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MAGNETIC PROPERTIES OF HOLMIUM
AND THULIUM

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MAGNETIC PROPERTIES OF HOLMIUM AND THULIUM*

by

B. L. Rhodes, Sam Legvold and F. H. Spedding

I. ABSTRACT

The magnetic properties of metallic holmium, 99.6% pure, and of metallic thulium, 99.4% pure, have been measured. The applied magnetic fields for this study were between 1,000 and 18,000 oersteds; the temperatures observed were in the range between 4.2°K and 300°K.

The experimental results indicate that both metals exhibit regions of paramagnetic (P) and antiferromagnetic (A) behavior. The Néel temperature for Ho was estimated to be $133 \pm 2^\circ\text{K}$, and for Tm $50.5 \pm 1.0^\circ\text{K}$. Each of the metals showed behavior immediately below the Néel temperature that was very similar to the reported behavior of dysprosium.

The ferromagnetic state was attained in holmium at 4.2°K, but the data between 20.4°K and 4.2°K were not available to determine the Curie point. Holmium showed considerable magnetic hysteresis in the temperature region below the Néel point. Thulium metal also showed magnetic hysteresis in the temperature region below the Néel point, but did not attain a ferromagnetic state in the temperature region of these investigations.

Values of the magnetic moment were observed for both metals that were larger than spin-only contributions would yield. Such observations indicate that there exists orbital contributions to the magnetic moment of the atoms of the elements studied.

In the paramagnetic region, holmium obeyed explicitly the Curie-Weiss law $\chi_A = 14.8/(T-87)$ with an indicated Bohr magneton number of 10.9. The theoretical calculations for the Ho tri-positive ion with a spectrographic state $^3\text{I}_8$ would indicate a

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value of 10.6. The difference between the two values is thought to be due to impurities in the sample or to exchange interactions between the atoms of the metal.

In the paramagnetic region, thulium obeyed explicitly the Curie-Weiss law $\chi_A = 7.26/(T-20)$ with an experimental Bohr magneton number of 7.6. This value is identical with that calculated for the spectrographical state of the tri-positive Tm ion 3H_6 .

Holmium, of the two metals studied, revealed the more interesting magnetic behavior because, principally, temperatures well below the Néel point were attained. Throughout the study the Ho metal showed magnetic behavior very similar to that of Dy.

The present theory of magnetic phenomena appears to be far from complete and adequate. It is hoped that the results of this study will be helpful in the establishment of a firm theory of magnetism. Such a theory could lend substantial support to the rich analogies which may be drawn between the fundamental properties of matter -- not only in the rare earth series but possibly for other members of the periodic table as well.

II. INTRODUCTION

A. Purpose of Investigation

The rare earth elements, which are now often termed the lanthanons, form a fascinating group of some fifteen members extending from lanthanum with an atomic number of 57 through lutetium with an atomic number of 71. The electronic configuration for this class of elements has been greatly clarified by exacting works performed since the beginning of the present century. In the specific electronic arrangements of the members of this group, and in the manner in which the properties of the individual elements are thereby altered, may well lie many keys to the storehouse of the knowledge of matter itself.

The central electronic core for the elements of the lanthanon series consists of 46 electrons populating and filling the shells from the 1s through the 4d. Around this central core lie the electrons of the 4f, 5s, 5p, 5d, and 6s shells. It is the electrons of the buried 4f shell which give rise to the interesting properties of the rare earth series. The electrons of the 5s and 5p shells act as a shield for the protection of the inner electrons; the electrons of the 5d and 6s shells play the role of valence electrons in the formation of chemical compounds, and form the conduction band for the metals.

The principal manner in which the configuration of electrons varies throughout the series is by a nearly monotonic increase in the number of electrons populating the 4f shell from 0 to 14 as the atomic number increases from 57 to 71. The exception to this monotonic increase, in the case of the rare earth metals, occurs in ytterbium and lutetium. Ytterbium, element 70, has two more 4f electrons than its neighbor thulium, element 69. Since this increase is sufficient to complete the 4f shell for the series, lutetium receives its additional electron in the conduction band.

The remarkable similarity in the chemical properties of the lanthanons is explained on the basis of the nearly identical electron configuration throughout the series for the 5d and 6s orbitals, that is, for the orbitals that participate in the chemical bonding.

The common valence exhibited by the lanthanon series is a +3, indicating that the incomplete 5d and the 6s shells are responsible for the principal chemical bonding. However, it is also found that cerium, praseodymium, terbium, and dysprosium may also exhibit a +4 valence while samarium, europium, thulium, and ytterbium may exhibit a +2 valence. These results show that although the outer electrons are responsible for the principal chemical properties of the series, additional chemical bonding may be contributed by the buried 4f electrons.

It was the purpose of this study to carry forward the program of investigation of the magnetic properties associated with the rare earth elements in their pure, metallic state. In doing so, the list of elements displaying ferromagnetism might be extended. This study was initiated at Iowa State College by Elliott, Legvold, and Spedding (1, 2, 3, 4) in their study of the metals of gadolinium, dysprosium, and erbium. Whether or not the characteristic magnetic properties of these elements can be correlated to the support or development of a fundamental law of magnetization awaits further work.

One would expect, however, that the direct correlation of the variation of the magnetic characteristics of the lanthanon series with the change in electronic configuration would be further complicated by the fact that there is present also a variation of the atomic radii. Bommer (5) and Herrmann (6) show that the atomic radii of this series decrease nearly smoothly and uniformly with the increasing atomic numbers.

B. Definition of Magnetic Terms¹

When a sample of material is placed in a magnetic field of strength H , there is present in the material a magnetic induction B , given by the relation

$$B = H + 4\pi I, \quad (1)$$

where I is the induced magnetization. Here the cgs. Gaussian system of units is employed, where H is in oersteds and B is in gauss. The quantity I may often be directly related to the magnetic field strength through a constant, K , the magnetic

¹Most of the information presented in this section may be found in Bozorth (7), Bates (8), and Selwood (9).

susceptibility per unit volume:

$$I = K H. \quad (2)$$

The magnetic susceptibility per gram, χ , is related to the constant K through the equation

$$\chi = K/d, \quad (3)$$

where d is the density of the material.

The atomic susceptibility, i.e., the susceptibility for one gram atomic weight, may be obtained by multiplying the susceptibility by the atomic weight of the substance. In a similar manner, the molecular susceptibility is the product of the susceptibility and the molecular weight.

A quantity which will be used quite extensively in this paper is the magnetic moment per gram, σ , defined by the relation

$$\sigma = \chi H. \quad (4)$$

The quantity will be of special value in the event that the susceptibility shows field dependence.

A quantity often encountered in the discussion of magnetic properties is the permeability, P, which is defined as the ratio of the magnetic induction to the applied field:

$$P = B/H. \quad (5a)$$

The introduction of equation (1) and (2) into (5a) yields

$$P = 1 + 4\pi K. \quad (5b)$$

Although the concept of permeability will not be used in the following work, it has been included here to show its relation to the quantities already presented.

C. Classification and Properties of Magnetic Substances

The classification of the magnetic properties of a sub-

stance may take one or more forms depending upon the sign, magnitude, and variation of the magnetic susceptibility. The susceptibility changes encountered in the study of the magnetic properties of holmium and thulium show that these elements may exhibit paramagnetic, antiferromagnetic, and ferromagnetic tendencies depending upon the field and temperature regions under investigation. However, the quartz rod used for the suspension of the sample in the work reported here showed diamagnetic behavior.

Experimentally, diamagnetism is detected by the repelling of the substance from the high field region of a magnet. The force of the repulsion is directly proportional to the diamagnetic susceptibility, which, in general, is independent of both the temperature and the field. Theory shows that diamagnetism is a fundamental atomic property of all matter. The effect is usually small and may be completely overshadowed and undetectable in magnetic studies of a substance that exhibits any of the other forms of magnetic behavior. Selwood (9, p. 32) derives the classical expression for the diamagnetism of matter following the technique developed by Langevin, and the results may be written in the form

$$\chi_A = -2.83 \times 10^{-6} \sum \overline{r^2}. \quad (7)$$

The final term represents a summation of the mean square orbital radii taken over all the orbits in the atom. From this expression it is apparent that the susceptibility of a diamagnetic substance should be independent of both the temperature and the field. However, Bozorth (7, p. 456) points out that in the cases of bismuth, gallium, tin, and graphite there is a field dependency encountered at low temperatures.

