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CRYSTAL STRUCTURE OF TERBIUM AT 120–300° K

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Low-temperature x-ray diffraction was used to study the crystal structure of terbium in the temperature interval 120–300° K. It is shown that a λ-anomaly of the linear-expansion coefficients, connected with the transition of the paramagnetic terbium into the antiferromagnetic state, occurs at 234° K. At 223° K there is observed a jump in the value of the atomic volume; this means that the transformation of the antiferromagnetic helicoidal structure into a ferromagnetic one (with collinear ordering) is a first-order phase transition. A small rhombic distortion of the hexagonal crystal lattice of terbium takes place below 223° K.

HEAVY rare-earth metals (REM) hold an unusual interest for the study of the connection between magnetic and crystalline structures of metals: hexagonal REM in the Gd–Tu series undergo a series of phase transitions connected with the change in the magnetic structure. The crystalline structure of the first of the heavy REM—gadolinium—was investigated by us earlier.[1] Unlike gadolinium, terbium experiences two magnetic transformations: from the paramagnetic into the antiferromagnetic state (Neel temperature $T_N = 229°\,K$[2]), and from the antiferromagnetic into the ferromagnetic state (Curie temperature $T_C = 221°\,K$[2]). It has been shown by neutron diffraction[2,3] that a helicoidal antiferromagnetic structure exists in terbium in the temperature interval 221–229° K, but this structure is destroyed in relatively weak magnetic fields ($H_C \sim 200$ Oe); below 221° K, collinear ordering takes place: the magnetic moments lie in basal planes of a compact hexagonal lattice or make a small angle with them.

The results of electric and magnetic measurements, carried out on polycrystalline and single-crystal terbium[4,11], point to the presence of anomalies of a number of properties at T_N and T_C. In addition, the plot of the temperature dependence of the specific heat of terbium shows a clearly pronounced peak at 229° K and a slight inflection at 221° K;[12] dilatometric measurements have revealed an anomaly of the coefficient of thermal expansion near the temperatures of magnetic transformations.[13,14] The results of the study of the influence of pressure on the magnetic-transformation temperatures of terbium are contradictory: some indicate an increase of the antiferromagnetism—ferromagnetism temperature under the influence of pressure ($dT_N/dp = -dT_C/dp = 0.7°\,K/kbar$[15]), while others claim a decrease ($dT_N/dp = -1.07°\,K/kbar$[16]).

According to x-ray diffraction investigations of terbium, rhombic distortion of the hexagonal lattice takes place in the basal planes[17] below 220° K; doubts concerning the possibility of a transition of terbium into a rhombic modification were raised in [15]. No singularities in the structure of terbium were observed at 229° K. The purpose of the present paper was to carry out a precision study of the crystalline structure of terbium in the temperature interval 120–300° K by the method of x-ray structure analysis.

We investigated 99.5% pure crystalline terbium (no analysis of the other REM was made). The procedure of low-temperature x-ray diffractometric investigations did not differ from that described earlier.[18] For a precision measurement of the change in the periods of the crystal lattice, x-ray diffraction peaks from the planes (104) and (203) were taken in chromium K_α radiation.

The temperature dependences of the interplanar distances are shown in Fig. 1. In the paramagnetic region, no anomalies were observed in the $d_{203}(T)$ and $d_{104}(T)$ curves; at 223–234° K, the interplanar distances increase with decreasing temperature. A small jump of the value of d_{104} takes place at T_C, as well as a noticeable change in the $d_{203}(T)$ curve. Below 223° K, a strong distortion of the profile of the diffraction peaks is observed, with the (203) line "breaking up" into two components, the distance between which increases with decreasing temperature. The less intense component of the (203) diffraction peak is located at smaller diffraction angles; the shape of the (104) line indi-

