CRYSTAL STRUCTURE OF TERBIUM-YTTRIUM ALLOYS AT 77—330°K

V. A. FINKEL' and V. V. VOROB'EV

Submitted

Zh. Eksp. Teor. Fiz. **53**, 1913—1919 (December, 1967)

The crystal structure of a number of solid solutions formed in the Tb—Y system is studied by low temperature x-ray diffraction. It is shown that alloying with yttrium lowers the Neel and Curie temperatures; the change of the atomic volume at the Curie point and the linear expansion coefficients along the hexagonal axis increase. No rhombic distortion of the hexagonal crystal lattice has been observed on going from the helicoidal antiferromagnetic structure to the collinear structure characteristic of pure rare earth metals.

X-RAY diffraction studies of the crystal structure of heavy rare-earth metals (REM)—gadolinium, terbium and dysprosium [1-3] —at low temperatures revealed a number of anomalies in the temperature dependences of the periods of the hexagonal close-packed (hcp) lattice and of the atomic volume, due to singularities of the magnetic and electronic structures of these metals. It was of interest to study the influence of the magnetic dilution on the crystal structure of these metals. The objects of investigations of this kind can be solid solutions of REM with nonmagnetic metals having the same valence (+3) and an hcp structure.

Apparently the optimal material for the investigation is a solution of terbium in yttrium: these metals form a continuous series of solid solutions [4], the magnetic properties of their alloys have been sufficiently well investigated [5,6], and the temperatures of the transition to antiferromagnetic (T_n) and the ferromagnetic (T_C) states are not very low. In addition, the helicoidal magnetic structures of the Tb-Y alloys are sufficiently simple: when $T_C < T < T_N$ an antiferromagnetic structure of the type of a simple helix is observed, and below T_C there is ferromagnetic collinear ordering of the spins in the basal planes [7]. The introduction of yttrium into the solid solutions leads to a lowering of the temperatures of the magnetic transitions and to an increase of the angle ω between the resultant magnetic moments and the neighboring basal planes; the character of the temperature variation of the angle of the helicoid $\omega(T)$ also depends on the yttrium concentration.

We investigated alloys containing 5, 10, 20, and 50, wt.% yttrium. With such a choice of compositions, all the qualitatively possible types of $\omega(T)$ dependences

are realized in the samples. Certain magnetic-structure properties of the alloys are listed in Table I.

EXPERIMENTAL PART

The alloys were melted in an arc furnace with a nonconsumable electrode in an argon atmosphere at a pressure 0.5—0.6 atm. The charged materials were of sufficiently high purity, 99.5% for terbium and 99.8% for yttrium. Samples measuring $10 \times 20 \times 2$ mm were cut from the obtained castings (weighing 10—20 g) by electroerosion, and were subsequently stabilized by annealing at 1200°C in a vacuum of 2×10^{-6} mm Hg for 10—50 hours (the annealing time had to be increased with increasing yttrium content in the alloys, since a strong decrease in the grain was observed). The grains in the annealed samples reached 0.2—0.5 mm. X-ray diffraction and metallagraphic tests established that all the samples are homogeneous solid solutions; no superstructure lines due to atomic ordering were observed on the x-ray pictures.

The procedure for low-temperature x-ray structure investigations of the Tb-Y alloys did not differ essentially from that described earlier [1-3]. The photographs were taken with the URS-50I setup, equipped with a low-temperature attachment. Peaks from the (203) and (104) planes of the hcp lattice were recorded in Cr-K_α radiation at large diffraction angles.

The results of the measurements of the interplanar distances (d_{104} and d_{203}) of the Tb-Y alloys at 77—300°K are shown in Fig. 1. We see that the $d_{104}(T)$ and $d_{203}(T)$ plots depend essentially on the degree of magnetic dilution. All plots reveal a sharp minimum at temperatures close to T_n (see Table I).

Table I

Content of Y in alloy		Effective atomic magnetic moment, μ_B [6]	Effective spin parameter G	T_N, °K [7]	$\frac{dT_N}{dp}$, deg kbar [8]	ω_N, deg [7]	T_C, °K [7]	$\frac{dT_C}{dp}$, deg kbar [8]	ω_C, deg [7]	Note
wt. %	at. %									
5.00	8.60	8.7	9.60	213	—0.78	27	160	—0.8	21	*
10.00	16.56	8.5	8.76	202	—0.68	30	100	—0.5	23	*
20.00	30.89	8.1	7.26	183	—0.51	40	—	—	—	**
50.00	64.12	5.5	3.77	120	—0.30	49	—	—	—	***

