Magnetization and Electrical Resistivity of Erbium Single Crystals*

R. W. GREEN,† S. LEGVOLD, AND F. H. SPEDDING
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa
(Received December 19, 1960)

The magnetic properties of erbium single crystals (hcp) grown by the Bridgman method have been determined in fields up to 18 kilo-oersteds with the field applied parallel to and perpendicular to the c axis at 4.2°K and between 20.4°K and 300°K. The c axis was found to be the direction of easy magnetization. A Néel point was observed at 85°K. The ferromagnetic-antiferromagnetic transition temperature inferred from the magnetic data was 19.6°K. The saturation moment, $\sigma_{\infty 0}$, obtained by extrapolation of the c-axis data was 8 Bohr magnetons compared to the theoretical 9. Electrical resistivity measurements from 1.3°K to 300°K with the current parallel to the c axis showed a sharp increase in resistivity at 20.4°K, the ferromagnetic-antiferromagnetic transition temperature; a large peak occurred at 53.5°K, and a minimum occurred at the Néel point. The a-axis resistivity curve showed a change in slope at the Néel point and was well behaved elsewhere.

INTRODUCTION

THE electrical resistivity of polycrystalline erbium has been reported by Legvold *et al.*[1] and by Colvin *et al.*[2] Legvold *et al.* found that there was a moderate change in the slope of the resistivity curve at about 80°K. Colvin *et al.*, using a sample prepared by improved techniques, found the temperature dependence of the resistivity of polycrystalline erbium to be significantly different. Their values for the resistivity and for the slope of the resistivity vs temperature curve at room temperature were approximately half the values previously reported. They also reported a minimum in the curve at 80°K.

The heat capacity of erbium has been measured between 15°K and 320°K by Skochdopole *et al.*[3] They found three peaks in the specific heat vs temperature: One peak occurred at 19.9°K; it was symmetrical and showed thermal hysteresis. A second peak occurred at 53.5°K, and this one had a rounded maximum. The third peak appeared at 84°K, where the heat capacity curve was flat for about one degree and then dropped very rapidly with increasing T.

Using the magnetic data for erbium determined by Klemm and Bommer,[4] Néel[5] predicted a Curie point of 40°K for this metal. Subsequently, Elliott *et al.*[6] reported the magnetic properties of erbium metal from 20.4°K to 90°K. The initial susceptibility vs temperature curve they obtained showed a maximum at 78°K. They concluded that erbium was antiferromagnetic from 78°K down to 20.4°K and that it was ferromagnetic below 20.4°K.

Koehler and Wollan[7] have reported neutron diffraction data on erbium. They found it to be ferromagnetic at 4.2°K, but at higher temperatures it was not possible to determine either the type of ordering or the magnetic lattice. Recently, however, Cable *et al.*[8] have obtained new data and concluded that a complex magnetic lattice is involved above 53°K. They indicate that a helical type of magnetic alignment might come close to fitting the observed diffraction patterns between 20°K and 53°K, and that there is a component of the magnetic moment perpendicular to the c axis at 4.2°K.

Banister *et al.*,[9] using x rays, determined the structure of erbium at low temperatures and found it to be hexagonal close-packed down to 40°K.

EXPERIMENTAL PROCEDURE

Four rectangular parallelepiped samples were cut from a large single crystal of erbium grown by the

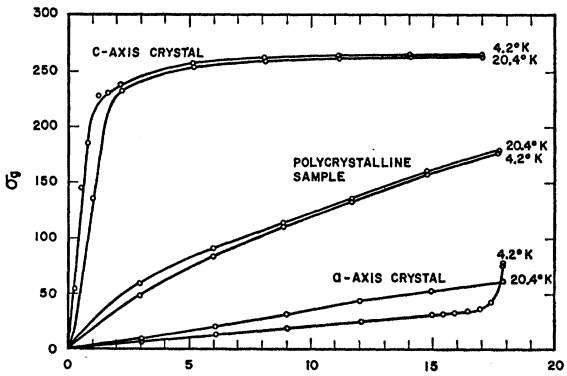

FIG. 1. Magnetic moment per gram of erbium samples vs field at 4.2°K, 20.4°K.

