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 $\Delta = \frac{1}{3}\Delta_{\parallel} + \frac{2}{3}\Delta_{\perp}$, where $\Delta_{\parallel}$ and $\Delta_{\perp}$ 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

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Magnetic Properties of Holmium and Thulium Metals*

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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 Bommer[1] 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, $\chi_{\text{at.}}(T\text{-}87) = 14.30$. The Curie constant in this relation corresponds to an effective moment of 10.6 Bohr magnetons and the value $\theta_p = 87$°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 toward 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 Bommer[6] 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.

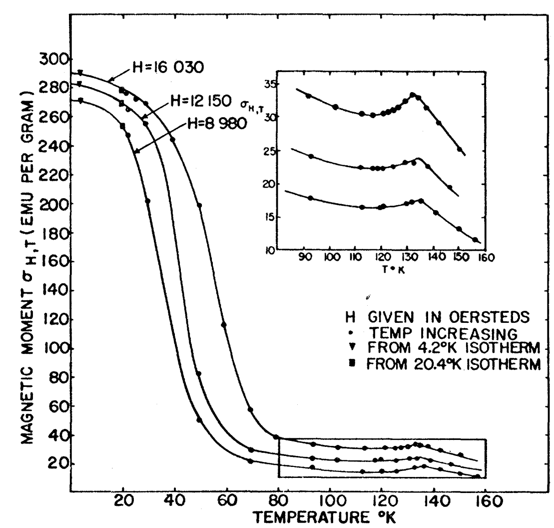

Fig. 1. Magnetic moment of holmium *vs* temperature at constant applied fields.

* Contribution No. 608 Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
[1] H. Bommer, Z. anorg. u. allgem. Chem. **242**, 277 (1939).
[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).

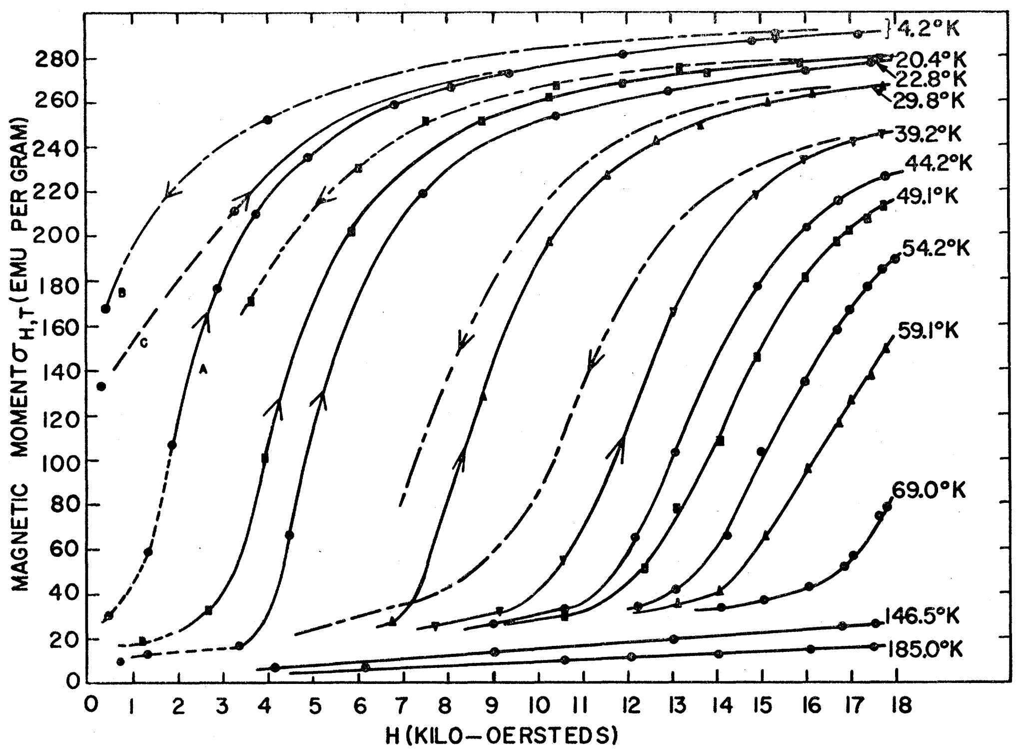

FIG. 2. Magnetization isotherms for holmium.