Nearly thirty elements are reported as displaying diamagnetic behavior, and the atomic susceptibilities of these lie in the region of -10^{-3} to -10^{-6} cgs. units. A curve showing the magnetic susceptibility of the elements as a function of the atomic number may be found in Bozorth (7, p. 456).

Paramagnetism is detected experimentally by the attraction of the substance toward the high field region of a magnet. In

general, paramagnetic behavior may be broken into two distinct classes, and these classes can in turn be associated with the origin of the phenomenon. Substances displaying "weak paramagnetism" include many of the metallic elements when they are in the form of solid conductors. The resulting behavior is explained on the basis of the magnetic contributions by the conduction electrons of the metal (7, p. 462). Experimentally, weak paramagnetic substances show very small susceptibilities that are generally quite independent of temperature.

"Strong paramagnetism" is displayed in the event that an atom of the substance has permanent magnetic moment due to a resultant of the sum of the spin and orbital moments of all its electrons. We shall consider, for the present, that the case of ferromagnetism is included in this class. The condition for the existence of such a resultant moment is that there must be present within the electron configuration certain shells that are not completely filled. Completed subshells can contribute only to the diamagnetism of the substance since all spin moments tend to cancel. The diamagnetic behavior, however, as previously mentioned, may be completely dominated if there exists a resultant moment for the atom. In general, the orbital moment plays little or no part in the contribution to the total magnetic moment of the atom. The exception occurs in the case of the rare earth group, however, as evidenced by the orbital contributions in the observations reported by Bozorth (7, p. 462) and Elliott (1, 4).

Such incomplete shells as mentioned here occur in the iron group, palladium and platinum groups, and in the rare earth series. In the iron group, it is the 3d unfilled shell that is responsible for ferromagnetism, while in the rare earth series the high values of the magnetic susceptibility are due to the incomplete 4f band. Elliott (1, 2, 3, 4) shows that the saturation magnetic moments for the metals Gd, Dy, and Er are respectively about 17%, 26%, and 32% greater than that for iron. It was formerly believed that the elements holmium and dysprosium might yield the largest magnetic moments of any of the atoms. There is evidence of this in the case of holmium, but perhaps there is a question in the case of dysprosium as compared to erbium.

In the preceding discussion it was more or less assumed that the strong paramagnetic substances included the class of materials which demonstrate characteristics attributed to ferromagnetism. However, in comparison, ferromagnetic substances differ in their magnetic properties principally in the fact that they show (a) marked field dependency of the susceptibility, (b) an approach to saturation of the magnetization, i.e., σ approaches a constant, maximum value as the field is increased infinitely and as the temperature approaches absolute zero, (c) the existence of local cells, called domains, containing many atoms and exhibiting spontaneous magnetization, even though the substance as a whole may show no resultant magnetization, and (d) the disappearance of these domains when the temperature is above a certain value which in this work will be called the "Curie point".

When the temperature is such that the substance exhibits paramagnetic behavior, theory and experiment indicate that fields of the order of 10^6 oersteds are necessary to produce alignment of the individual atomic moments in order to yield resultant moments as large as those encountered in the ferromagnetics. Thus, the basic problem of ferromagnetism has been to explain satisfactorily how such alignment can occur spontaneously. Elliott (1) gives an excellent review of the progress and success of the theories developed to explain this phenomenon. Additional information concerning the present state of the theory of ferromagnetism may be obtained from the reviews of Stoner (10) and Van Vleck (11) as well as from the works of Bates (8), Bozorth (7), and Selwood (9), and a very recent book by Stewart (12).

In addition to diamagnetism, paramagnetism, and ferromagnetism, there is also a form of magnetic behavior termed antiferromagnetism. The state of the present theory indicates that while the individual domains of a ferromagnetic substance are aligned to yield large resultant moments, the atomic moments within a domain in the antiferromagnetic substances are arranged in such a way as to produce zero magnetization. This appears experimentally in the following manner: as the temperature of the material is reduced from some point in the paramagnetic region, the susceptibility increases as a smooth, monotonic function of the temperature until a certain critical temperature is attained. At this point, which shall hereafter be called the Néel point, the susceptibility shows a marked decrease as the temperature is further reduced. There is

evidence that these materials display both field dependence and magnetic hysteresis in the region just below the Néel point.

The temperature dependence of the antiferromagnetic salts of MnO, MnS, MnSe, and MnTe have been determined by Squire (13). Similar studies have been reported by Föex and Graff (14) for the compounds Cr_2O_3 and CrSb; by Föex and La Blanchatais (15) for NiO; by Bizette and Tsai (16) for FeO and FeF_2 , and by Néel (17) for Fe_2O_3 . In all of these cases except one, (14), the susceptibility of the substance decreased continuously and smoothly below the Néel point. In these singular cases researchers find a marked susceptibility plateau at very low temperatures.

Although antiferromagnetism seems to appear in the members of the rare earth series, there is a definite and fundamental difference in the picture that they present as compared with that of the salts above. In the antiferromagnetic regions of the rare earth metals erbium, holmium, thulium, and dysprosium, there is a tendency for the antiferromagnetism to be destroyed at certain critical temperatures and fields.

The general approach to the problem of detecting the presence of antiferromagnetic states of substances has been through the indirect methods such as the magnetic and the specific heat measurements. In 1949 Shull and Smart (18) conceived the possibility of directly determining antiferromagnetism by the means of neutron diffraction. Later investigations employing this detection technique have been presented by Shull, Strauser, and Wollan (19), and they report very successful results.

The theory of the antiferromagnetism of matter has been reviewed by Van Vleck (20) and investigated further by Yin-Yuang Li (21). In the latter article it is shown that, with the application of the Heisenberg model, the Néel point of an antiferromagnetic should be dependent upon the applied field.

D. Equations Describing Magnetic Phenomena

Experimental results show that the magnetic susceptibility of many substances in the paramagnetic region may follow the

form of the Curie law

$$\chi_A = C_A/T, \quad (8)$$

where χ_A is the atomic susceptibility of the substance, T is the absolute temperature, and C_A is the Curie constant which theory shows to be related to the magnitude of the atomic moments. Many substances, including praseodymium among the lanthanons (22), are known to follow this relation, especially in the region of high temperatures. The form of this equation indicates that no interaction occurs between neighboring atoms so that the atomic moments remain uncoupled.

The classical theory developed by Langevin shows that the atomic susceptibility may also be expressed in the form

$$\chi_A = N_0 \mu_A^2 / 3KT, \quad (9)$$

where μ_A is the magnetic moment per atom and N_0 is Avogadro's number. If the atomic susceptibility is thus known from experiment, the magnetic moment per atom is easily determined. This moment is often expressed in terms of an effective number of Bohr magnetons per atom, μ_{eff} , given by the relation

$$\mu_{\text{eff}} = \frac{\mu_A}{\beta} = \left(\frac{3K\chi_A T}{N_0 \beta^2} \right)^{\frac{1}{2}} = 2.83 (\chi_A T)^{\frac{1}{2}} = 2.83 \sqrt{C_A}, \quad (10)$$

where β is the Bohr magneton number defined as the magnetic moment associated with a single spinning electron.

Other substances, including the metals of this study, may follow a paramagnetic behavior described by the Curie-Weiss relation

$$\chi_A = C_A / (T - \theta). \quad (11)$$

The quantity θ is often called the "molecular field", but in the following work it shall be termed the "paramagnetic Curie temperature" or simply the "Curie temperature".

The existence of the Curie temperature indicates that some interaction between neighboring atoms is present and results in a coupling of the individual atomic moments in some manner.

It may happen that the value of the quantity Θ occurs very near the ferromagnetic Curie point for the substance, if the ferromagnetic state exists. However, it must be recalled that the existence of a value Θ in equation (11) does not predict that the substance will become ferromagnetic below the temperature $T = \Theta$. It is observed, rather, that the simple Curie-Weiss law is no longer obeyed in the neighborhood of the Curie temperature.

Néel (23, 24) predicts that the Curie temperature may be given by the relation

$$\Theta = n \frac{4\beta^2}{3R} \frac{S^2(J+1)}{J}, \quad (12)$$

where S is the total spin quantum number, J is the total angular momentum quantum number, R is the gas constant and n is a constant. In this formulation he assumes that in the rare earths (a) the magnetic moment is composed of both orbital and spin contributions which add vectorially, (b) the atoms are coupled only through the total spin quantum number, and (c) the magnetic energy can be expressed in terms of the magnetic intensity through a constant, n , identical for all members of the series. He then uses the experimental results of gadolinium to determine n , and proceeds to calculate Θ for all the lanthanons. These calculations show, for several cases, results which are very close to the experimental values.