* Contribution No. 965. This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

† National Science Foundation Science Faculty Fellow, now at Morningside College, Sioux City, Iowa.

[1] S. Legvold, F. H. Spedding, F. Barson, and J. F. Elliott, Revs. Modern Phys. **25**, 129 (1953).

[2] R. V. Colvin, S. Legvold, and F. H. Spedding, Phys. Rev. **120**, 741 (1960).

[3] R. E. Skochdopole, M. Griffel, and F. H. Spedding, J. Chem. Phys. **23**, 2258 (1955).

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

[5] L. Néel, Z. Elektrochem. **45**, 378 (1939).

[6] J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **100**, 1959 (1955).

[7] W. C. Koehler and E. O. Wollan, Phys. Rev. **97**, 1177 (1955).

[8] J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, J. Appl. Phys. **32**, 49S (1961).

[9] J. R. Banister, S. Legvold, and F. H. Spedding, Phys. Rev. **94**, 1140 (1954).

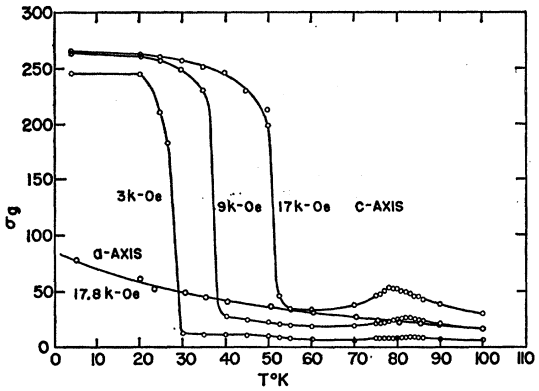

FIG. 2. Constant field plot of magnetic data taken with the field along the length of the *c*-axis crystal. The 17.8 koe data for the *a*-axis crystal are also shown.

Bridgman method, two with the *a* axis parallel to the long dimension and two with the *c* axis parallel to the long dimension. One pair, an *a*-axis crystal 1 mm×1 mm ×11 mm and a *c*-axis crystal 1 mm×1mm×6 mm, was used for magnetic measurements. The other pair, an *a*-axis crystal of effective dimensions 2.0 mm×3.0 mm×4.6 mm and a *c*-axis crystal of effective dimensions 1.5 mm×2.4 mm×4.6 mm, was used for resistivity measurements. Pieces of the crystal next to one of the samples used were analyzed for impurities. A spectrographic analysis showed: Yb<50 ppm; Tm≲20 ppm; Ho≲80 ppm; Dy≲50 ppm; Y detected but

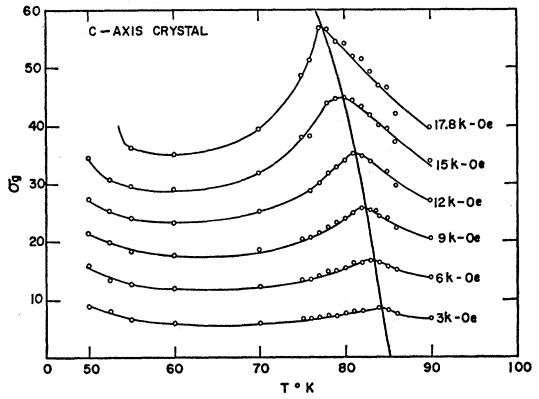

FIG. 3. An enlargement of the constant field plot shown in Fig. 2.

<100 ppm; Ca<100 ppm; Fe≲50 ppm; Si≲200 ppm; Mg detected but <200 ppm; Cr~500 ppm; Cu not detected; Ni not detected. A vacuum fusion analysis showed: N, 0.84 ppm; O, 1200 ppm; H, 11 ppm. A semiquantitative analysis for Ta on a small portion of the crystal yielded an estimate of the Ta content to be ~5000 ppm although it was not detected spectrographically.

