

Magnetic Properties of Dysprosium Single Crystals*

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(Received November 4, 1957)

Single crystals of metallic dysprosium have been grown by the Bridgman method and their magnetic properties have been determined in different crystallographic directions of the hexagonal close-packed structure. Below the Néel point of 178.5°K the individual magnetic moments are aligned perpendicular to the c_0 axis. The moments are aligned in an antiferromagnetic manner from 178.5°K down to 85°K and in a ferromagnetic manner below 85°K. Measurements with the field parallel and perpendicular to the c_0 axis reveal magnetic anisotropy at all temperatures. Below 110°K magnetic anisotropy is also observed in the basal plane. The direction of easy magnetization is along an a_0 axis. In the c_0 direction the crystals are extremely "hard" magnetically, the magnetization curves being linear as in the case of a paramagnetic material. The saturation moments follow the T^2 law.

I. INTRODUCTION

THE magnetic properties of metallic dysprosium have been investigated by Trombe¹⁻³ and by Elliott, Legvold, and Spedding.⁴ Trombe found it to have an anomalous peak in the susceptibility near 179°K, which indicates the presence of an antiferromagnetic Curie point (Néel point). Below 85°K he reports dysprosium to be ferromagnetic, this being the zero-field transition temperature from antiferromagnetism to ferromagnetism. Above 179°K Trombe reports it to be paramagnetic, following the Curie-Weiss law between 250°K and 750°K. In the temperature range 179°K to 250°K he finds that it departs somewhat from this law. The paramagnetic Curie temperature was reported to be 157°K, and the effective number of Bohr magnetons was found to be 10.64 from the slope of the $1/X$ vs T plot.

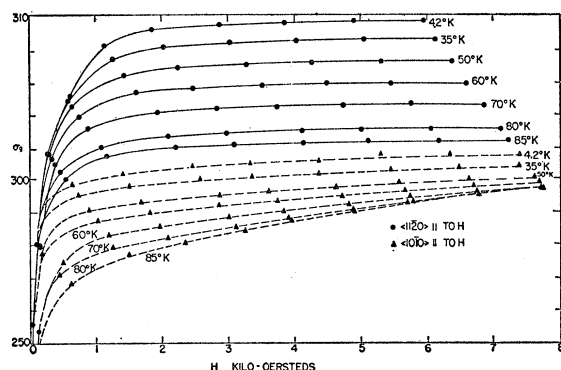


FIG. 1. Magnetization isotherms below 85°K with H along two different directions in the basal plane. The upper ordinate number should be 350, not 310.

* Contribution No. 606 from the Institute for Atomic Research and Department of Physics, Iowa State College, Ames, Iowa. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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¹ F. Trombe, *Compt. rend.* **221**, 19 (1945).

² F. Trombe, *J. phys. radium* **12**, 22 (1951).

³ F. Trombe, *Compt. rend.* **236**, 591 (1953).

⁴ Elliott, Legvold, and Spedding, *Phys. Rev.* **94**, 1143 (1954).

Elliott, Legvold, and Spedding⁴ have confirmed Trombe's results and have carried the measurements to lower temperatures and to higher fields. They report the Néel temperature to be 176°K and find the transition temperature from antiferromagnetism to ferromagnetism to be 92°K in a field of 1200 oersteds.

II. CRYSTAL PREPARATION

Two single crystals were studied in this investigation, one being roughly a cube and weighing 0.5 g and the other a sphere weighing 0.1 g. These crystals were grown by the Bridgman method in an atmosphere of argon with equipment described in a previous paper.⁵ After a melt the tantalum crucible was removed and the bulk material was etched with a solution of 40% nitric acid and 60% glacial acetic acid to reveal the grain structure. The largest grains were then cut out with a jeweler's saw and again etched. The spherical crystal was ground from a cube by the methods described by Bond.^{6,7}

The larger of the two single crystals had the following spectroscopic analysis: Si, detectable but less than 0.02%; Cr, detectable but less than 0.008%; Y, detectable but less than 0.02%; Er and Ho, detectable but less than 0.05%; Ta, 0.25%; Ca, Tb, Yb, Gd, and Tm, not detected. The smaller crystal showed the same analysis except for tantalum which was reported to be 0.15%.