If the susceptibility should show field dependence, the above formulas are no longer applicable. It is then found more basic to consider the magnetic moment as expressed by equation (4). In general, then, the magnetic moment may be a function of the temperature and the field, and this dependency is designated by subscripts:

$$\sigma = \sigma_{H,T}. \quad (13)$$

Not much can be said of this quantity in the region where it changes most rapidly, until, as in the case of ferromagnetism,

magnetic saturation begins to occur. As early as 1910 Weiss (12, p. 34) showed that the approach to saturation at a particular temperature may take the form

$$\sigma_{H,T} = \sigma_{\infty,T}(1-a/H^2), \quad (14)$$

where (a) is some constant value and may be termed the coefficient of magnetic hardness.

However, experiment shows that observations most often conform to the relation

$$\sigma_{H,T} = \sigma_{\infty,T}(1-a/H). \quad (15)$$

Bloch (7, p. 719) has made a quantum mechanical derivation of the variation of the saturation moments in the neighborhood of absolute zero and expresses the approach to absolute saturation magnetization in the form

$$\sigma_{\infty,T} = \sigma_{\infty,0}(1-bT^{3/2}). \quad (16)$$

The symbols in these equations have the following meaning:

$\sigma_{\infty,T}$ is the saturation magnetization at the temperature T;
 $\sigma_{\infty,0}$ is the absolute saturation magnetization at zero degrees absolute.

Experimentally, the observations for iron and nickel (6, p. 720) obey a T^2 law as well as, if not better than, the $T^{3/2}$ law. The rare earth metals Gd and Dy have shown variations according to equation (16).

The absolute saturation magnetization may be used to obtain the effective number of Bohr magnetons per atom from the relation

$$\mu_{\text{eff}} = \frac{\mu_A}{\beta} = \frac{A\sigma_{\infty,0}}{N_0\beta} = \frac{A\sigma_{\infty,0}}{5587}. \quad (17)$$

The result of equation (17) may be compared with the determination of the same relation from the paramagnetic data applied in equation (10); however, since it is very difficult to say just what role the exchange forces play in these determinations, one does not know what agreement the two results should display.

The quantum theory (34) predicts a magnetic moment for one gram-atomic weight to be given by

$$\mu_A = g\beta\sqrt{J(J+1)} \quad (18')$$

in regions far from saturation, but for regions near to magnetic saturation

$$\mu_A = g\beta J \quad (18'')$$

Here g is the gyromagnetic ratio determined by the quantum theory to be

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (19)$$

but in general defined by the relation

$$g = \frac{2mc}{e} \cdot \frac{\text{Magnetic moment}}{\text{Angular momentum}}, \quad (20)$$

where m and e are the mass and charge of the electron, respectively, and c is the velocity of light. In equations (18), (19), and (20), the quantity S represents the total spin quantum number; L , the total angular momentum quantum number; and J , the total quantum number, given by the vector sum of S and L .

The knowledge, therefore, of the spectral state of the lanthanons makes possible the theoretical determinations of their atomic moments.

III. REVIEW OF LITERATURE

Although a considerable amount of research has been reported in connection with the physical properties of the lanthanon elements, it has been only recently that the pure metals have been available in quantities sufficient to permit extensive investigations of their metallic states. A very careful digest of the reported magnetic, electrical resistivity, Hall effect, specific heat, and thermal expansion properties of the lanthanons has been compiled by Barson (25).

Furthermore, Selwood (9, p. 193) has prepared a summary of the knowledge of the rare earth properties which was available up to 1943.

In this review we are concerned only with the magnetic and related properties of the elements holmium and thulium. It must be recalled that the experimental observations in the following reports should be received with some caution when used in comparison with the results of this research. The reason for this caution is that most of the properties reported were obtained from the measurements upon the salts of the respective elements. In such a system the rare earth atoms may be sufficiently separated to dispel interactions which may occur when the element is in the metallic state.

In 1937, Cabrera (26) reported the Curie constant, C_A , for the tri-positive ions of Dy, Ho, and Er from measurements on the respective oxides. Bates (8, p. 147) reviews the work of Cabrera and submits the effective number of Bohr magnetons per atom for Ho to be 10.50. The calculated value by Van Vleck is reported to be 10.60. Trombe (27) reports an experimental value of 13.53.

In 1939, Néel (23, 24) reported the theoretical values of the Curie temperature, θ , for members of the heavy lanthanon group using equation (12), the known spectral terms, and the value of "n" as determined from the measurements on gadolinium. He reports the value of the Curie temperature for Ho to be 86°K. Although Klemm and Bommer (22) have determined the Curie temperature for many of the rare earth elements, they have not included holmium in their study.

Bommer (28) has reported the crystal structure of Ho to be the hexagonal closest packed arrangement. He has found that the magnetic susceptibility, which was obtained from the

measurements on the metal mixed with potassium chloride, obeyed the Curie-Weiss law in the temperature region from 550°K to about 200°K. The effective number of Bohr magnetons per atom in this region was determined to be 10.6. Below about 200°K there was an indication of departure from the Curie-Weiss law, but the number of observations in the low temperature region were insufficient to determine just where the departure began.

More recent determinations of the crystal structure and lattice parameters of the lanthanon metals have been made by Herrman et al. (6). He reports the lattice constants for Ho to be $a_0 = 3.5775$ and $c_0 = 5.6158$. The crystal structure for metallic Ho was found to be hexagonal closest packed.

The specific heat of Ho has been measured over the temperature range from 12°K to 300°K at this institution (28). The curve resembles very closely the specific heat curve for Dy except that the peaks are displaced toward lower temperatures. For holmium the two peaks occur at about 19.4°K and 131.6°K. There is indication that the study of the specific heat measurements for Ho is not quite complete since there is evidence of slight irregularities in the temperature range between 80°K and 110°K.

From the experimental viewpoint, it appears that Tm has perhaps received somewhat less attention than has holmium. Klemm and Bommer (22) report a Curie point for thulium at 10°K whereas Néel (23, 24) finds the calculated value to be 22°K. In their work, Klemm and Bommer show that in the paramagnetic region thulium definitely obeys the Curie-Weiss law, equation (11). Trombe's review (27) indicates the number of Bohr magnetons per atom for thulium to be about 6.45, whereas Cabrera (26) shows a value of 7.27.

Legvold and Spedding (35) have reported the Hall voltage for thulium from room temperature to 20.4°K. The results show that thulium has a negative Hall coefficient that is temperature dependent. Although this indicates extraordinary internal magnetic moment effects, there was no indication of peculiar behavior in the region where the present study indicates the occurrence of an antiferromagnetic transition.

Herrman et al. (6) reports the crystal structure of metallic thulium to be the hexagonal closest packed arrangement. He determined the lattice parameters to be $a_0 = 3.5375$ and $c_0 = 5.5546$.

IV. MATERIALS

The rare earth metals employed in this investigation were subjected to spectrographical analysis to determine their impurity content. The samples were analyzed for about 45 elements, special attention being directed to other rare earths present, and to iron, nickel and cobalt.¹

The analysis of the Ho metal used in this research indicated that the sample was about 99.6% pure. The detected impurities consisted of Ca and Mg, 200 ppm each; Fe, Si, and Ta, 500 ppm each; Dy, 1,000 ppm; and Er, 2,000 ppm. Other elements, including Co, Ni, and other rare earths, were not detected.

The analysis of the Tm metal used in this research indicated that the sample was about 99.4% pure. The detected impurities consisted of Cr, 50 ppm; Si and Fe, 100 ppm each; La, 200 ppm; Er, Yb, Y and Lu, 250 ppm each; Mg 500 ppm; and Ca and Ta, 200 ppm each. Other elements including Co, Ni and other rare earths, were not detected.

V. APPARATUS

A. Electromagnet and Power Source

The magnetic fields needed in the course of this study were produced by a 20 kw Weiss-type electromagnet designed and constructed at this laboratory. The yoke of this magnet is constructed of three rectangular slabs of mild carbon steel, two of which form the upright arms that are held rigidly to the third, the base slab, by means of heavy steel plates and bolts. The cores of the magnet are constructed of soft iron formed into cylinders one foot in diameter and fourteen inches in length. The cores are held to the yoke arms by means of heavy steel bolts.

The pole tips used in this research are of the Sucksmith type originally designed by Elliott (1), and recently machined

¹Complete spectrographical standards have not yet been devised for the determination of the quantity of impurities present in holmium and thulium. This analysis, given in parts per million, submits the best estimate possible with the current standards.

to better symmetry and to a form producing a more uniform gradient. By adjusting the current, the gradient can be varied from nearly zero to about 550 oersteds per cm., while the field varies in proportion from nearly zero to about 18,000 oersteds. The maximum gradient is sufficient to give rise to a force of some 10 gm. on a 0.08 gm. iron sample.

