OF EXPERIMENTS

A. Temperature Dependences of the Tb-Y Alloy Crystal Lattice Parameters

The results of the measurements of the crystal-lattice parameters of the Tb-Y alloys at temperatures 77–300°K are shown in Figs. 1 and 2. For comparison, the same figures show plots a(T), b(T), and c(T) for pure Tb[15]

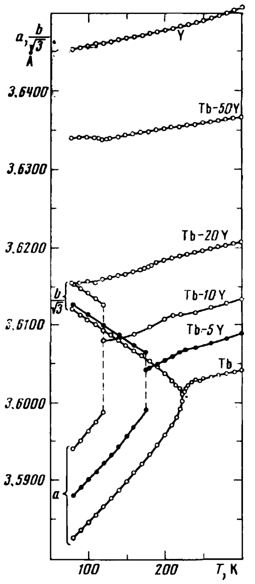

FIG. 1

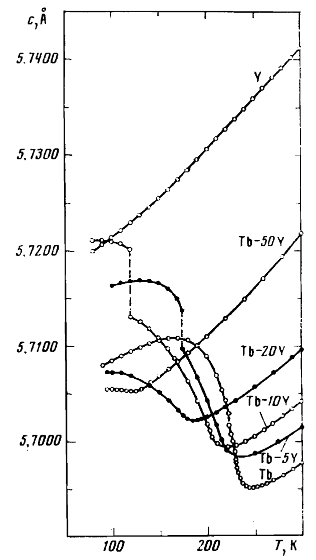

FIG. 2

FIG. 1. Temperature dependence of the parameters a and b of the crystal lattices of Tb-Y alloys.

FIG. 2. Temperature dependence of the parameter c of crystal lattices of Tb-Y alloys.

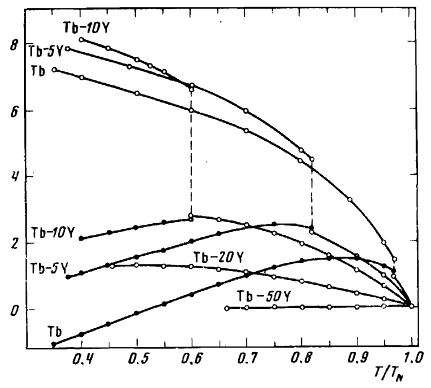

FIG. 3. Temperature dependence of the axis ratios c/a and b/a of Tb-Y alloys. The light circles denote the values of $\{[c/a - (c/a)_N]/(c/a)_N\} \times 10^3$, and the dark circles the values of $c/b\sqrt{3}$.

and Y[16]. For alloys, the temperature dependences of the lattice parameters are similar: at $T > T_N$ the a(T) and c(T) curves have positive slopes; near T_N, a noticeable change of the slope is observed (the values of T_N themselves correspond to inflection points of the curves); at $T < T_N$ the coefficient of thermal expansion along the c axis ($\alpha_{\parallel}$) is negative, and the a(T) curves are steeper than at $T > T_N$; at T_C, the symmetry of the crystal lattice is reduced to rhombic (in which case the parameter a decreases jumpwise, while the parameters b and c increase); at $T < T_C$ the values of b and c increase with decreasing temperature (at sufficiently low temperatures, the slope of the c(T) curves changes from negative to positive).

With decreasing temperature, the axis ratio c/a increases in the same manner as when the Tb content of the alloys is increased (Fig. 3). In the ferromagnetic state, the degree of rhombicity of the lattice (the ratio b/a) increases almost linearly with decreasing temperature (Fig. 4).

The temperatures of the alloy transitions from the paramagnetic to the antiferromagnetic state (T_N) and from the antiferromagnetic to the ferromagnetic state (T_C) are the following:

	Tb [15]	Tb–5% Y	Tb–10% Y	Tb–20% Y	Tb–50% Y
T_N, K:	230	213	200	175	120
T_C, K:	222.5	175	120	–	–

B. Effect of Magnetic Field on the Crystal Structure of Tb-Y Alloys

Figure 5 shows the c(H) isotherms for different Tb-Y alloys. In view of the relatively low accuracy with which the magnetostriction was measured in the para-, antiferro-, and ferromagnetic states, the c(H) plots were approximated as a rule by straight lines. The jumplike increase of the parameter c (accompanied by the splitting of the diffraction lines of the (hki*l*) type) was attributed to the antiferromagnetism—ferromagnetism transition with respect to the magnetic field.