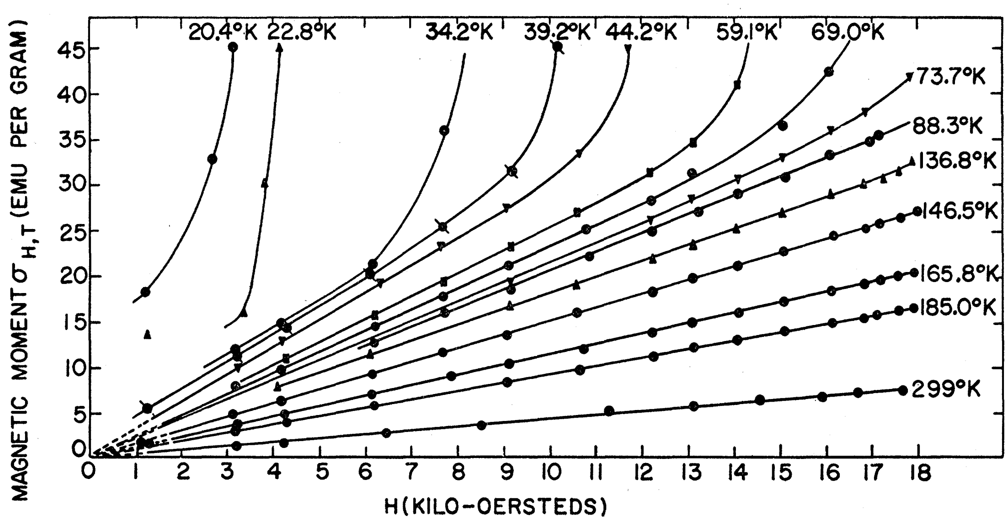

FIG. 3. Expanded magnetization curves for holmium in the region of low magnetic moment.

II. EXPERIMENTAL PROCEDURE

The rare-earth metals employed in this investigation were prepared by methods previously reported.[7-10] Holmium contained the following spectrographic impurities: Ca and Mg, 0.02% each; Fe, Si, and Ta, 0.05% each; Dy, 0.1%; and Er, 0.2%. Other elements, including Co, Ni, and other rare earths, were not detected. Thulium contained the following impurities: Cr, 0.05%; Si and Fe, 0.1% each; LaEr, Yb, Y, and Lu, 0.025% each; Mg, 0.05%; and Ca, La, and Ta, 0.02% each. Other metallic elements were not detected.

The experimental procedure followed has been described by Elliott *et al.*[11] The addition of a current control which held the magnetic field constant within one oersted improved the apparatus considerably. Samples 1mm×1mm×1cm were used.

[7] F. H. Spedding *et al.*, J. Am. Chem. Soc. **69**, 2777, 2786, 2812 (1947).

[8] F. H. Spedding and A. H. Daane, J. Am. Chem. Soc. **74**, 2783 (1952).

[9] F. H. Spedding and A. H. Daane, J. Electrochem. Soc. **100**, 442 (1953).

[10] J. E. Powell and F. H. Spedding, U. S. Atomic Energy Commission Report ISC-617, 1956 (unpublished).

[11] Elliott, Legvold, and Spedding, Phys. Rev. **91**, 28 (1953).

For most of the measurements the sample was placed in the gas stream above a vessel of boiling liquid nitrogen or liquid hydrogen. A heater in the gas stream was used to obtain temperatures up to 350°K. In addition, measurements were made in liquid hydrogen and liquid helium baths.

III. RESULTS

Figure 1 shows the magnetic moment of holmium *vs* temperature at constant applied fields. These data were obtained with increasing temperatures. Near 133°K the magnetic moment of holmium attains a sharp maximum value, indicating the onset of an antiferromagnetic state similar to that found in dysprosium,[12–14] in erbium,[15] and, as will be shown later, in thulium. Below the Néel temperature, 133±2°K, the magnetic moment of holmium tends to decrease until a temperature of about 115°K is attained. As the temperature is decreased below this value, the moment begins a temperature-dependent rise, indicating a transition from the antiferromagnetic to the ferromagnetic arrangement. Below 20.4°K, the magnetic moment tends to level off and approach the saturation moment for the fields plotted. It is apparent from the curves in the insert in Fig. 1 that there exists a shift in the Néel temperature with applied field.

