Magnetic phase transitions in a dysprosium single crystal in a weak magnetic field

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Structural investigations have been carried out on a dysprosium single crystal near the helical antiferromagnetism-collinear ferromagnetism and paramagnetism-antiferromagnetism phase transition points in magnetic fields up to intensities of 1 kOe. A region of stability of the magnetically heterogeneous state (ferromagnetism-antiferromagnetism point) on the H-T diagram was observed. It is found that the transformation at T_N still remains a second order phase transition in an external magnetic field. It is shown that T_N depends strongly on H, with the values of the critical index being anomalously high ($\omega = 2.83$).

Magnetic phase transitions in the rare earth metal dysprosium in zero magnetic field have been rather well studied: a paramagnetism-helical antiferromagnetism (P-AF) second-order phase transition occurs at $T_N \approx 180$ K, while at $\Theta \approx 90$ K there is a helical antiferromagnetism-collinear ferromagnetism (AF-F) first-order phase transition. The AF-F transition is accompanied by a reduction in the crystal symmetry from hexagonal to rhombic.[1] Applying an external magnetic field reduces the temperature range within which helical antiferromagnetism exists and, apparently, causes the appearance of a fan-shaped structure intermediate between the AF and F states, predicted by theory.[2] The H-T diagrams of Dy obtained experimentally[3–6] are incomplete and in large part contradictory. In particular, questions of the possibility of a direct AF-F transition in a magnetic field, of the existence of a magnetically heterogeneous state and of the construction of the H-T diagram near T_N, etc., remain open.

Using a method for x-ray diffraction in a magnetic field developed earlier,[7] it was possible to construct the general outlines of the H-T diagram of polycrystalline Dy, to study the thermodynamic features of the AF-F transition in a magnetic field and to find a number of effects associated with the reorientation of ferromagnetic domains. However, the experimental technique used (photographic recording of the diffraction picture in strong magnetic fields and a large "step" in the variation of magnetic field strength H, and a relatively low accuracy in stabilizing the temperature) prevented detailed study of structural effects near the critical temperatures T_N and Θ. The aim of the present work is a precision investigation of the crystal structure of Dy in weak magnetic fields in the neighborhood of the critical points, on the basis of which it is possible to elucidate the details of the course of the magnetic phase transitions and to determine the H-T phase diagram more accurately.

The essence of the experiments carried out comes down basically to obtaining the temperature (for $H = \text{const}$) and field (for $T = \text{const}$) dependences of the parameter c for the hexagonal (in the P and AF states) or rhombic (in the F state) lattice of Dy in weak magnetic fields, when the magnetic field strength vector **H** is directed along the basal plane (001). In the F and AF phases the magnetic moment lies in this plane and also, supposedly, in the intermediate fan phase.[8]

1. METHOD OF INVESTIGATION

The specimen studied was a Dy single crystal of $\approx 99.8\%$ purity. A specimen in the form of $2 \times 2 \times 2$ mm^3 cube was cut out of a single crystal, bounded by (100), (110) and (001) crystallographic planes. We note at once when a specimen of this shape is in the ferromagnetic state, the demagnetizing field H_0 should be fairly large. Unfortunately, an accurate calculation of H_0 is practically impossible since, as well be shown below, the amount of ferromagnetic phase in the specimen near the temperature Θ depends on the strength of the magnetic field; for $T > \Theta$ the value of H_0 is, naturally, small.

A special apparatus was developed based on the URNT-80 attachement to a DRON-2.0 x-ray diffractometer, for precision structural investigations $80 \leqslant T \leqslant 300$ K, $0 \leqslant H \leqslant 1000$ Oe. A brass holder with a specimen was placed between the poles of a miniature magnet. The field could be controlled to within an accuracy of 5 Oe by changing the current through the windings of an electromagnet. Temperatures were measured with a copper-constantan thermocouple, one junction of which was in immediate contact with a section of the specimen made by the (001) plane; a Shch 68002 voltmeter used as measuring instrument gave a measuring accuracy of ± 0.02 K. The temperatures were stabilized with an accuracy of at least ± 0.2 K.

The x-ray diffraction was carried out with monochromatized CuK_α radiation. The (006) reflection was recorded at a diffraction angle $2\theta \approx 109.7°$. Photographs were taken under stepwise scanning (stepsize 0.01°, exposure time 4 s). The accuracy in measuring the parameter c was at least $\pm 2 \times 10^{-4}$ Å.

In studying the magnetic phase composition it was necessary to measure the intensity of the partially overlapping (006) reflections from the hexagonal (antiferromagnetic) and rhombic (ferromagnetic) phases. A method was developed to solve this problem, close in essentials to the well known Rachinger method (see, for example, Ref. 9), but enabling not two (the K_{α_1} and K_{α_2} components of the spectral doublet) but four (two doublets) lines to be resolved. The accuracy in measurements of intensity was no better than 5–10%.