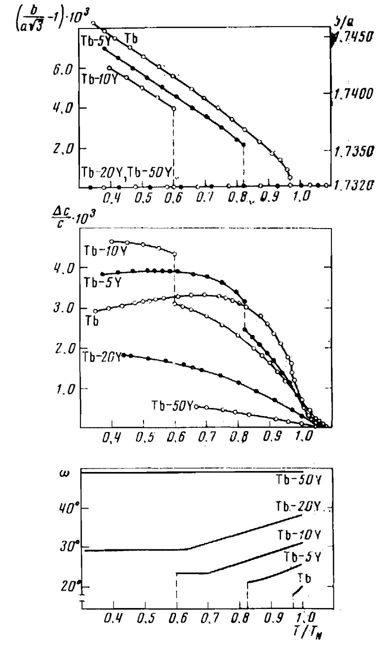

FIG. 4. Temperature dependence of the helicoid angle ω [3] and of the spontaneous magnetostriction deformations ($\Delta c/c$ and $\Delta b/a\sqrt{3}$) of Tb-Y alloys.

The c(H) isotherms revealed the following regularities:

a. At $T > T_N$ the isotherms have a small negative slope. In the immediate vicinity of the Neel point, $dc/dH > 0$. Maxima of the magnetostriction are observed at T_N.

b. At $T_c < T < T_N$ and $H < H_{cr}$, the isotherms have a positive slope. Lowering the temperature and increasing the Y content in the alloys decreases the slope.

c. The jumps of the parameter c during the antiferromagnetism-ferromagnetism phase transition (i.e., at $H = H_{cr}$) increase both when the transformation temperature is lowered and when the Y content in the alloys is increased.

d. At $T < T_C$ and $T_C < T < T_N$ we have $H > H_{cr}$ and $dc/dH < 0$. The isotherms c(H) have a tendency to increase in slope with increasing Y content in the alloys. At a Y content 20% the c(H) isotherms have already a positive slope.

Discontinuities of the parameter, accompanied by rhombic splitting of the diffraction lines from the hcp lattice, were observed also for the alloy Tb + 20% Y in the temperature interval 77—140°K. This is a direct

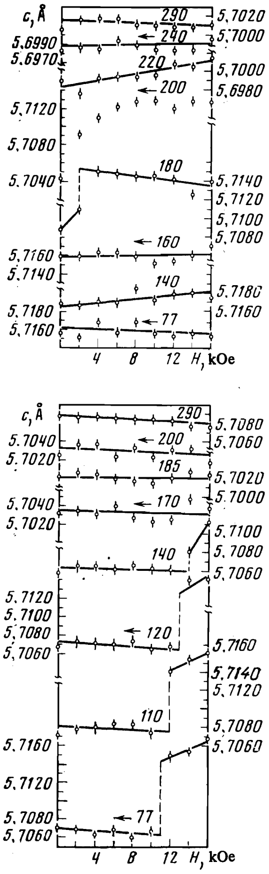

FIG. 5

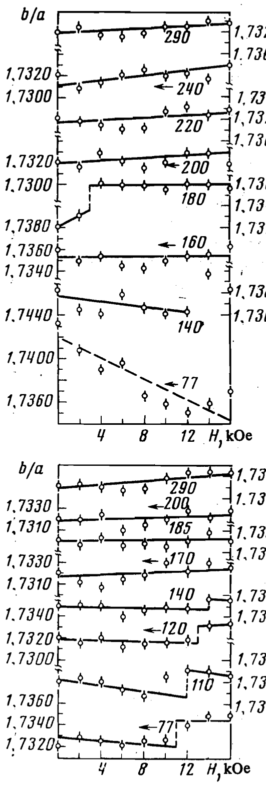

FIG. 6

FIG. 5. Isotherms of the field dependences of the parameter c of the crystal lattices of the alloys Tb + 5% Y (upper plots) and Tb + 20% Y (lower plots). The number at the curves indicate the temperature (°K); the left-hand scale is for the temperatures 240, 200, 170, 160, 120 and 77°K (marked by an arrow), and the right-hand scale is for the remaining temperatures.

FIG. 6. Isotherms of the field dependences of the b/a axis ratios of Tb-Y alloys. The notation is the same as in Fig. 5.

structural confirmation of the feasibility of a first-order antiferromagnetism-ferromagnetism transition with respect to the magnetic field in a material that does not go over spontaneously into the ferromagnetic state.[6]

No analogous effect was observed for the alloy Tb + 50% Y.

