

## CRYSTAL STRUCTURE OF DYSPROSIUM AT 77–300°K

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The low-temperature x-ray diffraction method was used to investigate the crystal structure of dysprosium in the temperature range 77–300°K. It was found that at 178°K there was a negative  $\lambda$ -anomaly of the thermal expansion coefficients, associated with a phase transition of the second kind from helicoidal antiferromagnetism to paramagnetism. At 85°K, a discontinuity in the values of the crystal lattice periods and atomic volume, as well as orthorhombic distortions in the hexagonal lattice, were observed, due to a first-order phase transition from antiferromagnetism to ferromagnetism.

DYSPROSIUM, like gadolinium and terbium investigated earlier,<sup>[1, 2]</sup> is one of the heavy rare-earth metals; at room temperature, it has the hcp lattice. The magnetic, electrical, and thermal properties of dysprosium at low temperatures have been investigated quite thoroughly.<sup>[3]</sup> From the anomalies of the temperature dependences of a number of physical properties and from the results of neutron-diffraction investigations,<sup>[4]</sup> it has been established that dysprosium is ferromagnetic below 85°K ( $T_C$ ): the magnetic moments are ordered collinearly; at 85–178.5°K, a helicoidal antiferromagnetic ordering is observed, with the helicoidal axis along the sixfold symmetry axis [001] and the angle between magnetic moments in neighboring planes ( $\beta$ ) almost linearly increasing with temperature from 26.5 to 43.2°; above 178.5°K ( $T_N$ ), dysprosium is paramagnetic.

In several papers, it has been shown that an increase in pressure shifts  $T_N$  toward low temperatures ( $dT_N/dp \approx -0.6$  deg K/kbar<sup>[5]</sup>), while the ferromagnetic–antiferromagnetic transition temperature depends nonmonotonically on pressure ( $dT_C/dp = +1.4$  deg K/kbar at  $p < 7$  kbar;  $dT_C/dp = -0.8$  deg K/kbar at  $p > 7$  kbar<sup>[6]</sup>). The results of x-ray diffraction investigations of dysprosium at low temperatures<sup>[7, 8]</sup> indicate an anomalous increase in the period  $c$  on cooling (at 85–178°K) and the presence of discontinuities in the values of the lattice constants at  $T_C$  (85°K) (however, the change in the atomic volume at this point is zero, within the limits of the experimental error<sup>[8]</sup>); orthorhombic distortions in the basal planes of the hexagonal lattice have been found at temperatures below 85°K. The purpose of the present

investigation was to study with precision the crystal structure of dysprosium at 77–300°K (in the ferro-, antiferro-, and paramagnetic states) using the x-ray diffraction method.

We investigated polycrystalline dysprosium of 99.2% purity. The low-temperature x-ray diffraction method did not differ basically from that described earlier.<sup>[1, 2, 9]</sup>

We used the  $K_\alpha$  radiation of chromium incident at large angles to obtain the diffraction peaks of the (104) and (203) planes of the hcp lattice of dysprosium. Below 85°K the diffraction peaks split into two components, which indicated an orthorhombic distortion of the crystal lattice. As mentioned in<sup>[2]</sup>, the orthorhombic indexing of the components of the peaks and the subsequent calculation of the lattice parameters did not yield unambiguous results; to decide on a particular indexing scheme, it was necessary to compare the results obtained with the data of macroscopic measurements. In the present study, we were able to obtain good correlation between the x-ray diffraction data and the results of dilatometric measurements carried out on dysprosium single crystals,<sup>[10]</sup> which supported our selection of the indexing scheme  $[(h0l)_h \rightarrow (hh)l_0 + (02h)l_0, \theta(hh)l_0 > \theta(02h)l_0]$ .<sup>1)</sup>

From the temperature dependences of the interplanar distances,  $d(T)$ , we calculated the values of the crystal lattice periods of dysprosium; the appropriate curves  $a(T)$ ,  $b(T)$ , and  $c(T)$  are shown

<sup>1)</sup>The subscripts "h" and "o" refer to the hexagonal and orthorhombic lattices, respectively;  $\theta$  is the diffraction angle.

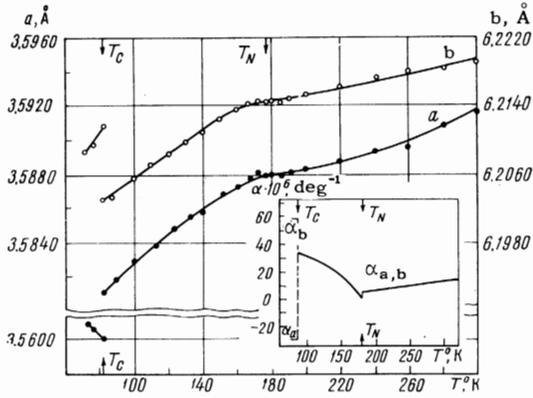


FIG. 1.

in Figs. 1 and 2. The same figures include the temperature dependences of the thermal expansion coefficients along the principal directions  $\alpha_a(T)$ ,  $\alpha_b(T)$ , and  $\alpha_c(T)$ , obtained by graphical differentiation of the curves  $a(T)$ ,  $b(T)$ , and  $c(T)$ .