The polycrystalline sample used for magnetic measurements was also a rectangular parallelepiped and was a portion of the sample used by Colvin *et al.*[2] in the work mentioned earlier. An analysis of this material showed: Tm≲20 ppm; Ho<80 ppm, Dy≲50 ppm; Yb≲50 ppm; Yb≲2 ppm; Y~400 ppm; Ca detected but <300 ppm; Mg detected but <300 ppm; Si detected but <300 ppm; Cr~500 ppm; Fe~500 ppm; C, 280 ppm; N, 79 ppm; Ag, Au, Be, Cd, Co, Ge, Hg, Ni, P, Ru, Sb, Te, Ti, V. W, not detected; La, very weak <500 ppm; Ta, very weak, <5000 ppm; Pb trace.

The magnetic measurements were made with fields up to 18 kilo-oersteds in magnitude applied parallel to the long dimension of the crystals at 4.2°K and between 20.4°K and 300°K. The magnetic moment per

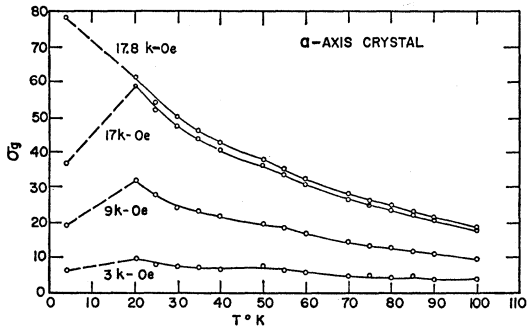

FIG. 4. Constant field plot of magnetic data taken with the field along the length of the *a*-axis crystal.

gram, σ_g, was measured isothermally as a function of field. Elliott *et al.*[10] have described the apparatus used in these measurements.

The electrical resistivities of the single crystals were measured as a function of temperature from 1.3°K to 300°K both with the current parallel to the *a* axis and with the current parallel to the *c* axis. The apparatus used in these measurements has been described by Colvin *et al.*[2]

RESULTS AND DISCUSSION

The *c* axis was found to be the direction of easy magnetization as is shown in Fig. 1, in which are

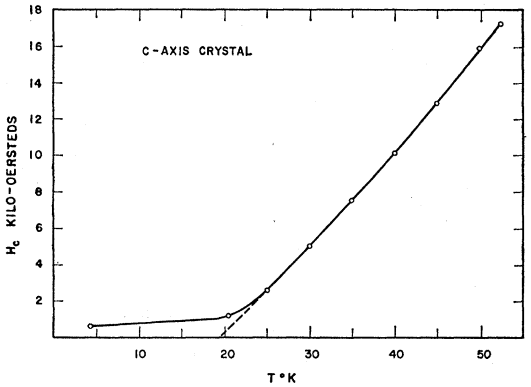

FIG. 5. The critical field, H_c, required to go from the antiferromagnetic state to the ferromagnetic state vs temperature.

[10] J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **91**, 28 (1953).