Magnetic measurements were made on the larger crystal above the Néel temperature and on the smaller spherical crystal below the Néel temperature. For both of the crystals the demagnetizing factor was taken to be $4\pi/3$. The method used to measure the magnetic moment was the same as that described in an earlier paper.⁵

III. EXPERIMENTAL RESULTS

Figures 1 and 2 show some of the σ , vs H isotherms obtained for the field parallel to two different crystalline

⁵ Behrendt, Legvold, and Spedding, *Phys. Rev.* **106**, 723 (1957).

⁶ W. L. Bond, *Rev. Sci. Instr.* **22**, 344 (1951).

⁷ W. L. Bond, *Rev. Sci. Instr.* **25**, 401 (1954).

directions in the basal plane of the hexagonal close-packed structure of dysprosium; σ_0 is the magnetic moment per gram and H is the magnetic field in kilo-oersteds. The notation used to designate the crystalline directions is as follows: the hkl in brackets are the coefficients of the three a_0 and the c_0 unit cell vectors, respectively. A crystalline direction is then defined by $[hkl]$, and this direction or an equivalent direction is then given by $\langle hkl \rangle$. From Fig. 1, which shows the isotherms in the ferromagnetic temperature range, it can be seen that the preferred directions (the directions of easy magnetization) are the $[11\bar{2}0]$ directions. Fig. 2 shows the isotherms obtained in the temperature range in which dysprosium is antiferromagnetic. Above approximately 110°K dysprosium is isotropic in the basal plane. The effects of the anisotropy

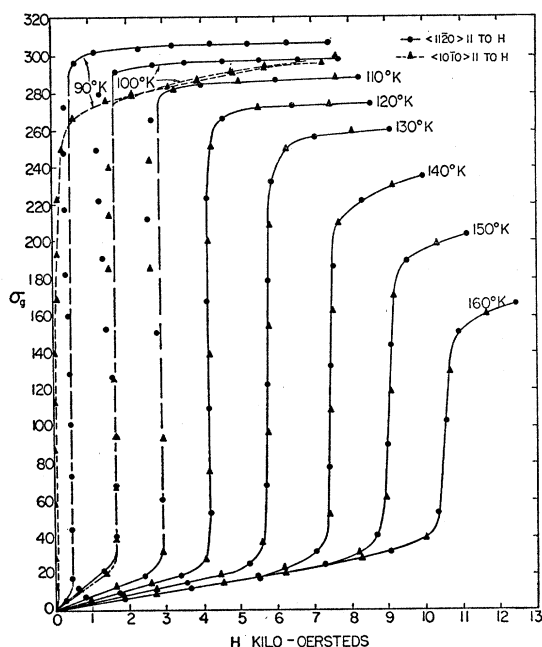


FIG. 2. Magnetization isotherms in the antiferromagnetic range from 90°K to 160°K with H perpendicular to c_0 .

in the basal plane are readily observed in the ferromagnetic temperature range and can be seen also in the antiferromagnetic temperature range below 110°K (Fig. 2). Figure 3 shows the magnetization curves obtained for temperatures near the Néel temperature with the magnetic field perpendicular to the c_0 axis.

With the magnetic field parallel to the c_0 axis, the magnetic moment was a linear function of the magnetic field for all temperatures investigated, and therefore the susceptibility was independent of the field. Figure 4 shows the variation of the parallel susceptibility (the susceptibility obtained when the field is parallel to the c_0 axis) with temperature over the entire temperature range investigated. Above the Néel temperature, the perpendicular susceptibility (the susceptibility obtained when

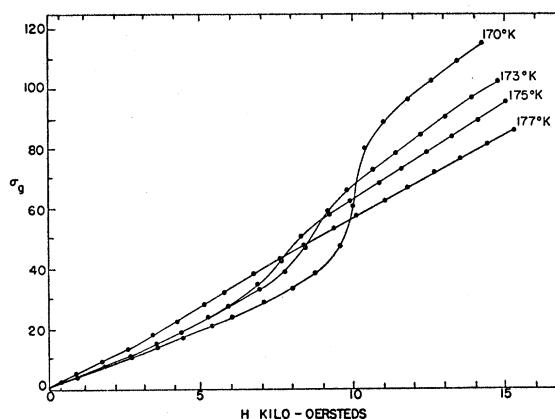


FIG. 3. Magnetization isotherms near the Néel point with H perpendicular to c_0 .