In Figs. 2 and 3 the magnetization curves for holmium are shown. Some representative data taken with the field decreasing are also shown as broken curves in Fig. 2. The upper (broken) curve B at 4.2°K in Fig. 2 represents the field-decreasing data while the center curve C shows the effect of remanent magnetism when the field is again increased from zero. The lower of the three curves, curve A, is the virgin run.

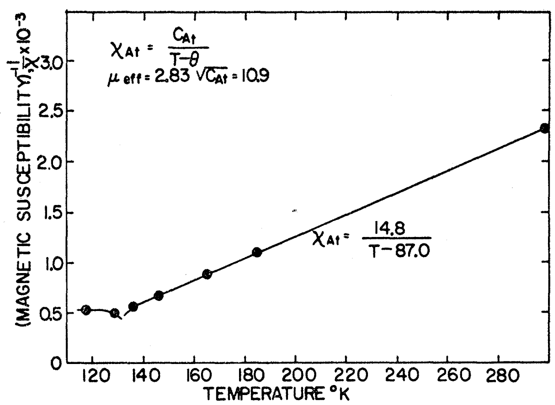

FIG. 4. Reciprocal of the magnetic susceptibility of holmium *vs* temperature.

Figure 4 shows the reciprocal of the magnetic susceptibility of holmium as a function of temperature. The data above 133°K obey the Curie-Weiss law with a Curie constant of 14.8, a result somewhat higher than that found by Bommer.[1] This result indicates an effective Bohr magneton number of 10.9, a value that is 3% larger than that resulting from the theoretical value of 10.6 for the holmium tripositive ion with spectroscopic state $^5I_8$. The extrapolation of the linear portion of the curve intersects the temperature axis to yield a paramagnetic Curie point of 87°K in agreement with the

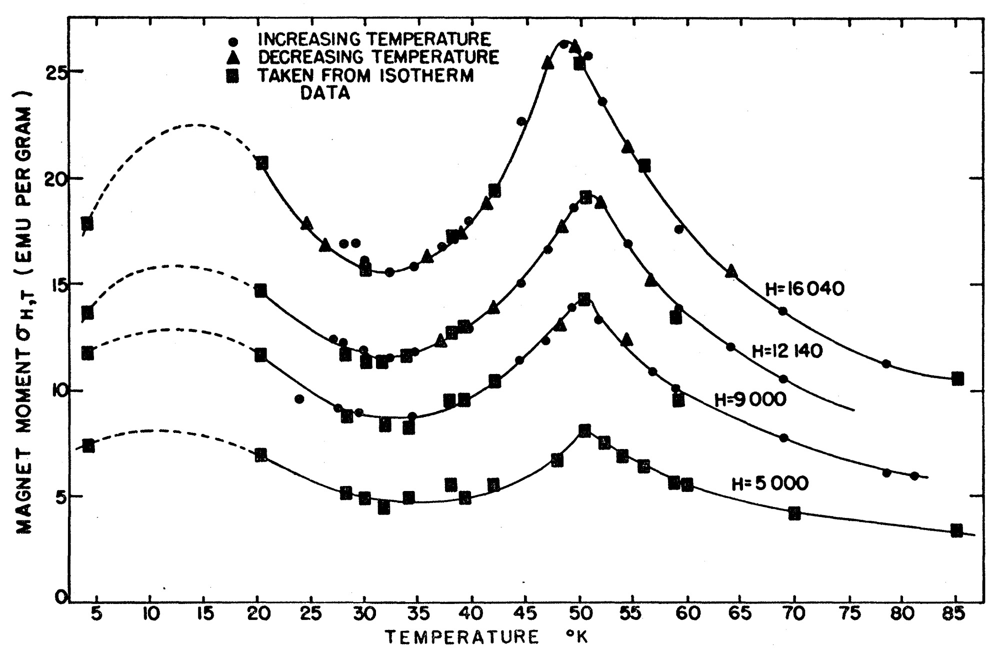

FIG. 5. Magnetic moment of thulium *vs* temperature at constant fields.