The variation of the b/a axis ratio in a magnetic field is shown for the Tb-Y alloys in Fig. 6. The maximal effects were observed at $H = H_{cr}$, when the axis ratios increased jumpwise ($b/a = \sqrt{3}$ for the hcp lattice).

Small deviations of b/a from $\sqrt{3}$ took place also in the antiferromagnetic state (the appearance of small rhombic deformations[17] λ^{γ} is connected with a certain distortion of the helicoidal structure in the magnetic field[13]). In the ferromagnetic state, we observed a decrease of b/a with increasing magnetic field intensity, and when the temperature was lowered the slope b/a of the isotherms increased.

An increase in the Y content in the alloys leads to a decrease in the values of $|d(b/a)/dH|$.

4. DISCUSSION OF RESULTS

When discussing the described results, attention must be paid first to the clearly pronounced general character of the behavior of the crystal structure of the alloys with decreasing temperature, with increasing magnetic field intensity, and with increasing content of the magnetoactive Tb atoms, i.e., as a result of the internal and external actions that leads to enhancement of the indirect sf-exchange interaction. The most general features of the behavior of the crystal structure—the expansion of the crystal lattice along the principal axis ⟨0001⟩ and its compression in the basal plane (0001). We note immediately that this character of the change of the structure is possessed by the Tb-Y alloy in both the antiferromagnetic and the ferromagnetic state, although at $T < T_C$ the situation is made complicated by the appearance of rhombic distortions of the lattice.

If account is taken of the most general and strongest effect—the magnetostriction along the principal axis[2] $\lambda_c = \Delta c/c$—then, judging from the results of the temperature measurements, the largest contribution to λ_c is made by the change of the period of the magnetic structure. It is seen from Fig. 4 that the maximum change of the helicoid angle ω corresponds to the maximum magnetostriction. At a helicoid angle that does not depend on the temperature (the alloy Tb + 50% Y), λ_c is minimal. It is obvious that the strong induced magnetostriction of alloys with large Tb contents, at temperatures close to T_N, can be attributed to a noticeable deformation of the antiferromagnetic structure (i.e., to a decrease of ω with increasing magnetic field intensity[14]), while the weak magnetostriction of the dilute alloys can be connected with the stability of their helicoidal magnetic structure (see Fig. 5).

The decrease of the helicoid angle with decreasing temperature or with increasing magnetic field intensity leads to a loss of stability of the antiferromagnetic structure[7,17] accompanied by a first-order phase transition. A clearly pronounced correlation is observed between the discontinuities of the helicoid angle ω in the antiferromagnetism-ferromagnetism transition and the jumps of the crystal-lattice parameters.

The increase of the degree of rhombic distortions ($b/a - \sqrt{3}$) in the ferromagnetic region with decreasing temperature (Fig. 4) can be connected (within the framework of the one-ion theory[18]) with the decrease of the local deviations of the magnetic moments **M** from the easy axis b ⟨01$\bar{1}$0⟩. This should be accompanied by an increase in the density of the magnetostriction energy (E_{ms}) in the basal plane, the dependence of which on the deformation $\lambda^{\gamma} = b/a - \sqrt{3}$ is given by[17]

$$E_{ms} = -c^{\gamma}(\lambda^{\gamma})^2/8, \tag{3}$$

where $c^{\gamma} = 2(c_{11} - c_{12})$ is the shear modulus.

Both the appearance of rhombic distortions of the crystal lattice at the phase-transition point, and their enhancement at $T < T_C$ are accompanied by an increase of the deformation of the c axis. The corresponding change of the energy of exchange interaction between the basal planes (E_{ex}) can be approximately expressed in terms of the magnetostriction work

$$E_{ex} = c_{33}(\lambda_c)^2/2, \tag{4}$$

where c_{33} is the elastic constant (Young's modulus for the principal axis).