*The helicoid angle ω increases linearly with the temperature.
**No ferromagnetic ordering was observed. At $T < 120$°K the angle ω does not depend on the temperature ($\omega = 31$), at $T > 120$° it increases linearly.
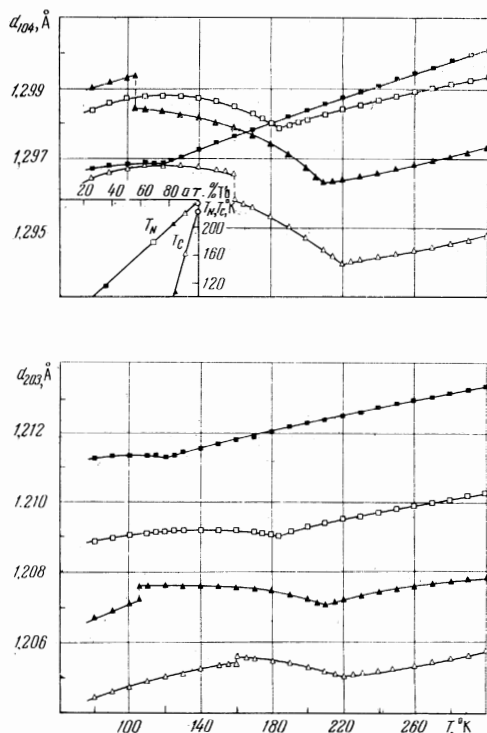***ω does not depend on the temperature.

FIG. 1. Temperature dependence of the interplanar distances from the planes (104) and (103) for the following alloys: Δ−Tb8.60 at % Y, ▲−Tb16.56 at % Y, □−Tb30.89 at. % Y, ■−Tb64.12 at % Y.

For terbium alloys with 8.60 and 16.56 at.% of yttrium there is observed, at lower temperatures, a discontinuity on the d(T) curves, evidencing also the presence of an ferromagnetism-antiferromagnetism transition[1]. The dependence of T_N and T_C of the alloys and of pure terbium on the degree of magnetic dilution is shown in the insert of Fig. 1. We see that T_C varies practically linearly with the atomic concentration of the yttrium, and the concentration dependence of T_N deviates slightly from linear.
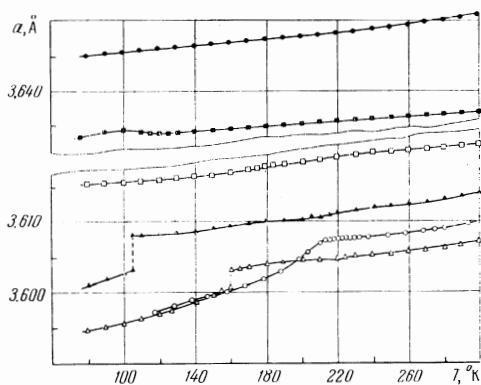

FIG. 2. Temperature dependence of the period a of the crystal lattices of the alloys: ○−Tb, Δ−Tb8.60 at % Y, ▲−Tb16.56 at % Y, □−Tb30.89 at % Y, ■−Tb64.12 at % Y, ⊙−Y.

With the aid of the curves of Fig. 1 we calculated the periods of the crystal lattices of the alloys; the corresponding a(T) and c(T) curves are shown in Figs. 2 and 3. For comparison, the same curves show the temperature dependences of the periods of pure terbium[5] and yttrium[9].

The c(T) curves (and to a lesser degree the a(T) curves) revealed anomalies in the transition from the ferromagnetic to the paramagnetic state (T_N), in the form of a sharp minimum (or inflection). As a rule, in the temperature interval of antiferromagnetic ordering ($T_C < T < T_N$), anomalous broadening of the hcp lattices takes place along the hexagonal axis ([001]) with decreasing temperature. However, the tendency towards anomalous broadening along the [001] axis decreases with decreasing temperature, and a broad maximum is observed on practically all the c(T) curves.

For terbium alloys with 8.60 and 16.56 at.% yttrium, a jumplike decrease of the periods of the crystal lattice occurs on going from the ferromagnetic into the antiferromagnetic state (T_C). A similar phenomenon takes place also in pure terbium[2].