2. RESULTS OF THE INVESTIGATION

As has already been mentioned, the main attention in the present work was paid to the study of structural effects in

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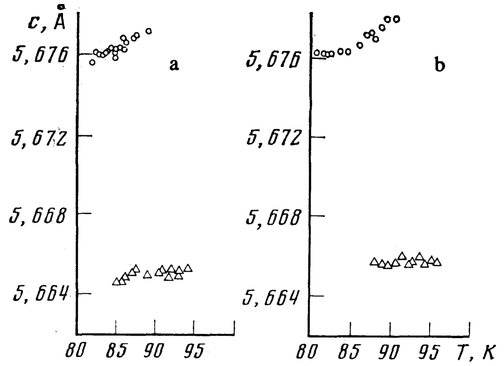

FIG. 1. The temperature dependence of the parameter c in the neighborhood of the temperature Θ in fields $H = 0$ (a) and $H = 835$ Oe (b); ○ F phase, △ AF phase.

Dy near the critical points. The results of measurements in two temperature ranges, ~80–100 and ~160–190 K, are given below; some results on the magnetostriction of Dy were also obtained at intermediate temperatures. To avoid hysteresis effects in phase transitions in Dy (Ref. 10), all experiments were carried out under conditions of increasing temperatures or magnetic field strength.

2.1 Phenomena in the neighborhood of the AF–F phase transition point

The results of measurements of the temperature dependences of the parameter c of dysprosium at $H = 0$ and $H = 835$ Oe are shown in Fig. 1. A discontinuity in the lattice parameter $\Delta c \approx 12\times 10^{-3}$ Å is observed, which is characteristic of a first order phase transition. The following two facts are noteworthy:

a) the existence of a fairly wide region within which the F and AF phases coexist (the splitting of the (006) diffraction line into two components $(006)_{AF}$ and $(006)_F$ is an unambiguous sign of the coexistence of phases);

b) a noticeable shift in transition temperatures (more precisely, the region within which the F and AF phases coexist) in the high temperature direction ($d\Theta/dH \approx 3\times 10^{-3}$ K · Oe^{-1}[1)]) and some reduction in the jump in the parameter c in a magnetic field.

Photographs at $T = 88.3$ and 89 K, corresponding to the region of the magnetically heterogeneous state of Dy enabled the effect of a strong change in the ratio of intensities of the diffracted lines $(006)_F$ and $(006)_{AF}$ in a magnetic field to be detected; the fraction X of the F phase grows with increasing H. With a fairly high degree of certainty (correlation coefficient $r \approx 0.95$), the value of X depends quadratically on the field:

$$\begin{aligned} &88.3\text{ K}: \quad X=0.176\pm0.024+(7.516\pm0.701)\cdot10^{-7}\, H^2, \\ &89\text{ K}: \quad X=0.073\pm0.019+(16.230\pm0.466)\cdot10^{-7}\, H^2. \end{aligned} \tag{1}$$

It can be seen from Eq. (1) that the value of H corresponding to a complete transition to the F state grows rapidly with increasing temperature (~1000 and 1500 Oe respectively at 88.3 and 89 K). Measurements of the field dependences of the parameter c of dysprosium in the F and AF phases at 88.3

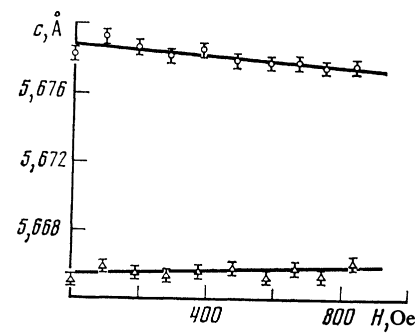

FIG. 2. The field dependence of the parameter c of dysprosium at 88.3 K, ○ F phase, △ AF phase.

showed that while c_{AF} grows with increasing field, c_F decreases (Fig. 2).

2.2. Phenomena in the neighborhood of the P-AF transition

The results of measuring the $c(T)$ relation in different fields H are shown in Fig. 3. All the $c(T)$ curves have a similar shape: the parameter c depends weakly on temperature for $T > 180$ K, while at lower temperatures c increases anomalously with decreasing T. No discontinuities on the $c(T)$ curves were found at any fields. A noticeable shift occurs in the critical points, which were determined by the appearance of kinks (shown by arrows in Fig. 3) on the $c(T)$ curves,[1] in the low temperature direction with increasing magnetic field strength. It is noteworthy that independent of the critical values of T and H, the kink is observed at practically one and the same value of the parameter c (see the inset of Fig. 3).