the field is perpendicular to the c_0 axis) was found to be independent of the field, and exhibited the dependence on temperature shown in Fig. 4. In Fig. 4 are also shown the inverses of the parallel and perpendicular susceptibilities as a function of temperature. From the slopes of these curves the effective numbers of Bohr magnetons were determined. With the field parallel to the c_0 axis a value of 10.64 Bohr magnetons was obtained, and with the field perpendicular to the c_0 axis the number of Bohr magnetons indicated was 10.65. These values agree very well with the free gas value for the tripositive ion which is 10.64 Bohr magnetons. The paramagnetic Curie temperatures obtained for the field parallel and perpendicular to the c_0 axis are 121°K and 169°K, respectively (Fig. 4).

Figure 5 is a plot of the magnetic moment $vs 1/H$ for several of the isotherms of Figs. 1 and 2. The saturation moments, $\sigma_{\infty, T}$, were found by extrapolating these curves to infinite fields ($1/H=0$).

In Fig. 6 the saturation moments obtained from Fig. 5 are plotted as a function of $T^{1/2}$ and T^2 to obtain the absolute saturation moment. The T^2 law appears to fit the experimental data better than does the $T^{1/2}$ law.

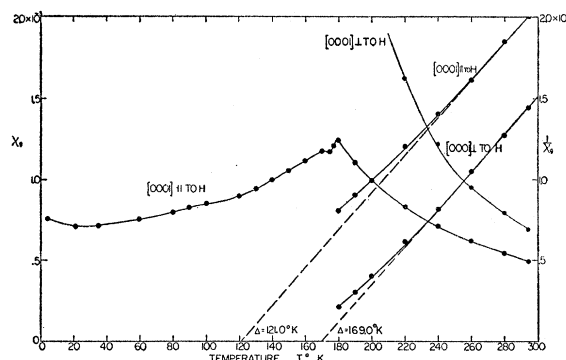


FIG. 4. Magnetic susceptibilities along c_0 and perpendicular to c_0 vs temperature and the reciprocal of these susceptibilities vs temperature.

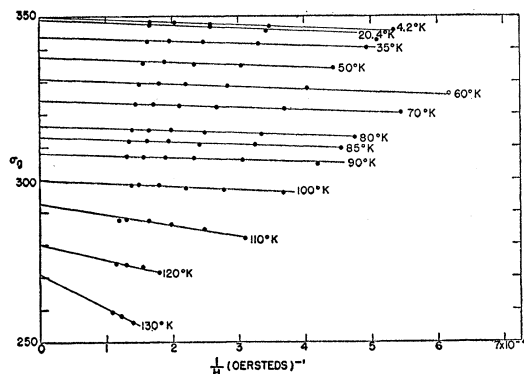


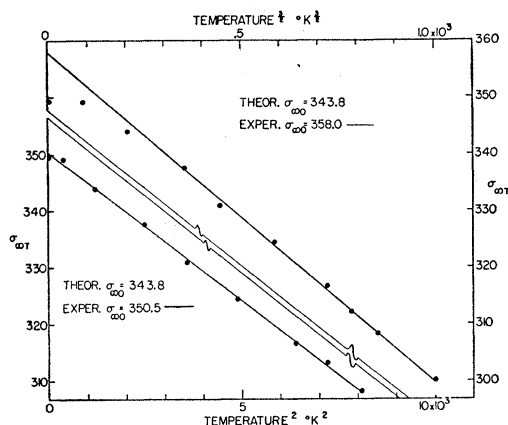
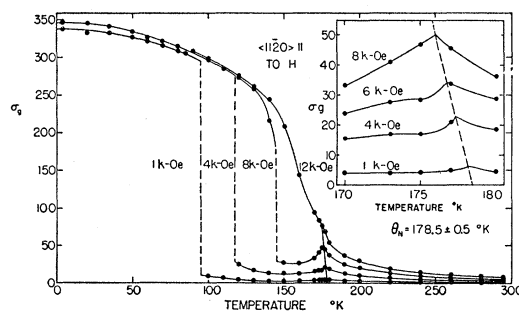
FIG. 5. Magnetic moment extrapolations to infinite field.