At the antiferromagnetism-ferromagnetism phase transition point, the following condition should be satisfied:

$$\Delta E_{ms} + \Delta E_{ex} = 0. \tag{5}$$

Unfortunately, the elastic moduli of the Tb-Y alloys have not been determined; on the other hand, if the values of c_{ij} for pure terbium [19] are substituted in Eqs. (3) and (4) the condition (5) is satisfied approximately.[3] This means that the work of the magnetostriction along the principal axis actually compensates for the change of the density of the magnetostriction energy in the basal plane. This circumstance is obviously also the cause of the absence of jumps in the $c/b = f(T)$ curves at the point T_C (Fig. 3) and the change of the "hierarchy" of the $\Delta c/c = f(T/T_N)$ curves for the alloys at $T < T_C$ (Fig. 4), when larger values of $\Delta(b/a)$ correspond to larger jumps of the parameter c at the point T_C.

For the induced antiferromagnetism-ferromagnetism transition in a magnetic field at $T_C < T < T_N$, the jumps of the lattice parameters are smaller than for the spontaneous transitions at the point T_C. This is in full agreement with the concepts developed in [14], according to which the magnetic-field phase transition is preceded by a noticeable deformation of the helicoidal magnetic structure (a decrease of the angle ω to a certain critical value at which the SS structure becomes unstable), accompanied by expansion of the crystal lattice along the principal axis. The discontinuity of the helicoid angle ($\Delta\omega$) is smaller here than at the point T_C, and the jumps of the crystal-lattice parameters are correspondingly smaller.

The decrease of the degree of rhombic distortions in the ferromagnetic state with increasing magnetic field intensity can be connected with rotation of the magnetic moment M in the basal plane in the direction of the projection of the magnetization vector of the magnetic field H. [15] In accord with the representations developed above, the decrease of b/a should be accompanied by a decrease of the parameter c, as is indeed observed in the experiments (Fig. 5). It appears that two effects become superimposed: the increase of c with the field because of the enhancement of the exchange interaction, and the decrease of c as a result of rotation of M in the basal plane. As a rule, the second effect is stronger, and this explains the rather paradoxical character of the functions c(H) in the ferromagnetic state.

The decrease of the derivative $|d(b/a)/dH|$ upon magnetic dilution indicates that this magnetostriction effect has a one-ion character.

5. CONCLUSION

The main result of the analysis of the structural aspects of the behavior of the Tb-Y alloys in external field (temperature and magnetic) is the construction of a qualitative picture of the dependence of the crystal-lattice deformations (λ_c and λ^γ) on the temperature and on the magnetic field intensity (Fig. 7). The constructed scheme applies to a large class of rare-earth magnets, in which helicoidal and collinear magnetic structures are realized. The observed striction effects are connected in the main with the change of the magnetic-structure parameters:

1) Decrease of the helicoid angle ω causes the appearance of positive magnetostriction along the principal axis, with λ_c proportional to $\Delta\omega$.

2) A temperature-induced or field-induced deformation of the helicoidal magnetic structure (a decrease of ω to a certain critical value) leads to instability of the crystal lattice, i.e., to a first-order antiferromagnetism-ferromagnetism phase transition.

3) Raising the degree of magnetic ordering with decreasing temperature is accompanied by an increase of the rhombic deformations of the hexagonal lattice ($\lambda^\gamma = b/a - \sqrt{3}$); application of an external field leads to a distortion of the collinear ferromagnetic structure and to a lowering of b/a.

4) A decrease of the distance between the magnetoactive atoms in the case of magnetic dilution stabilizes the helicoidal antiferromagnetic structure, as a result of which the spontaneous and induced magnetostriction are noticeably decreased and the jumps of the lattice parameters in the antiferromagnetism-ferromagnetism transformation are increased.

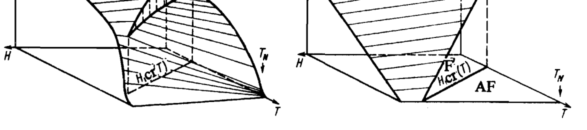

FIG. 7. Change of the magnetic deformation of the crystal lattices along the principal axis ($\lambda_C = \Delta c/c$) and of the rhombic distortions ($\lambda^\gamma = b/a - \sqrt{3}$) vs. the temperature and the magnetic-field intensity.

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[1] The authors consider it their pleasant duty to thank V. V. Vorob'ev for help with the preparation of the alloys.

[2] Δc is the difference between the measured value of the parameter and the value obtained by extrapolation from the paramagnetic region.

[3] The condition (5) is satisfied, naturally, only approximately, since at the phase-transition point there is a thermal effect connected with the small change of the volume in T_C. [2] This effect, however, is energy-wise much smaller than the change of the magnetoelastic energy.

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