A noticeable kink is observed on the $c(H)$ isotherm at $T = 178$ K for $H \approx 700$ Oe (Fig. 4), while for $H > 700$ Oe the slope of the $c(H)$ curves is less than for $H < 700$ Oe. The dif-

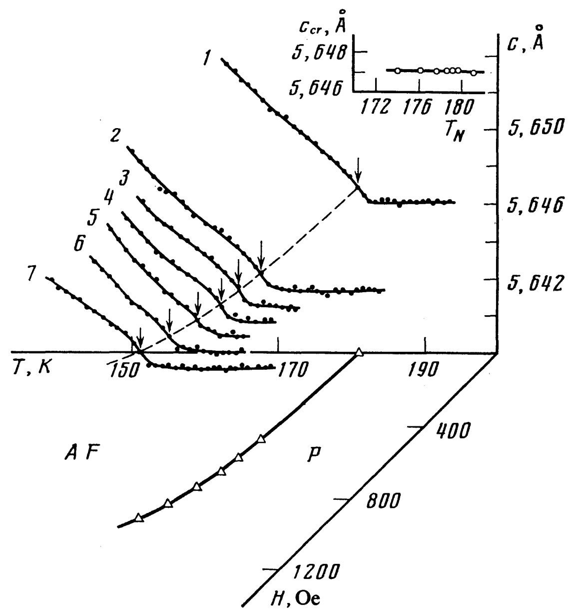

FIG. 3. The c-H-T diagram of Dy near T_N: 1) $H = 0$; 2) 480 Oe; 3) 580 Oe; 4) 665 Oe; 5) 745 Oe; 6) 835 Oe; 7) 920 Oe. The inset shows the dependence of c_{cr} (at the P-AF transition point) on the temperature of the phase transition.

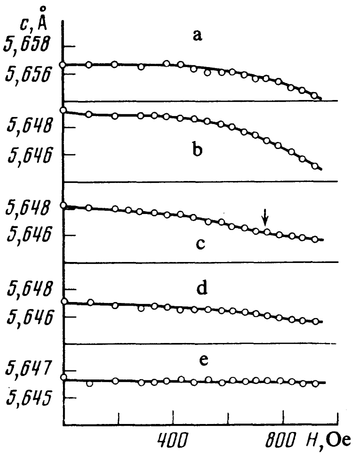

FIG. 4. The $c(H)$ isotherms of dysprosium near T_N: a) $T = 148.3$ K; b) 172 K; c) 178 K; d) 180.5 K; e) 184.2 K.

ference in the slope of the $c(H)$ curves at $H \lesssim 700$ Oe exceeds possible experimental errors ($\simeq 2\times10^{-7}$ Å Oe^{-1}). Anamalies are not observed in the $c(H)$ curves at lower or at higher temperatures. The parameter c is practically independent of magnetic field strength at $T > T_N$. The $c(H)$ relation has an appreciably nonlinear form for $T < T_N$ (see Fig. 4) and can be described by a relation of the type

$$c = c_0 + bH + dH^2,$$

with the contribution of the quadratic term increasing appreciably on approaching T_N:

T, K	c_0, Å	$b\cdot10^6$, Å/Oe	$d\cdot10^9$, Å/Oe^2	
125,7	5,6631±0,0002	2,127±0,193	−2,711±0,307	(2)
148,3	5,6590±0,0002	2,115±0,219	−4,715±0,354	
172,0	5,6523±0,0002	3,032±0,231	−7,479±0,381	

3. DISCUSSION

The essentially new result obtained from the x-ray diffraction study of a Dy single crystal in weak magnetic fields is the direct confirmation of the existence of a region for the magnetically heterogeneous state in the H-T diagram, i.e, the coexistence of AF and F structures[2)] near the temperature Θ. Unlike the closest physical analog—the intermediate state of type I superconductors—a region within which the AF and F phases coexist is also realized at $H = 0$, broadening evidently as the magnetic field strength increases.

When phases which differ in specific volume coexist, the proportions of the phases in equilibrium along the phase equilibrium line (in the present case, along the $H_{cr}(T)$ line) should be inversely proportional to the ratio of the specific volumes ("the leverage rule" (Ref. 11)), or to a first approximation the lattice parameters. As can be seen in Fig. 5, the correlation between the quantities c_F/c_{AF} and $(1-X)/X$ is not bad. It is evident that the possible direct observation of the coexistence of the AF and F phases in Dy is, in fact, due to the large difference between the lattice parameters of these phases and the relatively low temperature of the phase transition.