By graphically differentiating the a(T) and c(T) curves we determined the coefficients of linear expansion $\alpha^\perp$ and $\alpha^\parallel$ respectively perpendicular and parallel to the hexagonal axis. The pattern of variation of the linear expansion coefficients with changing temperature is shown in Fig. 4; the main characteristics of the termal expansion ($\bar{\alpha}_F$, $\bar{\alpha}_{AF}$, $\bar{\alpha}_p$—the mean values of α in the ferromagnetic, antiferromagnetic, and in the paramagnetic regions; $\Delta\alpha_C$ and $\Delta\alpha_N$—the
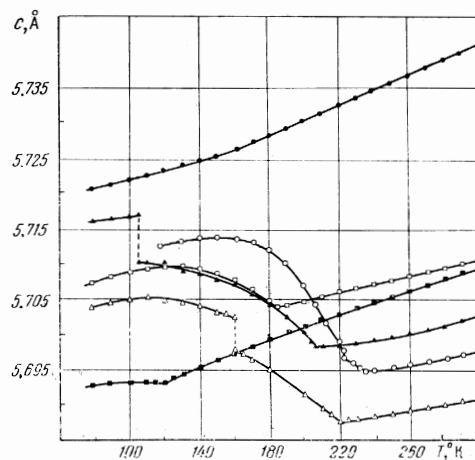

FIG. 3. Temperature dependence of the period c of the crystal lattices of the alloys. The notation is the same as in Fig. 2.

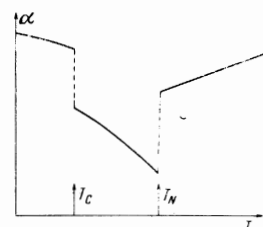FIG. 4. Scheme of variation of the coefficients of linear expansion of the alloys with the temperature.

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[1]We note immediately that in Tb-Y alloys, unlike in terbium[2] and dysprosium[3], the transition at the Curie point is not accompanied by a rhombic splitting of the diffraction lines.

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Table II.

Alloy	Coefficient of linear expansion, $\alpha \times 10^6$, deg^{-1}									
	$\bar{\alpha}_F^\perp$	$\Delta\alpha_C^\perp$	$\bar{\alpha}_{AF}^\perp$	$\Delta\alpha_N^\perp$	$\bar{\alpha}_P^\perp$	$\bar{\alpha}_F^\parallel$	$\Delta\alpha_C^\parallel$	$\bar{\alpha}_{AF}^\parallel$	$\Delta\alpha_N^\parallel$	$\bar{\alpha}_P^\parallel$
Tb [²]	α (a) : 26.87 / α (b) : 24.99	28.00	0.00 *	−8.32	8.72	−27.27	−54.57	−19.49 *	−25.41	7.0
Tb 8.60 at. % Y	19.42	14.00	7.31	−4.16	7.49	−3.11	7.74	−29.92	−30.94	7.83
Tb 16.56 at. % Y	22.43	26.00	6.10	−19.10	5.29	−8.82	16.10	−14.72	−27.06	9.06
Tb 30.89 at. % Y	—	—	6.03	−0.?6	6.45	—	—	−5.94	−52.09	10.07
Tb 64.12 at. % Y	—	—	0.96	−10.73	4.32	—	—	3.43	−20.6?	15.67
Y [²]	—	—	—	—	6.80	—	—	—	—	16.89

*The coefficients $\bar{a}_{AF}^\perp$ and $\bar{a}_{AF}^\parallel$ could not be measured accurately because of the narrowness of the region of antiferromagnetic ordering in terbium[2] (~11°K).

"jumps" of α at the points T_C and T_N) are given in Table II. At the Curie point, the $\alpha^\perp(T)$ and $\alpha^\parallel(T)$ curves experience a discontinuity and at T_N there are observed negative λ-anomalies of the thermal expansion coefficients.

DISCUSSION OF RESULTS

The results of the study of the crystal structure of four solid solutions produced in the Tb-Y system at low temperatures indicate that the character of the structure changes occurring during the ferromagnetism-antiferromagnetism and antiferromagnetism-paramagnetism transformation in each of the alloys is the same as for the pure REM, terbium[2] and dysprosium[3], which have similar types of helicoidal magnetic structure in the magnetically ordered state. The presence of negative λ-anomalies of the coefficients of thermal expansion for all the alloys at T_N signifies that the transition from the antiferromagnetic state (helicodial structure of the simple helix type) into the paramagnetic state is a second-order phase transition. The "sign" of the anomalies agrees, in accordance with the well known Ehrenfest equation,

$$\Delta a_N = \frac{\Delta C_p}{T_N V}\frac{dT_N}{dp},$$

with the negative values of dT_N/dp[8] for the Tb-Y alloys (Table I), and the jump of the specific heat ΔC_p at the Neel point is always positive.

At the Curie point of the alloys of terbium with 8.60 and 16.56 at. % yttrium, a jumpwise change takes place in the periods of the crystal lattices (Figs. 2 and 3) and in the atomic volume ($V = a_2 c \sqrt{3}/4$) (Fig. 5), pointing to the presence of a first-order phase transition. However, unlike terbium and dysprosium[2,3], the ferromagnetism-antiferromagnetism transition in the alloys is not accompanied by a rhombic distortion of the hcp lattice in the basal planes, i.e., the change in the magnetic symmetry in the first-order phase transition occurs without a change of the crystal symmetry, in analogy with the transition in chromium at 168 °K[10].