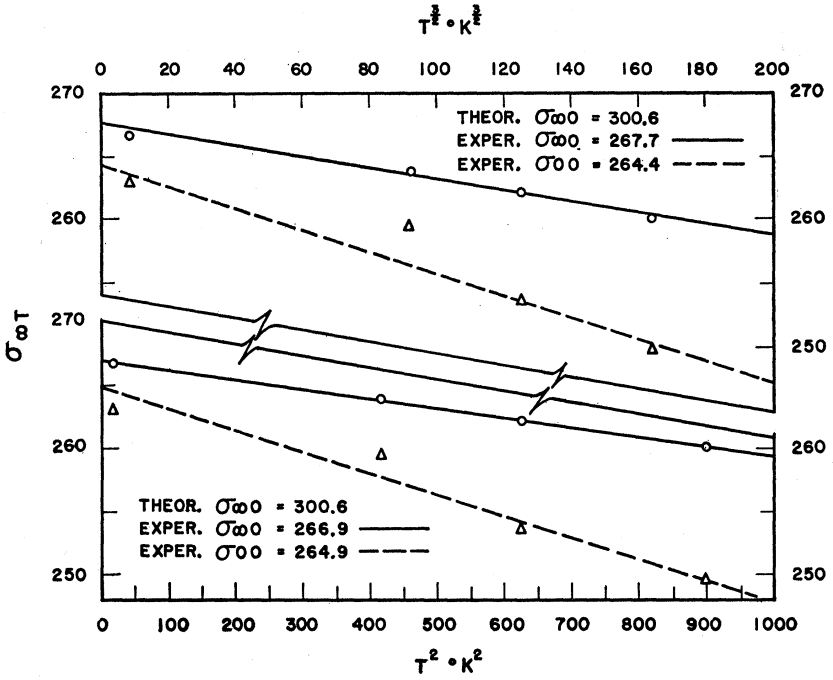

FIG. 6. The saturation magnetic moments vs T^2 and vs $T^{\frac{3}{2}}$.

plotted the low-temperature isotherms for the three magnetic samples. The plots of σ_g vs temperature at constant fields were determined from the isothermal measurements (Figs. 2–4). A ferromagnetic-antiferromagnetic transition temperature of 19.6°K was obtained by extrapolating the H_c vs T curve shown in Fig. 5. The critical field for a temperature T, H_c, is the field at which the magnetic moments suddenly align themselves with the applied field and the sample appears to go ferromagnetic. In Fig. 6 are shown extrapolated σ_{0T} and $\sigma_{\infty T}$ values vs $T^{\frac{3}{2}}$ and vs T^2. A plot of $1/\chi_g$, the reciprocal of the magnetic susceptibility, vs temperature in the paramagnetic temperature range is shown in Fig. 7 for the three magnetic samples used.

The results of measurements of resistivity of the single crystals as a function of temperature, temperature increasing, are shown in Fig. 8. Residual resistivity values of 19.50 μohm-cm and 16.32 μohm-cm have been subtracted from the observed data for the a-axis crystal and c-axis crystal, respectively. It was observed that there were some oxide platelets in the single crystals. The plane of the platelets was observed to lie in the basal plane. These platelets, formed in the crystal growing process, probably contributed to the high residual resistivities observed.

In Fig. 9 are plotted data taken from the curves reported by Colvin *et al.*[2] for the polycrystalline sample of erbium as well as the calculated polycrystalline data determined from the relationship

$$\rho_{\text{poly}} = \tfrac{2}{3}\rho_{\perp} + \tfrac{1}{3}\rho_{\parallel}.$$

Here for any given temperature ρ_{poly} is the calculated resistivity value of a polycrystalline sample of erbium, and $\rho_{\perp}$ or $\rho_{\parallel}$ is the resistivity value perpendicular or parallel to the c axis.

A Néel point for erbium was observed at 85°K. This is shown in Fig. 3, where a curve drawn through the peaks in the isofield curves has been extrapolated to $\sigma_g = 0$. This temperature agrees with the minimum observed in the $\rho_{\parallel}$ vs temperature curve shown in Fig. 8. It also agrees closely with one of the anomalies in the heat capacity vs temperature curve of erbium measured by Skochdopole *et al.*[3]

The experimental value of the saturation magnetic moment at infinite field and 0°K, $\sigma_{\infty 0}$, was 266.9 cgs units/g by the T^2 plot and 267.7 by the $T^{\frac{3}{2}}$ plot. These values are close to 8 Bohr magnetons. If the influence of the crystalline fields can be neglected and if it is assumed that the low-lying state is the spectroscopic state $^4I_{15/2}$, we then find $\mu_{\text{eff}} = gJ = 9$ Bohr magnetons.

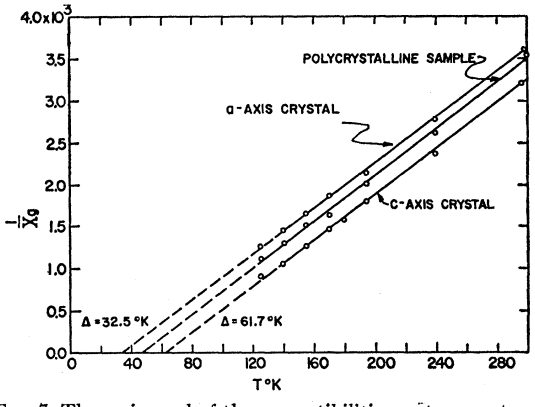

FIG. 7. The reciprocal of the susceptibilities vs temperature.