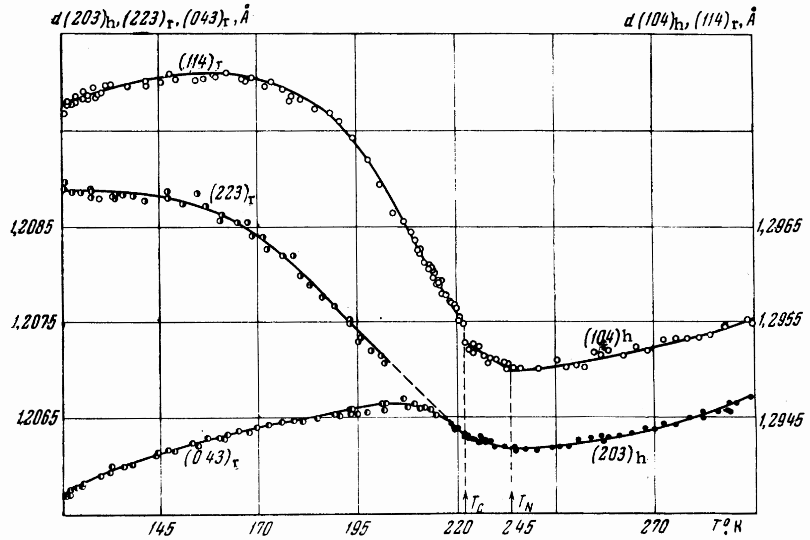

FIG. 1. Temperature dependence of the interplanar distances of the planes $(104)_h$, $(203)_h$, $(223)_r$, $(043)_r$, and $(114)_r$. The curve $d(024)_r(T)$ is not plotted because of the impossibility of accurately determining the values of $d(024)_r$.

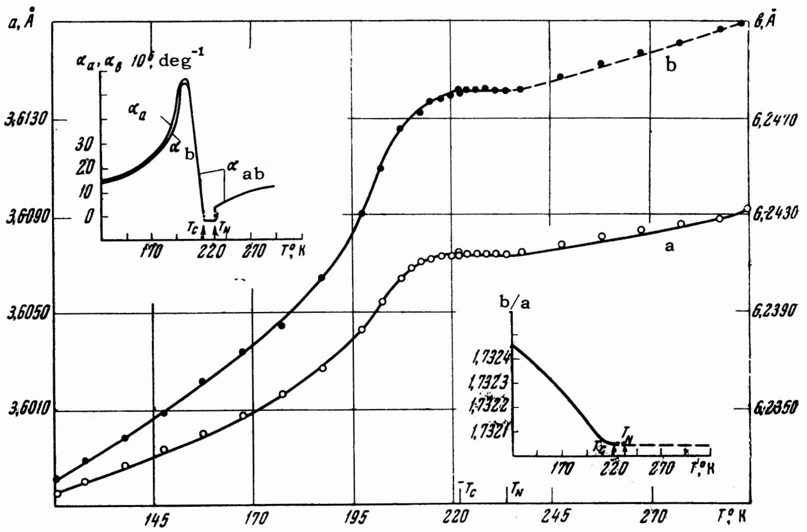

FIG. 2. Temperature dependence of the periods a and b, the ratio of the axes b/a, and the coefficients of linear expansion α_a and α_b.