No features were found on the $c(T)$ and $c(H)$ curves ob-

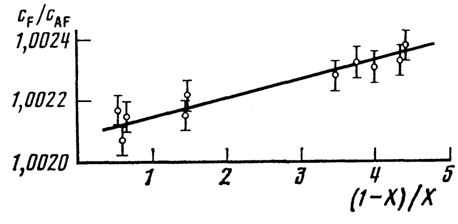

FIG. 5. The dependence of c_F/c_{AF} on $(1-X)/X$ at 88.3 K.

tained near the temperature Θ which could be connected with the appearance of a fan structure. This means that there is a direct AF-F transformation in the temperature and field regions studied. It should, in general, be noted that a variant of the phase diagram could evidently be constructed adequately describing the behavior of the physical properties of Dy, in which the hypothetical region where the fan shaped magnetic structure exists is absent.

Investigation of the structure of Dy in weak magnetic fields near T_N showed that the form of the $c(T)$ relation does not change qualitatively when a magnetic field is turned on; in all cases there was no discontinuity in the lattice parameter on the $c(T)$ curves, the behavior of the curves leads to the appearance of λ-anomalies in the thermal expansion coefficient $\alpha_\parallel$ (Fig. 6), the "sign" of which, in conformity with the Ehrenfest equation for the case of uniaxial stress,

$$\Delta\alpha_\parallel = \frac{\Delta C_p}{VT_N}\frac{dT_N}{d\sigma_{33}} \tag{3}$$

(C_p is the specific heat at constant pressure, V is the specific volume, σ_{33} is the uniaxial stress, directed along the c axis), agrees with the nature of the shift in T_N under the action of uniaxial stress applied along the ⟨001⟩ axis [$dT_N/d\sigma_{33} < 0$ (Ref. 12)]. All this means that the P-AF transformation in weak magnetic fields, as for $H = 0$, is a second-order phase transition.

When studying Dy it was possible to observed a second-order AF-P phase transition with magnetic field. The change in shape of the $c(H)$ isotherm at $T = 178$ K (see Fig. 4) indicates the existence of a jump in the magnetostriction coefficient $d\lambda/dH$, the second derivative of the thermodynamic potentials.[11] The fact that the second order AF-P phase transition occurs for a value of the parameter c which is practically constant along the critical line (see Fig. 3) means, apparently, that the critical values of the parameters of the helical magnetic structures along the critical line of the phase transition also remain constant. The noticeable

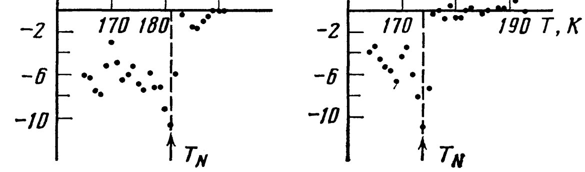

FIG. 6. The temperature dependences of the linear expansion coefficient $\alpha_\parallel$ of dysprosium near T_N for $H = 0$ (a) and $H = 920$ Oe (b).

growth in the parameter c with decreasing T in the region $T < T_N(H)$ is evidence of a faster reduction in helix angle as H is increased.[7]

A fairly strong shift in the temperature of the second order phase transition was found near T_N (see the H-T phase diagram in Fig. 3), which can be well described ($r \approx 0.98$) by the equation

$$T_N(H) - T_N(0) = (2.682 \pm 0.094) \cdot 10^{-4} \; H^{2,83 \pm 0,01}. \quad (4)$$

The value of the critical index obtained experimentally ($\omega = 2.83$) is larger than follows from the hypothesis appropriate to an antiferromagnet ($\omega = 2$, Ref. 13). The value of ω obtained for Dy is closest to the experimental value of the critical index of the rare earth ferromagnet Gd ($\omega = 2.53$, Ref. 14).

CONCLUSIONS

1. Structural investigations have been carried out on a dysprosium single crystal at $T \sim 80$–200 K and field strengths up to 1 kOe.

2. It has been shown that the first-order helical antiferromagnetism-collinear ferromagnetism phase transition is spread out in temperature ($\Delta\Theta \approx 4$ K). A magnetic field considerably affects the ratio of volumes of the ferro- and antiferromagnetic phases in the magnetically heterogeneous state.

3. The paramagnetism-helical antiferromagnetism transformation is a second-order phase transition both at $H = 0$ and in an external magnetic field.

4. The strong shift of T_N in a magnetic field is described by a power law with critical index $\omega = 2.83 \pm 0.01$. The value of the crystal lattic parameter c is constant along the critical line of the second order phase transition.

1) For the start of the F-AF transitions
2) The existence of such a state could be indirectly judged on the basis of results of magnetic and galvanomagnetic measurements[10]

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