The electrical current from the power source passes through a system of three pairs of field coils, all of equal resistance and connected in parallel. (Originally there were four sets of coils in this array, but the inner pair was disconnected because of shorting at high currents.) The current to these coils is supplied by a large motor-generator set capable of supplying a maximum operating current of 150 amperes at 120 volts. The field current of the large generator unit is supplied by a small motor-generator set, and the field current of the small generator is in turn supplied and controlled by an electronic unit built at this institution. With the electronic unit controlling the stability of the voltage across a 0.01 ohm shunt in series with the electromagnet, the field of the magnet can be maintained to within an estimated 1 oersted variation, except for spurious fluctuations, over the entire field range up to 18,000 oersteds.

The heat developed in the coils of the electromagnet is dissipated by means of transformer oil which circulates through "cans" enclosing the magnet coils. The oil then passes through a water-cooled heat exchanger before returning to the magnet. Even at the highest currents of about 125 amperes, the efficiency of the cooling system is adequate to maintain the enclosing "cans" as cool as desired.

B. Sample Weighing, Suspension, and Centering

Forces acting on samples placed in the inhomogeneous field were obtained by direct weighing, using a Voland Speedigram Analytical Balance, Model "750-D. Under stable conditions the least count of weights was 0.1 mg., and weighings could be made rapidly.

A sample-height-adjustment mechanism replaced the left-hand scale pan of the balance, and to this mechanism was suspended a fused quartz rod 3 mm. in diameter. The quartz rod was long enough to extend into the region of the field gradient, and the sample was attached to the rod by means of

a special, lightweight brass holder. This holder was designed to have a low heat capacity so as to minimize time lag in thermal drifts. The brass had been previously tested for a minimum of magnetic properties.

One problem which appeared very early in the course of these measurements was the tendency of the sample to be attracted toward one or the other pole piece, due to the unstable equilibrium at the center of the field. High in the field there was found a region which exhibited a self-centering effect, but in this region the weighing was unstable. Since a mathematical analysis showed that the simultaneous existence of both weighing stability and self centering could not be expected, we were forced to incorporate some centering device in order to weigh the sample.

The system finally adopted employed four lengths of a very fine gold chain. The chain allowed ample vertical motion of the sample for accurate weight measurements, but restricted the lateral motion to within a very small region. The centering mechanism was mounted within a thin brass sheath which surrounded the sample, and the sheath in turn was attached to a quartz tube which surrounded the quartz suspension rod and extended to the table supporting the balance.

A discussion of the possible errors introduced by the centering device will be found in the appropriate position of section VII.

C. Temperature Control and Measurement

There were two fundamental types of cryogenic systems employed in these experiments. The first of these consisted of a dewar especially designed for liquid-bath measurements; the second was designed for gas-stream measurements.

The bath measurements were more simple in nature and provided the more stable temperature; however, this system introduced certain undesirable problems such as liquid level fluctuations in the centering tube, and the collection of gas bubbles on the weighing components. Actually, a more serious problem at first was the formation of solid air throughout the dewar interior. Solid air could not be tolerated, of course, because of the possibility of solid oxygen adhering to the

sample and adding both weight and magnetic properties to that of the metal. The situation was finally remedied by the insertion of a baffle system to exclude the air. Further precaution was taken by flushing out the system with gaseous hydrogen immediately preceding the introduction of the liquid hydrogen.

The second method of temperature control was to regulate the temperature of the gas which flowed by the sample. The dewar itself was constructed in the form of an enlarged, double-walled Florence flask, such as found in the chemistry laboratory, except that the bottom was round. Since the bulb of the dewar occupied the region just below the pole pieces of the magnet, its volume was limited to about two liters.

In the bottom of the dewar was placed a heating element constructed of constantan wire of sufficient resistance to provide adequate boiling of the liquid used. A similar element was positioned in the neck of the dewar just below the sample to heat the evolved gas. Trials for optimum boiling rates were made with a view to good temperature correspondence between the thermocouple and the sample, along with easy temperature control. Thereafter each liquified gas was boiled at its specified rate.

With the use of liquid hydrogen in this dewar, it was possible to regulate the temperature from about 22°K to 350°K within an accuracy of about 0.5°K . Liquid nitrogen provided about the same response, but allowed temperature variations over the range from about 100°K to 350°K .

The temperature was determined by means of a copper-constantan thermocouple calibrated against a standard platinum thermometer. In our latest work, the sample was imbedded in a thin brass ring immediately surrounding the sample and sample holder. This improvement provided a more accurate means of determining the temperature of the sample than was previously possible when the thermocouple was simply exposed to the gas stream.

VI. METHOD OF PROCEDURE

A. Preparation of Sample

The rare earth metals were shaped into samples that were 1 mm. by 1 mm. in cross section and 10 mm. in length. This was accomplished by filing the rough metals in a simple form made of forged steel. During the experiment, the samples were protected by a liberal coating of G. E. Adhesive #7031. When not under test, they were stored in an evacuated desiccator.

There was no attempt made to anneal the samples at high temperature before they were subject to the experimental observations.

B. Method of Measurement

When an experimental sample is placed in a region with a magnetic field gradient, the force exerted upon it is given by the expression

$$F = \Delta M_c g = \sigma_{H,T} m (dH/dZ), \quad (21)$$

where dH/dZ is the field gradient, m is the sample mass, $\sigma_{H,T}$ is the magnetic moment per gram, and g is the gravitational constant. The quantity ΔM_c is the change in the effective mass of the sample due to a variation in either the temperature or the field gradient, but which has been corrected for the diamagnetic lift on the suspension rod and, in the case of liquid-bath measurement, for change in the liquid level.

In an actual experiment, the weight may be observed as a function of the temperature (isofield data¹), or it may be observed as a function of the field (isotherm data). We shall present results of both forms of observations.

¹We will use the term "isofield" to designate a curve obtained with a constant magnetic field, just as the term "isotherm" shall be used to designate a curve obtained for a constant temperature.

In the initial investigation of a material, the technique which has proved the most fruitful and advantageous has been to perform an isofield measurement with a step-wise variation of the temperature. A quick plot of the observed quantities during the course of the experiment provided a quantitative picture of the response of the material and indicated the region requiring specific attention.

C. Calibration of Magnet

The magnet field, H , was calibrated from 100 to 18,000 oersteds by means of a Rawson rotating flux coil and meter. The limit of accuracy of this instrument is about 1.5% over its entire range, but many of the recordings agreed to within 0.2% of standard field values calibrated by a proton resonance instrument. Assuming that a smooth curve of calibration points yields better accuracy than the most inaccurate points, we estimate that the limit of accuracy of the recorded value of H is about 0.5%. Although the values of the field are given in the appendices to the nearest 10 oersteds, their magnitudes should not be trusted to an accuracy greater than our estimate.

The magnetic field gradient, dH/dZ , was determined over the entire field range using a sample of 99.99% pure iron. In this calibration, the sample of iron was placed in the same position as the experimental sample, and, with the sample at room temperature, the weight was recorded as a function of the "relative current" which was proportional to the current exciting the magnet. The application of the basic relation, equation (21), to the experimental results, using a value of 217.8 for the saturation moment of iron, yielded the desired field gradient. Thus the magnetic properties of the metals here investigated have been, in effect, compared with that of iron.

One question which immediately arose was concerned with the accuracy of the assumption that the iron has a saturation moment of 217.8 over the entire field range. Actually, the value of this quantity has been assumed to be an average of many reported determinations. In this investigation, we have assumed that this quantity is known to an error not more than 0.02% for fields over 4,000 oersteds. At 1,000 oersteds the error increases to about 1%. Somewhat below 1,000 oersteds the magnetic moment of iron becomes so uncertain that the field gradient cannot be determined by the method described here.

The errors encountered in the calibration of the field gradient will be discussed in an appropriate part of Section VII.

D. Determination of Temperature Correspondence

It was not feasible to attach the thermocouple directly to the experimental samples because of the magnetic properties of the constantan wire. Instead, the thermocouple was attached to a brass ring surrounding the sample; however, even with this arrangement, the ring and sample temperatures were not quite the same. A series of "temperature-correspondence" determinations were therefore obtained by temporarily attaching a difference-thermocouple between the sample and the experimental thermocouple. The results indicated that the sample was cooler than the thermocouple by about 1.5°K at 25°K . This temperature difference gradually decreased and vanished at about 200°K . The temperature difference has been attributed to the character of the gas flow and the heat influx into the system.