The change in the character of the temperature dependence of the helicoid angle ω in the terbium alloy with 30.89 at.% yttrium at ~120 °K leads only to a small inflection on the $a(T)$ and $c(T)$ curves (Figs. 2 and 3) and cannot be classified as a second-order phase transition.

When yttrium is added to terbium, an increase takes place in the jumps of the periods of the hcp lattice and of the atomic volume at the Curie point (see Table III). The same table shows for comparison the values of the jumps of the quantities a, c, and V for terbium and dysprosium. We see that with decreasing effective spin parameter $G = c(g-1)^2 J(J+1)$ (where c is the atomic concentration, g the spectroscopic splitting factor (the Lande factor), and J the resultant mechanical angular momentum; in the case of REM this is the sum of the spin and orbital angular momenta: $J = L + S$) the volume effect in the ferromagnetism-antiferromagnetism transformation increases, thus indicating an increase in the heat of the transition (see Table III). The increase of the heat of the transition $q_C = T_C \Delta V (dT_C/dp)$, as well as the lowering of the temperature T_C, may be connected with the fact that the transition at the Curie point occurs between more stable magnetic structures as a result of the magnetic
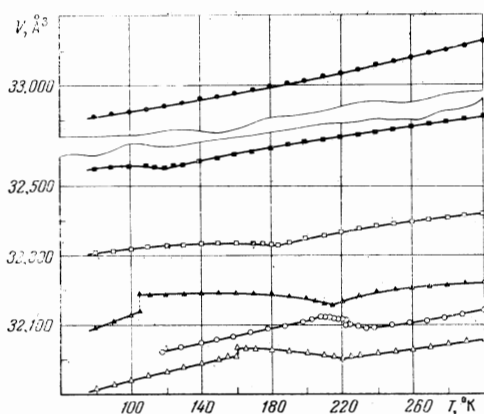

FIG. 5. Temperature dependence of the atomic volumes of the alloys. Notation is the same as in Fig. 2.

Table III.

Alloy	G	T_c, °K	Δa, Å	Δc, Å	ΔV, Å³	$\frac{\Delta V}{V}$, %	q_C, kcal/mole
Tb[²]	10.50	223	0.00003	−0.00032	−0.00273	−0.0085	0.01±0.02
Tb 8.60 at. % Y	9.60	160	0.00260	−0.00460	0.02039	0.6370	−0.06±0.02
Tb 16.56 at. % Y	8.76	105	0.00485	−0.00658	0.04967	0.1546	−0.15±0.02
Dy[³]	7.08	85	0.02066	−0.00766	0.09360	0.2986	−0.20±0.02

dilution. Indeed, in the series consisting of Tb, Tb with 8.60 at.%, Y, Tb with 16.56 at.% Y, and Dy the value of the helicoid angle ω at the Curie point increases and approaches the value (48°) at which the energy of the exchange interaction is minimal[11], i.e., the helicoidal structure of the simple helix type is stable.

Magnetic dilution leads to an increase of the coefficients $\alpha^{\|}$ of the thermal expansion along the hexagonal axis in the ferromagnetic, antiferromagnetic, and paramagnetic states (see Table II). Obviously, this is the consequence of the change of the normal (phonon) part of the coefficient of thermal expansion, which increases monotonically with increasing yttrium concentration, as well as of the decrease of the exchange interaction between the atomic layers (the basal planes (001)), which leads to anomalous deformation of the crystal lattices of the REM[12]. The coefficient $\alpha^{\perp}$ (in the antiferromagnetic region) decreases as a result of magnetic dilution, since the exchange interaction and the basal planes leads to an increase of the coefficient of linear expansion in directions perpendicular to the hexagonal axis.

Unlike the pure REM—gadolinium, terbium and dysprosium[1-3]—the temperature dependence of the atomic volume (5) of the Tb-Y alloys shows no clearly pronounced maxima, this being apparently the consequence of changes in the topology of the Fermi surface, leading to the appearance of singularities in the thermodynamic quantities[13]. This is obviously connected with the distortion of the Fermi surface during the alloying.

In conclusion, we note that the shift of the temperature boundaries of the regions of magnetic ordering, the change in the degree of the stability of magnetic states, and the values of the exchange interaction between the atomic layers (the (001) plane) and inside the layers, all lead to strong violation of the additivity in the values of the linear and volume parameters of the crystal lattices of the Tb-Y solid solutions in the ferromagnetic and antiferromagnetic states. At small yttrium concentrations, the deviations from additivity are observed in the paramagnetic state.

The authors are grateful to V. S. Belovol and M. I. Palatnik for help with the experiments.

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