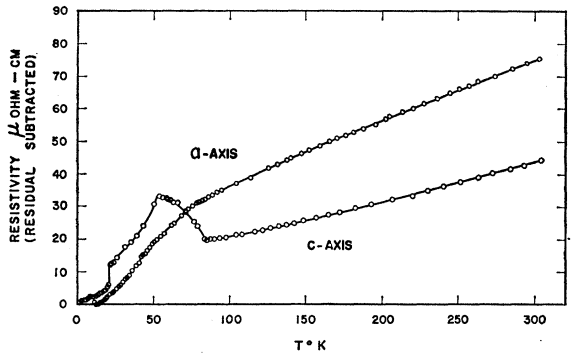

FIG. 8. Resistivity (residual subtracted) as a function of temperature.

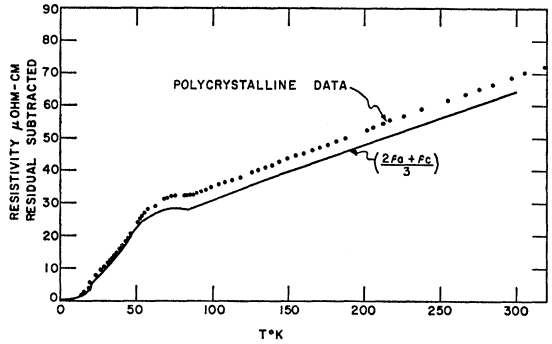

FIG. 9. Polycrystalline data vs temperature obtained from Colvin compared with $\frac{2}{3}\rho_{\perp}+\frac{1}{3}\rho_{\parallel}$ vs temperature.

This 1 Bohr magneton difference could be associated with the alignment of the spins which Koehler and Wollan[7] and Cable *et al.*[8] have observed by neutron diffraction studies. They report that a component of the moment is perpendicular to the c axis. The sharp upturn in the magnetic moment along the a axis at 4.2°K when the applied field reaches 17 kilo-oersteds (Fig. 1) suggests that the magnetic moments can be at least partially aligned along the a axis and that in sufficiently high fields the full 9 Bohr magnetons might be reached.

In the paramagnetic temperature range, above 140°K, the effective number of Bohr magnetons was obtained from the plot of $1/\chi$ vs T shown in Fig. 7. The value obtained was 9.9 ± 0.2 Bohr magnetons. This if to be compared with the theoretical value of 9.6 Bohr magnetons.

The anisotropy in the resistivity is defined by the ratio $\rho_{\perp}/\rho_{\parallel}$. For room temperature $\rho_{\perp}/\rho_{\parallel}=1.72$. Anisotropy is apparent not only in the room-temperature values of the resistivity, but also in the behavior of the resistivity in the neighborhood of the three specific heat anomalies[3] observed at 20.4°K, 53.5°K, and 85°K.

At the Néel point, 85°K, $\rho_{\perp}$ vs T has a small change in slope, while $\rho_{\parallel}$ vs T goes through a sharp minimum.

At 53.5°K no anomaly was observed for $\rho_{\perp}$ vs T, but for $\rho_{\parallel}$ vs T a peak occurred. The occurrence of this broad unsymmetrical peak might indicate that the ordering or disordering of the spins through the antiferromagnetic-paramagnetic transition occurs over a wide temperature range, or it might indicate that the spins are changing from one type of antiferromagnetism to another. Further neutron diffraction studies in this temperature region, perhaps on single crystals of erbium, might help to clarify the situation.

In the paramagnetic temperature range, $\rho_{\perp}$ vs T has a slope of 0.185 μohm-cm/°K, $\rho_{\parallel}$ a slope of 0.122 μohm-cm/°K.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to J. E. Powell for preparing the rare-earth salts and to A. H. Daane and C. Habermann for preparing the metals. One of us (R. W. G.) wishes to express his sincere gratitude to the National Science Foundation for granting him a National Science Foundation Science Faculty Fellowship for the year 1958-59.