The absolute saturation moment is found to be 350.5 ± 2 cgs units per gram for dysprosium. This is to be compared with the theoretical saturation moment at absolute zero of 343.8 cgs units per gram, which is the free-gas value for the tripositive ion of dysprosium.

A similar plot of the spontaneous magnetization $vs T^2$ yields a value of 346.4 ± 2 cgs units per gram for the saturation moment at absolute zero. The spontaneous moment at a given temperature was obtained by extrapolating the high-field data of the isotherms of Fig. 1 to $H=0$. These values were then plotted against T^2 to find the absolute saturation moment.

Figure 7 shows the magnetic moment per gram plotted against temperature for various fields. The determination of the Néel temperature, which is $178.5 \pm 0.5^\circ\text{K}$, is shown in the insert. This graph also shows the dependence of the transition temperature from antiferromagnetism to ferromagnetism on the magnetic field, the transition temperature decreasing as the field is made larger.

In Fig. 8 is shown the critical field, H_c , plotted against temperature. The critical field is defined as the magnetic field at which the magnetic moment rises discontinuously (Figs. 2 and 3) from an antiferromagnetic to

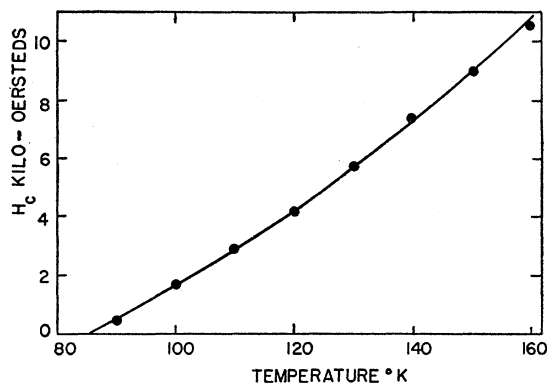
FIG. 6. The saturation magnetic moments taken from Fig. 5 $vs T^2$ and $vs T^{1/2}$.FIG. 7. Constant field plot of the dysprosium data with H along an a_0 axis. The insert is an enlargement of the data near the Néel point.

a ferromagnetic state. For $H_c=0$ the zero-field transition temperature is seen from Fig. 8 to be $85 \pm 0.5^\circ\text{K}$.

IV. DISCUSSION

An interpretation of the experimental results of this study in terms of the molecular field theory will be given in a subsequent paper. Here we only point out certain of the salient conclusions. Dysprosium is magnetically very hard along the c_0 axis, the magnetic moment being about 7% of the absolute saturation value for a field of 20 kilo-oersteds at low temperatures. In order that the absolute saturation moment obtained here may be compared with that found by Elliott, Legvold, and Spedding⁴ we make the approximation that for small fields the magnetic moment is confined to a plane which is perpendicular to c_0 . Then for a polycrystalline sample the apparent absolute saturation moment will be $\pi/4$ times the true absolute saturation moment.

Elliott, Legvold, and Spedding⁴ have found the apparent saturation at absolute zero to be 273 ± 3 cgs units per gram for fields less than 14 kilo-oersteds, and 299 ± 5 cgs units per gram for fields from 14 to 18 kilo-oersteds. Taking their low-field value and multiplying it by $4/\pi$, we find the true saturation moment at absolute zero to be 347.6 ± 4 cgs units. This is within

FIG. 8. The critical field, H_c , required to go from the antiferromagnetic state to the ferromagnetic state vs temperature.

experimental error of the value 350.0 ± 2 cgs units per gram obtained in this investigation.