All the curves in Figs. 1 and 2 are complex; we can identify three regions, depending on the type of magnetic ordering:

178° K < T < 300° K —paramagnetic state. There are no anomalies in the temperature dependence of the hexagonal lattice periods;

85° K < T < 178° K —antiferromagnetic helicoidal ordering. There is an anomalous expansion of the hexagonal crystal lattice along the principal axis [001] on cooling ( $\alpha_c < 0$ ). Over this whole range of temperatures, the values of  $\alpha_a$  and  $\alpha_c$  decrease and a negative  $\lambda$ -anomaly appears at 178° K ( $T_N$ );

77° K < T < 85° K —ferromagnetic collinear ordering. When the temperature is lowered, to 85° K ( $T_C$ ), the value of the period  $a$  decreases suddenly, while the periods  $b$  and  $c$  suddenly increase. The degree of the orthorhombic distortion in the basal planes of the crystal lattice of dysprosium is quite large [ $\Delta(b/a) = (b/a)_{80^\circ K} - \sqrt{3} = 0.0118$ ];  $a_b > 0$ ,  $\alpha_a$  and  $\alpha_c < 0$ .

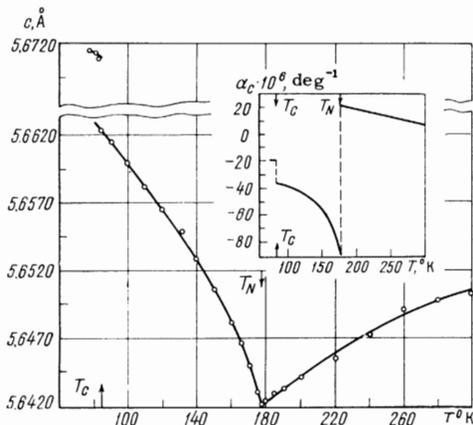


FIG. 2.

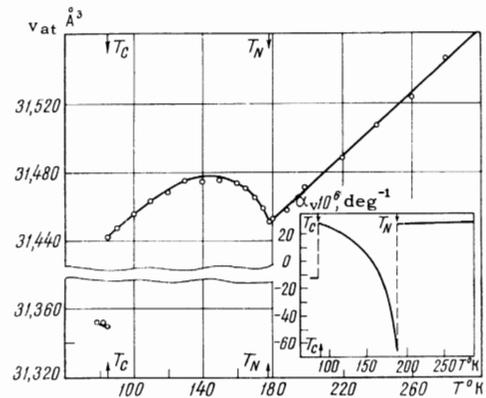


FIG. 3

It is evident that all the quantities characterizing the linear expansion of dysprosium (the lattice periods and the linear expansion coefficients) exhibit a strong anisotropy. Therefore, it is desirable to consider, as in the case of gadolinium and terbium,<sup>[1, 2]</sup> the temperature dependences of the atomic volume [ $v_{at} = 1/4(abc)$ ] and of the volume expansion coefficient ( $\alpha_v = v_{at}^{-1} dv_{at}/dT = \alpha_a + \alpha_b + \alpha_c$ ) (Fig. 3). The  $v_{at}(T)$  curve has a discontinuity at  $T_C$  ( $\Delta v_{at}/v_{at} \approx 0.2\%$ ), a flat maximum at  $\approx 145^\circ$  K, and a sharp minimum at  $T_N$ . The volume expansion coefficient  $\alpha_v$  is negative in the ferromagnetic region; between 85 and 178° K, the value of  $\alpha_v$  decreases, passing through zero at 145° K; at 178° K, a negative  $\lambda$ -anomaly is observed; in the paramagnetic region  $\alpha_v > 0$ .

The results of our investigation of the crystal structure of dysprosium at low temperatures indicate that this structure is affected by changes in the magnetic structure. The negative  $\lambda$ -anomaly of the thermal coefficients ( $\alpha_a$ ,  $\alpha_c$ ,  $\alpha_v$ ) at  $T_N$  (178° K) indicates that the transition from the helicoidal antiferromagnetic to the paramagnetic state is a phase transition of the second kind. The "sign" and magnitude of  $\Delta\alpha_v$  agree, in accordance with the well-known equation of Landau's theory of phase transitions of the second kind<sup>[11]</sup>

$$\Delta\alpha_v = \frac{\Delta c_p}{T_N v} \frac{dT_N}{dp},$$

with the value of  $\Delta c_p$ , reported in<sup>[12]</sup>, and with the value of  $dT_N/dp$  given in<sup>[5]</sup>. The transition from the ferromagnetic to the antiferromagnetic state at 85° K ( $T_C$ ) has all the characteristics of a phase transition of the first kind: the atomic volume has a discontinuity (Fig. 3) and the crystal lattice symmetry changes. An estimate of the heat of transition in accordance with the Clapeyron–Clausius equation (using the volume discontinuity at 85° K found in the present study and the published value

of  $dT_C/dP$ <sup>[6]</sup> gives about 0.1 kcal/mole, which is comparable with the heat of polymorphic transitions.

It is worth noting the maximum in the  $v_{at}(T)$  curve at  $\sim 145^\circ\text{K}$  (Fig. 3), which corresponds to the beginning of the distortion of the helicoidal antiferromagnetic structure<sup>[4]</sup> and to the appearance of anomalies of a number of physical properties.<sup>[3, 6]</sup> The same effect has been found for gadolinium at  $\sim 200^\circ\text{K}$ <sup>[1]</sup> and for terbium at  $\sim 210^\circ\text{K}$ <sup>[2]</sup> in the ferromagnetic region. The cause of the anomalous temperature dependence of the atomic volume of rare-earth metals is not yet clear. It is possible that the appearance of maxima in the  $v_{at}(T)$  curves, like changes in the magnetic structure and magnetic properties, is a consequence of changes in the Fermi surface topology, causing the appearance of singularities in the thermodynamic properties.<sup>[13]</sup>

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