E. Treatment of Data

It is the magnitude of the effective number of Bohr magnetons per atom, μ_{eff} , which yields information concerning the ways in which the electron spin and orbital moments combine to give the total atomic moments for the substance. Although μ_{eff} had already been determined for Ho and Tm from measurements made upon their salts, it was considered desirable to make new measurements on the pure metals. Two methods by which experimental data may be used to yield values for μ_{eff} are available. The first method applies equation (11) to the data obtained in the paramagnetic region; the second applies equation (17) to the experimentally determined absolute saturation magnetization.

The second method, of course, can be used only when the metal exhibits ferromagnetic characteristics, where complicated exchange interactions aid in aligning individual atomic moments to produce saturation. In the approach to saturation, equations (14), (15) or (16) may aid in the extrapolation of the plot of the experimental data to obtain the saturation magnetization at infinite field and absolute zero.

The basic relation which has been applied to the treatment of the initial data has been equation (21). Since the magnetic

field and magnetic field gradient are known functions of the relative current in field coils, the magnetic moment per gram is given by the relation

$$\sigma_{H,T} = \Delta Mc / \frac{m}{g} \frac{dH}{dZ} . \quad (22)$$

The quantity $\sigma_{H,T}$ may then be plotted as either a function of the field, maintaining a constant temperature, or as a function of temperature, maintaining a constant field. As heretofore mentioned, both of these techniques will be used in the treatment of the data.

One correction for the field was necessary before plotting the final data. The magnetizing field H , that is effective in a given sample, differs from the applied field H_a by the amount of a demagnetizing factor that is directly proportional to the magnetization per unit volume. This correction is negligible until the experimental substance shows ferromagnetic behavior. The expression used for obtaining the true magnetizing field in these experiments may be written in the form

$$\begin{aligned} H &= H_a - NI \\ &= H_a - Nd \sigma_{H,T} . \end{aligned} \quad (23)$$

where I is the magnetization per unit volume, d is the density of the substance, and N is the demagnetization constant which is assumed to have a value of 0.0875 for samples having the same dimensional ratios as in this experiment. Information concerning N may be found in Beorth (7, p. 846).

VII. RESULTS

A. Holmium

Figure 1 shows the magnetic moment per gram of holmium as a function of the absolute temperature for three different fields. There are four features which are immediately observable from this figure:

Figure 1. Magnetic Moment of Holmium as a Function of Temperature for Constant Fields.

First, holmium exhibits an antiferromagnetic state similar to that of dysprosium but with a Néel point very near 132°K.

Second, there is a temperature hysteresis observable below about 100°K for each of the given fields, though the plot is shown only for the lowest curve. The data from the isotherms and the data from the decreasing and increasing isofields all concur to support the nature of the curve between 100°K and room temperature. Below 100°K the points from the isotherm curves agree well with the points taken from decreasing temperature isofields.

Third, the magnetic moments at the 20°K peaks attain values some 20% greater than the saturation moment for pure iron, and we have reason to believe that holmium, even at 20°K, does not exhibit true ferromagnetic behavior. Contrary to the response found in dysprosium and thulium, holmium does not show a sharp drop in the low-temperature region as the temperature decreases.

Fourth, there seems to be a very definite shift in the Néel point with the magnitude of the field.

Figure 2 gives the manner in which the magnetic moment varies as a function of the applied field at a number of different temperatures. When any isotherm run had been completed for a temperature in the region below the Néel point, the sample was always warmed to well above 150°K before the next isotherm was taken. This insured that the magnetic history had a minimum influence on the following isotherm curve.

In general form, these curves resemble closely those for dysprosium published by Elliott et al. (1, 4).

The remarkable feature of these curves is the manner in which the antiferromagnetic behavior of the magnetic moment resembles those of the paramagnetic region until at some particular, critical, high, temperature-dependent field the antiferromagnetic alignment is destroyed and ferromagnetic behavior appears. This type of behavior has only been apparent, to the author's knowledge, in the case of the rare earth metals.

Squire (13) has reported the existence of a hysteresis phenomenon in the region just slightly below the Néel point for MnSe. To detect the possible presence of hysteresis in the case of holmium, we have, for certain isotherms, recorded observations for both increasing and decreasing fields. Plots for decreasing fields, indicated by the dashed lines in Figure 2, have been shown for only a few chosen temperatures. Because

Figure 2. Magnetic Moment of Holmium as a Function of Field for Several Temperatures.

of the inaccuracy of the magnet's calibration with decreasing currents, we estimate errors in the decreasing field data of about two percent due to calibration alone. The experimental points for the decreasing field have not been included in either the appendix or the final graph.

At 4.2°K , the liquid helium bath temperature, we have included two increasing-field plots and one decreasing field plot. Run #1 was taken immediately after cooling the sample from room temperature to 4.2°K in a zero magnetic field; the dashed curve represents points taken on decreasing the field from its maximum value; and Run #2 represents again increasing-field data. The difference between the increasing-field curves represents the effect of magnetic remanence.

At 20.4°K , the liquid hydrogen bath temperature, we have shown three increasing-field curves and one decreasing-field curve. Run #1 and Run #2 and the decreasing-field curve have the same sequence as given above. The curve designated as Run #3 differs from the others in that these data were taken in the hydrogen bath immediately following the helium bath runs. It is clear that additional magnetic remanence is indicated under these conditions.

Figure 3 shows details of the low-magnetic-moment region of Figure 2. It is remarkable that the low-field antiferromagnetic magnetic moments vary in the manner of true paramagnetics, i.e., they are linear with field and pass through the origin.

Figure 4 shows the reciprocal of the magnetic susceptibility of holmium as a function of the temperature. The data above the Néel point obey explicitly the Curie-Weiss law, equation (11), with a Curie constant of 14.8. The extrapolation of the linear portion of the curve intersects the temperature axis to yield a paramagnetic Curie temperature of 87.0°K . The results indicate an effective Bohr magneton number for holmium of 10.9.

Figure 5 shows an attempt to fit the approach to saturation of the lowest temperature isotherms of holmium to equation (14). This attempt was made after it was found that the correspondence according to equation (15) proved unsatisfactory. Extrapolation to infinite fields has yielded intercepts which, when plotted as a function of $T^{3/2}$, indicate an absolute saturation moment of about 293. This value is to be compared with the value

Figure 3. Magnetic Moment of Holmium on Expanded Scale as a Function of Applied Field.

Figure 4. Reciprocal of Magnetic Susceptibility of Holmium as a Function of Temperature.

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Figure 5. Approach to Saturation of the Magnetic Moment of Holmium as a Function of H^{-2} .

of 338.7 derived for a free ion $5f_8$ in equation (18"). The data at 4.2°K fit a H^{-1} plot much better than a H^{-2} plot. A plot of the infinite-field intercepts of Figure 5, along with a value of 312 for the saturation moment at 4.2°K, yields a curve satisfying equation (16) quite well. This plot indicates an absolute saturation magnetic moment is 314.

B. Thulium

Figure 6 shows the variation of the magnetic moment of thulium as a function of the temperature for four different fields. In the case of thulium, as with holmium, there exists an antiferromagnetic region, and the indicated Néel point is in the neighborhood of 50°K.

An extensive plot of the compiled data has indicated that below about 30°K thulium also shows a temperature hysteresis, although it is considerably less pronounced than in the case of holmium where the temperature range of observations below the Néel point is much greater. Again there is evidence of a definite transition from the antiferromagnetic state to ferromagnetic behavior. By using points from the 20.4°K and the 4.2°K isotherms (Figure 7) the curves of Figure 6 have been shown extended on down to very low temperatures. No data could be taken between 20.4-4.2°K with the present apparatus to show the form of the lower anomaly peak.

Figure 7 shows the variation of the magnetic moment of thulium as a function of the magnetizing field for several isotherms. Down to 60°K there is true paramagnetic behavior; however, between 60-52°K the data are linear with field but intersect the magnetic moment axis between the origin and unity. Below 50.5°K the data are not linear with the field and the extrapolation of the low-field data shows that these curves do not intersect the origin.

In this figure, as in the similar one for holmium, there appears to be a critical field value, depending upon the temperature, at which the susceptibility attains a very marked field dependence. This again is attributed to the destruction of the antiferromagnetic state with a transition towards ferromagnetic behavior.