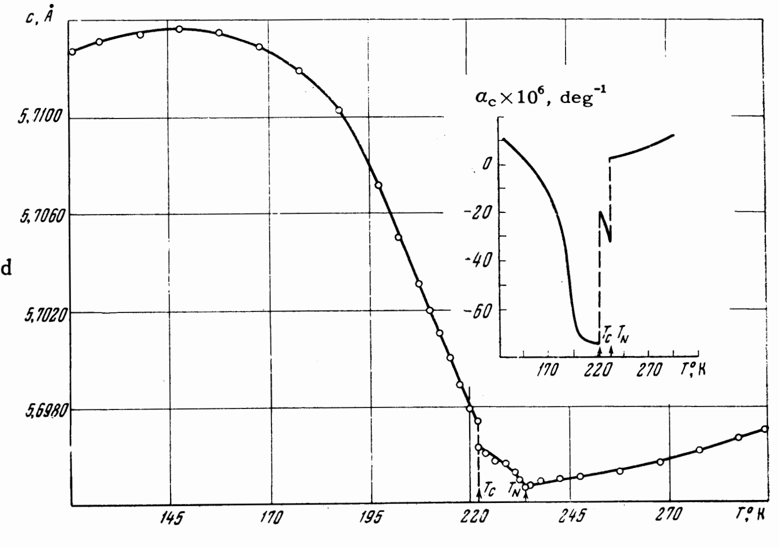

FIG. 3. Temperature dependence of the period c and of linear expansion α_c.

cates that a similar ratio of intensities would be observed in the case of total separation of this peak.

The components of the doubled diffraction lines cannot be indexed uniquely. Although the peak doubling scheme—$(104)_h \rightarrow (024)_r + (114)_r$, $(203)_h \rightarrow (0.43)_r + (223)_r$, where the indices "h" and "r" pertain respectively to the hexagonal and rhombic lattices—is subject to no doubt, it is not clear whether the lines at large diffraction angles are of the type $(h\,h\,l)$ or $(0\;2h\;l)$. This introduces a certain indeterminacy in the calculation of the periods a and b of the rhombic lattice and does not influence the determination of the value of the period c. The identification scheme proposed in Fig. 1 leads apparently to better correlation with the results of other physical investigations (see below). In the ferromagnetic region, the dependence of the interplanar distances on the temperature has a rather complicated character.

With the aid of the curves shown in Fig. 1, we calculated the parameters of the hexagonal and rhombic lattice of terbium (Figs. 2, 3). By graphic differentiation of the a(T), b(T) and c(T) curves we determine the values of the linear-expansion coefficients α_a (in the (001) plane of the hexagonal lattice or along the [100] direction of the rhombic lattice), α_b (which is equal to α_a for hexagonal crystals or measured along [010] for rhombic crystals), and α_c (along the [001] direction in hexagonal or rhombic lattices). The values of the coefficients of linear expansion are shown on the inserts in Figs. 2 and 3.

The temperature dependences of the lattice constants and of the coefficient of thermal expansion of terbium are quite complicated. In the paramagnetic region, normal thermal expansion of terbium takes place ($\alpha_a = \alpha_b > 0$, $\alpha_c > 0$). In the region of existence of the helicoidal antiferromagnetic structure (223–234°K), the coefficient of expansion along the hexagonal axis is negative, and in the basal planes there is practically no expansion. A sharp minimum is observed on the c(T) curve at T_N (Fig. 3); a minimum is observed in less pronounced form also on the a(T) curve (Fig. 2). The consequence of such a behavior of the a(T) and c(T) curves is the presence at T_N of negative λ-anomalies of the coefficients of linear expansion (see the inserts in Figs. 2 and 3).

At T_C (223° K), a jump takes place in the value of the period c, and one can also assume the presence of jumps in the periods a and b, but the effects observed in the investigation do not go beyond the limits of possible measurement errors. We note that at the chosen scheme for indexing the diffraction lines, the coefficients of linear expansion α_a and α_b become positive values in the ferromagnetic region. The small difference in the temperature variation of α_a and α_b leads to a decrease in the degree of rhombic distortion with increasing temperature: near T_C we have $b/a = \sqrt{3}$ (see Fig. 2, insert). In the same indexing scheme it turns out that $\alpha_a > 0$ and $\alpha_b < 0$, and $\alpha_a(T)$ has a maximum while $\alpha_b(T)$ has a minimum; on the other hand, the degree of distortion of the hexagonal structure greatly increases: $\Delta(b/a) = (b/a)_{120^\circ K} - \sqrt{3} = 0.0004$ at the chosen indexing scheme, and 0.0101 for the opposite indexing. This circumstance, and also the qualitative agreement of the a(T) and b(T) curves with the results of the measurements of thermal expansion in single-crystal terbium[10] offer evidence in favor of the chosen indexing scheme of the diffraction lines at $T < T_C$.