[12] F. Trombe, Compt. rend. **221**, 19 (1945).
[13] F. Trombe, Compt. rend. **236**, 51 (1953).
[14] Elliott, Legvold, and Spedding, Phys. Rev. **94**, 1143 (1954).
[15] Elliott, Legvold, and Spedding, Phys. Rev. **100**, 1595 (1954).

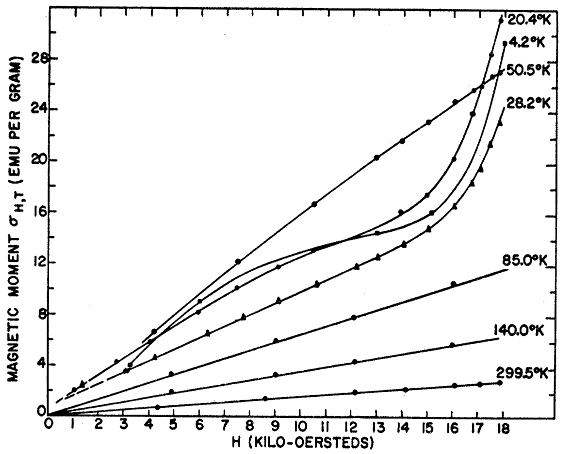

FIG. 6. Magnetization isotherms for thulium.

result of Bommer.[1] In addition, the magnetic data on holmium agree well with the thermal data of Gerstein *et al.*[4]

Figure 5 shows the variation of the magnetic moment of thulium with temperature at constant field. For thulium, as for holmium, there exists an antiferromagnetic region with the indicated Néel point very near 51°K. At the lower temperatures there is some evidence of a tendency toward ferromagnetism. The low magnetic moments observed at 4.2°K indicate that an additional transition of some kind must occur between 20.4°K and 4.2°K.

Figure 6 shows the result of the isothermal measurements of the magnetic moment of thulium. The data from room temperature down to 60°K show strictly paramagnetic behavior, i.e., the plots are linear and pass through the origin. Between 60–52°K the plots are linear, but tend to intersect the magnetic moment axis between the origin and unity. Below 50.5°K the data are like those for holmium in the antiferromagnetic region.

Both the 20.4°K and the 4.2°K isotherms show curvature toward the field axis in the range below 13 000 oersteds and curvature away from the field axis above 13 000 oersteds. In the high-field range of these two isotherms there is a marked, abrupt trend toward ferromagnetic-like behavior, but the applied fields were not high enough to attain any approach to magnetic saturation. Not shown here are data taken with fields decreasing from the maximum value which indicate that magnetic hysteresis is present at 20.4°K and at 4.2°K.

Figure 7 shows the reciprocal of the magnetic susceptibility of thulium *vs* temperature. The data satisfy the

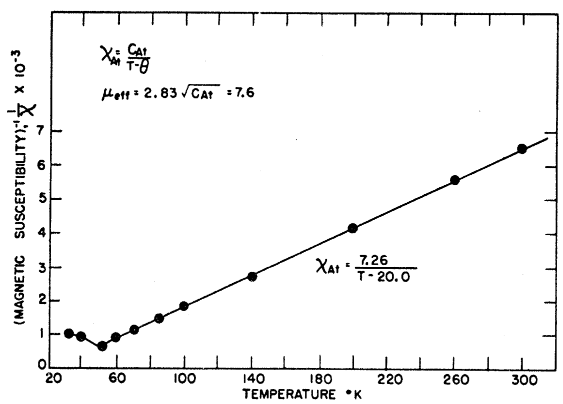

FIG. 7. Reciprocal of the magnetic susceptibility of thulium *vs* temperature.

Curie-Weiss law in the temperature region above the Néel point. The indicated Curie constant corresponds to an effective Bohr magneton number of 7.6 as compared with the theoretical value of 7.6. Extrapolation of the linear portion of the curve to the temperature axis indicates a paramagnetic Curie temperature of 20°K. Our Bohr magneton number agrees well with that found by Klemm and Bommer,[6] but our paramagnetic Curie temperature is 10° higher than theirs and is very close to the 22°K value predicted by Néel.[2,3]

The authors wish to thank Jack Powell for preparing the rare-earth salts and A. H. Daane for preparing the metal samples from the salts.