A plot of the points from the decreasing-field data shows that thulium has definite magnetic hysteresis at both 20.4°K and at 4.2°K. The increasing- and decreasing-field plots

Figure 6. Magnetic Moment of Thulium as a Function of Temperatures for Constant Fields.

Figure 7. Magnetic Moment of Thulium as a Function of Field for Several Temperatures.

join at about 17,000 oersteds. Although the decreasing-field data are not shown, they, as do the increasing-field data, show a curvature toward the magnetic field axis in the field region below 13,000 oersteds.

Figure 8 shows the reciprocal of the magnetic susceptibility of thulium plotted as a function of temperature. The data satisfies the Curie-Weiss law, equation (11), in the temperature region above the Néel point with an indicated Curie constant of 7.26 and an effective Bohr magneton number of 7.6. Extrapolation of the linear portion of the curve to the temperature axis indicates a paramagnetic Curie temperature of 20.0°K.

VIII. DISCUSSION OF RESULTS

A. Holmium

The magnetic data for holmium show that the pure metal exhibits a transition from the paramagnetic state (P) to the antiferromagnetic state (A) in the region of 132°K. Since this transition, P-A, is of the nature of a disorder-order transition, it should be accompanied by an entropy change and appear as a characteristic peak on the specific heat curve. It has been shown that there exist two such peaks in the specific heat curve for Ho, one at 19.4°K and one at 131.6°K (29).

Thus, there are indications that there are at least three possible magnetic states for the metal Ho, the A and P states mentioned above and the ferromagnetic state (F) existing below 19.4°K.

Our measurements show that the P-A transition temperature, i.e., the Néel temperature, is probably at $133 \pm 2^\circ\text{K}$. The magnetic curves indicate a very definite shift of the Néel point to lower temperatures as the field increases. This is in agreement with the present theory of the behavior of systems like that of Ho. Hendrickson (30) points out that the F-A transition temperature is increased with increasing fields, and that the A-P transition temperature is decreased with increasing fields.

A comparison of the magnetic properties of Ho with those of Dy (1, 4, 31) shows that the two metals differ principally

Figure 8. Reciprocal of Magnetic Susceptibility of Thulium as a Function of Temperature.

in their transition temperatures. Whereas the F-A transition temperature for Dy occurs at about 85°K in zero field, the F-A transition temperature for Ho probably occurs at about 19.4°K.

Hendrickson (30) has proposed a theoretical model which qualitatively interprets the magnetic behavior of Dy as determined by experiment. His approach has been to apply the molecular field approximation, following a method by Smart (32), to the hcp structure.

Hendrickson (30) accounts for the minimum (Figure 1 for Ho) just below the Néel point as due to short range ferromagnetic ordering.

That holmium, in particular, shows considerable temperature hysteresis in the region A below about 100°K, is quite evident in Figure 1. The presence of such a phenomenon is not at all surprising and may be interpreted as being due to magnetic history in the sample. That is, on the increasing isotherms the sample is influenced by a history of much smaller magnetic moments than on the decreasing isotherm; thus, the decreasing temperature curves fall below the increasing temperature curves.

In Figure 2, the presence of magnetic hysteresis in Ho is quite evident as the area between the solid and dashed lines for selected temperatures. Those are very odd hysteresis loops if compared to those of a ferromagnetic substance, but such an odd effect may be expected in a region such as state A. Certainly the differences between the corresponding lines cannot be due to experimental error.

There appears to be a gradual change in the characteristics of the hysteresis as the temperature decreases. Perhaps this can be interpreted as naturally accompanying a gradual shift from state A to state F.

The Curie temperature for metallic holmium was determined to be 87°K. This is precisely the value as determined by Néel (23) and measured by Trombe (27).

The spectroscopic state of the holmium ion is given by Vickery (33) to be a $5I_8$, and the paramagnetic theory of Hund and Van Vleck (34) indicates that the effective Bohr magneton number would be 10.6. The experimental determination here of 10.9 may be interpreted as probably due either to sample impurities or to exchange interactions in the atoms of the metal rather than as experimental error.

The theoretical value of the absolute saturation magnetic moment for the free Ho ion $5I_8$, according to equation (18"), is 338.7. We have attempted, partially in Figure 5, to determine the absolute saturation moment from the data taken. The data in the temperature region between 20°K and 25°K closely fit a H^{-2} plot, whereas at 4.2°K the data fit the H^{-1} plot best. The intercepts at infinite field from Figure 5, along with a value of 312 for the saturation moment at 4.2°K, were plotted against $T^{3/2}$ according to equation (16). The extrapolation to zero degrees Kelvin indicated an absolute saturation magnetic moment of 314. This is about 7% below the theoretical value.

Theory indicates that if the magnetic moment of Ho were due only to electron spins the effective Bohr magneton number would be 4.9. Such a value would yield a saturation magnetic moment per gram of 161 cgs. units. Since much larger values of the magnetic moment have been measured in this study, it is apparent, experimentally, that there are also orbital contributions to the magnetic moment of the Ho atoms.

Hendrickson (30) has shown possible theoretical basis for a shift in the F-A transition to higher temperatures with increased fields. The experimental evidence of this shift is apparent when the Ho isotherm plots begin their sudden rise with increasing fields in the temperature region below the Néel point.

The magnetic curves for Ho down to 20.4°K do not show the type of magnetic behavior one would expect for a true ferromagnetic substance below its Curie point. However, the F-A transition point has evidently been shifted to fields so low that we are able to attain an approach to saturation in fields available for these investigations.

At 4.2°K the element shows the behavior of a typically hard ferromagnetic substance. The data below 20.4°K, however, are not sufficient to determine the Curie point for Ho. One can, perhaps, rely on the knowledge of the specific heat anomaly at 19.4°K (29) to indicate a ferromagnetic Curie point.

B. Thulium

In the preceding section we have made reference to the similarity between the magnetic properties of Ho and Dy. In

one respect the magnetic behavior of Tm more closely resembles that of Dy than does Ho. In the Dy and Tm the data at 4.2°K fall below those at 20.4°K and this gives rise to an additional, peculiar hump at low temperatures. This behavior is not completely understood at the present time, but Elliott (1,4) gives four possible explanations for the behavior in Dy: (1) the existence of ferromagnetism with two sublattices accounting for the decreased saturation moment with decreasing temperatures, (2) the change in the population of split 4f electron states of different magnetic moments by temperature decrease, (3) variation of the Heisenberg exchange integral due to a temperature variation of the crystalgraphic axis, and (4) impurities, such as iron, affecting the magnetic properties of the rare earth metal.

This author will not attempt to submit a theoretical explanation for the very complicated magnetic behavior of these elements.

The Néel point for the pure metallic Tm may be quoted as 50.5 ± 1.0°K. There appears to be a very definite shift in the Néel point between 12,000 and 16,000 oersteds. Since these curves have been repeated several times and with the same results, we are sure that this temperature shift is real.

The negative curvature seen in the 4.2°K and 20.4°K isotherms of Figure 7, and which is also shown in the decreasing-field data, was verified to be correct by a check on the apparatus and by repetition of the data. This is probably a typical behavior of these elements in the antiferromagnetic state. The same curvature is noticed at 50.5°K also.

The paramagnetic data indicate a Curie point of 20°K that agree very well with the experimental values obtained from measurements on salts (21).

The spectrographical state of the thulium ion is given by Vickery (23) to be 3H_6 . The magnetic theory of Hund and Van Vleck (34) indicates an effective Bohr magneton number for such an ion to be 7.6. This is exactly the value determined by the paramagnetic data of this investigation.

Calculations from equation (18") for the free 3H_6 ion indicates a saturation magnetic moment for Tm of 230.8. The maximum moments measured were about 33, indicating that the thulium was far from magnetic saturation. From the given figures

it is apparent that thulium does not go ferromagnetic; however, the sudden rise of the magnetic moment near 16,000 oersteds at 20.4° K and 4.2° K show that perhaps ferromagnetism was beginning. What might happen in the temperature region between 20.4° K and 4.2° K is very difficult to say. Experimental observations somewhere in this region would be helpful in determine the magnetic state of thulium at very low temperatures.

Theory indicates that if the magnetic moment of Tm were due only to electron spins the effective Bohr magneton number would be 3.5. Such a number would yield a saturation magnetic moment per gram of 27 cgs. units. Since larger values of the magnetic moment have been measured in this study, it is apparent, experimentally, that there are also orbital contributions to the magnetic moment of the Tm atoms.