The average or polycrystalline paramagnetic Curie temperature can be obtained from the single crystalline Curie temperatures by use of the relation $\Delta = \frac{1}{3}\Delta_{11} + \frac{2}{3}\Delta_{12}$, where Δ_{11} and Δ_{12} are, respectively, the Curie temperatures obtained with the field parallel and perpendicular to the c_0 axis. Using the values 121°K and 169°K as the single crystalline paramagnetic Curie temperatures,

we find that their polycrystalline average value is 154°K , which is to be compared with the value of 157°K which Trombe reports.

V. ACKNOWLEDGMENTS

The authors wish to express their appreciation to J. E. Powell for preparing the rare-earth salts and to A. H. Daane and J. Hanak for preparing the polycrystalline metal from the salts.

Magnetic Properties of Holmium and Thulium Metals*

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(Received August 12, 1957)

The magnetic moments of holmium and thulium metals have been measured in applied fields of 3000–18 000 oersteds, over the temperature range of 4.2 – 300°K . Holmium, paramagnetic above 133°K , appears to be antiferromagnetic between 20°K and 133°K , and ferromagnetic below 20°K . Thulium was found to be paramagnetic above 51°K and possibly antiferromagnetic below 51°K .

I. INTRODUCTION

THE magnetic properties of holmium have been studied by Bommer¹ over the temperature range 90 – 515°K . From his investigation of a powdery mixture of the rare-earth metal with an alkali chloride, he found that the magnetic susceptibility of holmium for temperatures above 195°K was in excellent agreement with the Curie-Weiss law, $\chi_{\text{at.}}(T-87)=14.30$. The Curie constant in this relation corresponds to an effective moment of 10.6 Bohr magnetons and the value $\theta_p=87^\circ\text{K}$ agrees well with the value calculated by Néel.^{2,3} Below 195°K there was evidence of a departure from the Curie-Weiss law.

The heat capacity of holmium has been measured by Gerstein *et al.*⁴ from 12°K to 300°K , and the curve is similar to that for dysprosium,⁵ except that the transformation peaks are displaced lower temperatures. For holmium, a large peak occurs at 131.6°K , indicating an order-disorder magnetic transition, and a small peak occurs at 19.4°K , indicating an order-order transition.

Klemm and Bommer⁶ have reported the magnetic properties of thulium from a powdery mixture of the

rare-earth metal with an alkali chloride. The magnetic susceptibility of thulium was found to be independent of the applied magnetic field over the temperature range of the investigation, 90 – 291°K . The paramagnetic Curie point was experimentally found to be 10°K , a value somewhat lower than the 22°K calculated by Néel.^{2,3} The results of Klemm and Bommer indicate an effective moment of 7.6 Bohr magnetons.

The results of magnetic measurements on holmium and thulium extending down to 4.2°K are reported in this paper.

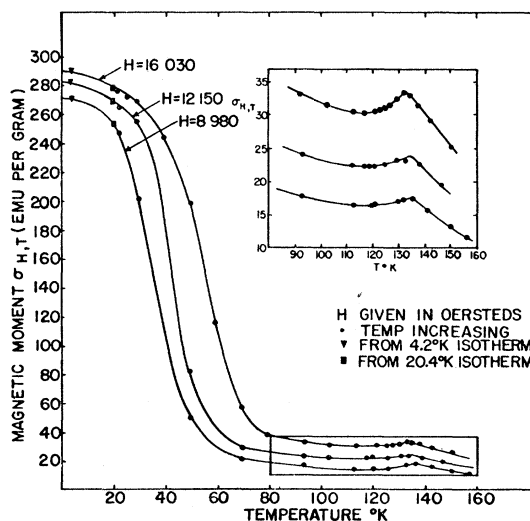


FIG. 1. Magnetic moment of holmium vs temperature at constant applied fields.

* Contribution No. 608 Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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² L. Néel, *Z. Elektrochem.* **45**, 379 (1939).

³ L. Néel, *Compt. rend.* **206**, 49 (1938).

⁴ Gerstein, Griffel, Jennings, Miller, Skochdopole, and Spedding, *J. Chem. Phys.* **27**, 394 (1957).

⁵ Griffel, Skochdopole, and Spedding, *J. Chem. Phys.* **25**, 75 (1956).

⁶ W. Klemm and H. Bommer, *Z. anorg. u. allgem. Chem.* **231**, 138 (1937).