The temperature dependence of the period c in the ferromagnetic region has a rather complicated character (see Fig. 3).

In view of the strong anisotropy of the temperature dependence of the periods of the crystal lattice and of the coefficients of linear expansion of terbium, it is advantageous to consider, just as in the case of gadolinium,[1] the temperature dependence of the atomic volume and of the coefficient of volume expansion (Fig. 4). On the $V_{at}(T)$ curve there is observed a maximum at 210° K, a jump at T_C (223° K), and a sharp minimum at T_N (234° K); in the paramagnetic region, no singularities are observed on the $V_{at}(T)$ curve. On the $\alpha_V(T)$ curve (Fig. 4, insert), there are jumps at the ferromagnetic and antiferromagnetic transformation temperatures.

The results of the study of the crystalline structure of terbium at low temperatures show that it depends strongly on the change in the magnetic structure. The anomaly of the thermal-expansion coefficients (α_V, α_a, α_c) observed at the point of transition from the paramagnetic into the helicoidal antiferromagnetic state indicates that the transformation at 234° K is a second-order phase transition. The "sign" of the anomaly, in accordance with the Landau theory of phase transitions,[19] agrees with the results of measurements of dT_N/dp, given in [16], but contradicts the results obtained in [15]. At 221° K, a jump takes place in the magnitude of the atomic volume, i.e., of the first derivative of the thermodynamic potential;[19] this signifies that in terbium the transformation for the helicoidal antiferromagnetic into the ferromagnetic structure, with collinear ordering of the magnetic moments in the basal

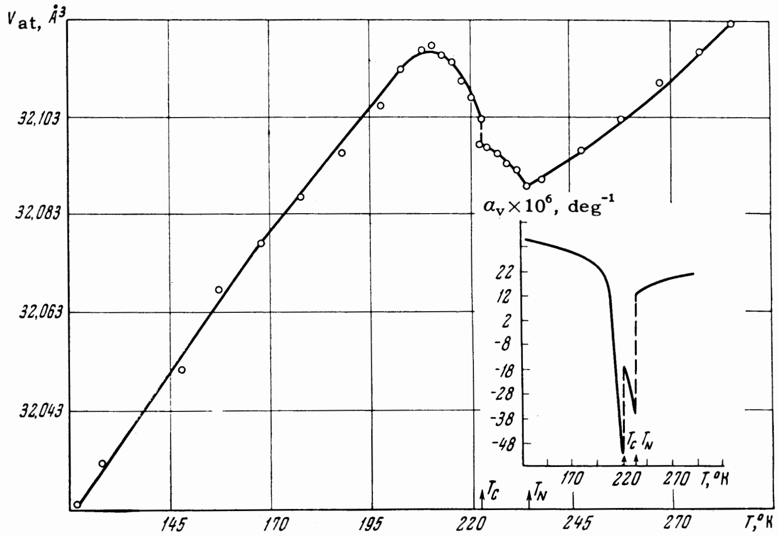

FIG. 4. Temperature dependence of the atomic volume and of the coefficient of volume expansion.

planes, is a first-order phase transition. The rhombic distortion of the crystal lattice below T_C is apparently connected with the fact that, in connection with the appearance of an easy-magnetization direction in the basal planes, the thermal expansion in these planes becomes anisotropic, i.e., the coefficient of thermal expansion along the magnetic moments is somewhat different from the coefficient in the perpendicular direction.

The nature of the maximum on the $V_{at}(T)$ curve near T_C is not perfectly clear. A similar effect, but more clearly pronounced, is observed also for gadolinium,[1] where it is connected with the "drift" of the direction of easy magnetization relative to the hexagonal axis. It is not excluded that a similar effect (but in the basal planes) takes place also in terbium, but a solution of this equation calls for further research.

The slight disagreement between the measured values of the temperatures of the ferromagnetic and antiferromagnetic transformations and the latest published data[2, 4] is probably connected with the different purity of the investigated terbium.

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