C. Discussion of Errors

The errors encountered in the measurement of the magnetic properties of Ho and Tm have been analyzed from the basic relation, equation (22). We shall here make a substitution of a parameter P for the gradient calibration, ($g^{-1} dH/dZ$). Equation (22) may then be written in the following manner:

$$\sigma_{H,T} = \Delta M_C / mP. \quad (24)$$

The magnetic moment may be expressed in terms of the experimental variables as

$$\sigma = \sigma(H, T, M_C, m, P). \quad (25)$$

In the treatment which follows we shall ignore the errors in m since its error is not greater than 0.05% and in P since its error is not greater than 0.1% with fields above about 3,000 oersteds.

Thus, equation (25) may be written as

$$\sigma = \sigma(H, T, \Delta M_C). \quad (26)$$

To insure that the centering device did not introduce systematic weight errors into this study, two calibration curves were made. The first determination of P was made using 99.99% pure iron; the second determination was made using 99.97% pure nickel. We chose Ni for this check because it possessed a saturation magnetic moment of about one-fourth that of iron. The resultant forces were thereby reduced; and any effect of the chains on the final weight could, if they existed, be detected by a difference in the calibration curves. Since the separate calibration curves agreed within the accuracy of the knowledge of the saturation moments of the standards, we assumed that the centering mechanism had negligible effect upon the results of this investigation. However, iron, of the two standards, was chosen for the calibrating element since the indication was that its saturation moment was better known. Repeated calibration checks during the experiment showed the existent error in the value of P to be not greater than 0.1%, indicating perhaps that small errors were present in the positioning of the sample.

The corrected mass change of the sample, ΔM_c , may be in error due to (a) gas flow fluctuations in the case of gas-stream cooling, (b) gradual shift in the "zero weight"¹ caused by thermal expansions in the suspension system following liquid transfer, and (c) spurious fluctuations in the case of liquid bath measurements, probably caused by the action of gas bubbles. These errors are small, to be sure, but they are not negligible, especially when the metal shows small weight changes. We estimate that the maximum error in the sample weight was about 4 mg. with an average of about 2 mg.

The fluctuation of the field, H , was determined indirectly by using the fluctuations in the relative current and the slope of the smooth field calibration curve. The field fluctuations, representing the control tolerance of the electronic equipment, were estimated to vary from ± 0.7 oersteds at 4,000 oersteds to a minimum of ± 0.4 oersteds at 13,000 oersteds and then back to ± 0.7 oersteds at 18,000 oersteds.

¹We shall define the weight taken with zero field to be the "zero weight".

In the gas-stream cryogenic system employed, it was virtually impossible to maintain a constant temperature during an "isotherm" run. However, the temperatures were not too unstable; they were maintained to within $\pm 0.7^\circ\text{K}$ at all isotherms. Indeed, most of the isotherms were maintained even more closely, within $\pm 0.3^\circ\text{K}$.

The standard deviation of the magnetic moment as expressed from equation (25) may be written

$$\text{S. D.} = \sqrt{\left(\frac{\partial \sigma}{\partial H}\right)^2 (dH)^2 + \left(\frac{\partial \sigma}{\partial T}\right)^2 (dT)^2 + \left(\frac{\partial \sigma}{\partial \Delta M_c}\right)^2 (d\Delta M_c)^2} \quad (27)$$

which we shall write, for simplicity, as

$$\text{S. D.} = \sqrt{U^2(dH)^2 + V^2(dT)^2 + W^2(d(\Delta M_c))^2} \quad (28)$$

In equation (27) and (28) dH , dT , and $d(\Delta M_c)$ represent, respectively, the incremental errors in the field, temperature, and corrected weight.

The variable U is the slope of an isotherm curve and becomes large only if the magnetic moment shows high field dependence; the variable V is the slope of an isofield curve and becomes large only if the magnetic moment shows high temperature dependence.

The third term on the right hand side of equation (28) sets the limit of accuracy of these experiments. By using equation (24) we may write this term, if we ignore the squared relation, as

$$W d(\Delta M_c) = \frac{d(\Delta M_c)}{mP} \quad \frac{0.004}{0.080P} = \frac{0.05}{P}, \quad (29)$$

where we have assumed that, in general, the mass of the sample is about 0.080 grams, and the error in ΔM_c is about 0.004 grams. The quantity P varies from 0.13 at 4,000 oersteds to 0.54 at 18,000 oersteds.

Thus, at 4,000 oersteds the limit in the accuracy of $\sigma_{H,T}$ is about 0.4 cgs. units. This error, of course, is increased if terms U and V are significant. It is obvious, then, that there must be high values of the moment exhibited if the percent error is to be small.

For holmium the percent error in the moment is about 4% at 4,000 oersteds and 0.5% at 18,000 oersteds, as calculated from equation (27) and the slopes U and V of the experimental curves. However, in the regions where the slopes of Figures (1) and (2) are large, the errors may increase to about 7%.

The percent errors of the magnetic moments for Tm are somewhat higher because the moments themselves are smaller. At 4,000 oersteds the error is about 9% and decreases to about 0.8% at 13,000 oersteds. However, the isotherms below the Neel point may show, at 17,000 oersteds, errors as large as 3% due to the terms U and V of equation (28).

Additional errors are encountered in the final plot of the data for the isotherms since the error in the field is estimated to be about 0.5%.

In general, the success of these measurements was very gratifying. It was a little surprising to discover that the experimental points formed such smooth curves. Rather large errors might easily have been expected (if judged from previous experiments) with such small samples as here used, when the forces were so small. However, there are improvements which could be incorporated.

D. Suggested Improvements

From the previous section it may be seen that the following improvements would be desirable:

- (a) more reliable weights
- (b) better temperature control at all temperatures
- (c) an extension of the possible temperatures to include the region between 20.4°K and 4.2°K
- (d) more accurate knowledge of the field H

- (e) extension of accurate field gradient calibration for fields well below 4,000 oersteds.

It appears that little can be done about the field fluctuations, dH of equation (28), since it is determined by the limitations of the electronic control unit, which is now adjusted for optimum performance.

For materials exhibiting large magnetic moments, such refinements are hardly necessary. However, samples exhibiting moments as low as T_m could be measured with an error of not more than perhaps 0.8% at 4,000 oersteds, rather than the estimated 9%, if suggestions (a) and (b) could be incorporated.

Certain steps have been taken toward incorporating suggestions (a), (b), and (c) in a single cryogenic device, and suggestions (d) and (e) with a direct measurement device. The details of the methods, which are only in the stage of development, will not be given here.

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X. APPENDICES

The following tables include the measured values of the magnetic moments of holmium and thulium as a function of the temperature holding the field constant (isofields) and as a function of the field holding the temperature constant (isotherms). The symbols given are those used throughout the text.

For the isofield data, we have given results of measurements with both increasing and decreasing temperatures; the data were taken in the order presented in the tables. The field values were not corrected according to equation (23).

The isotherm data are given with corrected fields according to equation (23) and with the corrected temperatures.

The magnet calibration curves, both of the field and of the field gradient, the temperature correspondence curves, and rod-correction curves together with the original calculations and rough graphs are all on file at the Low Temperature Laboratory, Institute for Atomic Research, Iowa State College, Ames, Iowa. Tracings for the final graphs are on file at the Technical Library, Institute for Atomic Research, Iowa State College, Ames, Iowa.

APPENDIX A. HOLMIUM

1. Isofield data for holmium.¹

H, T	T°K	H, T	T°K
H=8,980		H=12,150	
247.1	22.1	265.4	22.7
212.6	29.7	255.1	29.6
31.4	49.3	83.1	49.4
21.8	69.1	29.7	69.1
17.8	93.1	24.1	93.1
16.5	112.5	22.4	112.5
16.4	120.2	22.3	117.3
16.6	125.1	22.3	119.2
17.1	129.9	22.3	121.2
17.4	132.3	22.7	125.1
17.6	136.0	23.4	129.9
15.6	142.1	23.3	133.1
13.4	149.9	22.8	138.1
11.7	156.2	19.6	146.0
16.9	138.1	23.2	138.1
17.0	129.9	22.8	127.7
16.3	117.3	22.2	121.2
18.0	93.1	24.6	93.1
20.9	69.0	28.7	69.1
26.1	49.2	58.7	49.4

¹Temperature first increasing, then decreasing.

H, T TOK

H=16,030

275.6	22.1
272.8	25.7
269.6	29.7
245.0	39.7
198.1	49.6
116.9	59.3
57.7	69.1
38.5	78.7
33.2	93.2
31.4	102.8
30.5	112.8
30.4	117.3
30.6	121.2
30.8	123.1
31.1	125.1
31.6	127.0
32.5	129.9
33.3	132.3
33.0	134.4
31.5	137.3
29.0	142.1
25.1	149.9
31.7	137.3
33.3	132.3
31.6	127.0
30.8	123.1
30.3	117.3
30.4	112.8
31.4	102.8
32.7	93.2
36.9	81.6
45.8	69.1
107.2	59.3
194.1	49.6

2. Isotherm data for holmium.

H, T	H
T=20.4°K	
(Run #1)	
18.7	1,200
32.8	2,690
100.7	3,950
202.6	5,830
251.8	8,770
261.6	10,290
268.0	11,910
271.0	12,770
273.5	13,780
275.8	14,800
277.4	15,870
278.7	16,560
279.1	16,860
279.7	17,280
280.2	17,620

T=22.8°K	
10.1	713
13.5	1,300
16.8	3,350
66.3	4,480
218.8	7,480
253.2	10,430
264.7	12,920
271.7	14,860
273.9	15,960
275.4	16,620
276.0	16,930
277.8	17,430

H, T	H
T=20.4°K	
(Run #2)	
28.1	1,010
47.3	2,670
123.3	3,940
210.2	5,830
239.1	7,330
253.5	8,780
262.8	10,290
268.7	11,930
271.3	12,830
273.8	13,790
275.9	14,810
277.7	15,870
278.8	16,590
279.2	16,870
279.9	17,350
280.2	17,630

T=25.0°K	
230.0	8,440
245.8	10,080
254.5	11,490
259.7	12,520
263.5	13,420
266.4	14,170
268.6	14,840
270.6	15,510
272.1	15,120
273.2	16,620
274.1	17,100
274.5	17,520
274.6	17,790

H, T H
T=29.8

37.4	6,780
137.5	8,770
196.7	10,280
226.1	11,560
241.6	12,660
249.4	13,660
255.0	14,370
259.3	15,120
262.3	15,670
263.7	16,110
265.4	16,670
266.8	17,670

H, T H
T=34.2

4.15	1,300
12.1	3,210
14.9	4,180
21.3	6,150
35.9	7,730
233.1	12,960
250.7	14,740
258.0	15,910
261.4	16,630
261.8	16,930
262.9	17,360
263.9	17,810

T=39.2°K

5.5	1,300
11.1	3,210
14.3	4,250
20.2	6,120
25.4	7,700
31.4	9,160
55.7	10,610
122.5	12,170
165.5	13,030
197.2	13,960
219.0	14,890
233.5	15,960
239.1	16,620
242.2	17,090
244.1	17,370
245.6	17,713

T=44.2°K

5.1	1,190
9.9	3,240
13.0	4,190
19.1	6,320
23.1	7,610
27.5	9,040
33.4	10,630
65.6	12,210
103.1	13,070
140.0	14,000
177.4	14,940
203.2	15,990
215.2	16,740
218.1	16,980
224.1	17,500
226.4	17,780

H,T H
T=49.1°K

3.7	1,270
9.4	3,210
12.3	4,270
17.3	6,120
21.7	7,660
27.0	9,310
30.2	10,590
51.5	12,410
77.4	13,100
108.9	14,040
145.2	14,909
181.8	15,950
197.6	16,670
201.8	16,960
208.2	17,370
212.8	17,710

H,T H
T=54.2°K

4.1	1,190
8.9	3,200
11.2	4,150
16.7	6,200
20.6	7,660
24.3	9,140
28.3	10,600
32.2	11,850
33.9	12,250
41.9	13,080
65.3	14,220
102.9	14,990
135.3	15,990
158.2	16,690
167.2	16,990
177.8	17,400
185.3	17,710
189.3	17,890

T=59.1°K

2.8	1,230
8.3	3,090
11.0	4,200
15.7	6,210
19.4	7,660
23.1	9,150
26.9	10,580
31.2	12,180
34.6	13,100
40.9	14,060
64.5	15,080
94.8	16,020
115.7	16,720
125.2	17,000
137.6	17,430
149.2	17,770

T=69.0°K

2.8	1,260
7.9	3,190
9.7	4,160
14.5	6,210
17.6	7,670
21.2	9,130
25.1	10,800
28.1	12,190
30.9	13,100
33.5	14,080
36.8	15,060
42.5	16,060
51.6	16,860
56.2	17,070
74.4	17,630
78.2	17,820

H, T H
T=78.7°K

2.3	1,200
7.3	3,260
8.8	4,130
13.1	6,130
16.5	7,650
19.5	9,120
22.6	10,570
25.9	12,190
28.4	13,100
30.7	14,070
33.3	15,070
36.1	16,070
38.1	16,790
38.9	17,100
40.6	17,540
42.0	17,860
42.8	18,020

H, T H
T=88.3°K

2.7	1,310
6.8	3,230
12.7	6,180
15.9	7,750
18.5	9,160
22.0	10,810
24.8	12,220
26.9	13,240
28.9	14,070
30.7	15,070
33.4	16,080
34.9	16,790
35.4	17,110

T=97.9°K

3.4	1,290
6.7	3,240
12.1	6,200
15.4	7,830
17.8	9,200
20.9	10,730
23.6	12,210
25.5	13,090
27.3	14,080
29.7	15,070
31.5	16,080
33.3	16,800
34.9	17,110
35.4	17,840
35.8	18,000

T=107.6°K

2.1	1,210
6.0	3,220
8.0	4,260
11.6	6,110
14.7	7,500
17.3	9,180
20.4	10,760
22.9	12,210
24.8	13,100
26.8	14,060
29.0	15,080
31.0	16,070
32.5	16,790
33.1	17,100
33.8	17,510
34.7	17,850
35.1	18,000

H, T H
T=117.3°K

2.9	1,100
6.3	3,210
7.8	4,160
11.6	6,090
14.8	7,670
17.1	9,080
19.9	10,500
22.9	12,170
24.8	13,100
26.8	14,060
29.0	15,060
31.1	16,080
32.3	16,800
33.2	17,100
34.2	17,520
35.1	17,910

H, T H
T=126.9°K

3.2	1,250
6.8	3,230
8.5	4,260
5.9	6,170
15.0	7,680
17.8	9,180
20.9	10,750
23.6	12,220
25.2	13,110
27.0	14,070
29.2	15,050
31.2	16,080
32.6	16,800
33.0	17,090
33.8	17,510
34.6	17,850
34.8	18,020

T=129°K

1.9	1,190
6.0	3,140
8.1	4,120
12.6	6,210
15.8	7,660
18.7	9,050
20.6	11,320
25.1	12,230
27.0	13,100
29.0	14,080
31.1	15,060
33.4	16,120
35.0	16,780
35.7	17,090
36.4	17,500
36.9	17,830
37.4	18,020

T=136.8°K

4.7	1,240
6.4	3,210
7.9	4,120
11.3	6,110
14.3	7,680
16.6	9,130
19.2	10,590
21.9	12,240
23.4	13,110
25.2	14,070
26.9	15,050
28.9	16,090
30.1	16,800
30.7	17,230
31.6	17,530
32.3	17,840
32.2	18,030

H,T H
T=146.5°K

1.8	1,100
4.8	3,110
6.3	4,170
9.3	6,120
11.5	7,660
13.7	9,050
15.8	10,560
18.1	12,200
19.6	13,080
20.8	14,050
22.6	15,050
24.3	16,110
25.1	16,840
25.6	17,100
26.3	17,560
26.7	17,860
27.0	17,960

H,T H
T=165.8°K

1.6	1,250
3.9	3,210
4.9	4,220
7.1	6,150
8.0	7,900
10.4	9,110
11.9	10,710
13.7	12,220
14.8	13,110
15.9	14,070
17.1	15,050
18.2	16,080
19.0	16,800
19.4	17,110
19.9	17,520
20.3	17,860

T=185°K

1.7	1,230
3.0	3,180
4.1	4,260
5.8	6,170
7.2	7,700
8.4	9,090
9.7	10,600
11.1	12,210
12.0	13,110
12.9	14,060
13.8	15,060
14.8	16,110
15.2	16,800
15.7	17,100
16.2	17,530
16.5	17,890

T=299.0°K

1.3	3,190
1.8	4,240
2.8	6,450
3.7	8,550
5.1	11,270
5.6	13,140
6.3	14,580
6.9	15,950
7.2	16,700
7.6	17,680
7.8	18,040

APPENDIX B. THULIUM

1. Isofield data for thulium.

H,T H=9,000	T°K	H,T H=12,140	T°K
9.7	24.0	12.5	27.1
9.2	27.5	12.3	28.1
9.0	29.6	12.0	29.9
8.7	32.0	11.7	32.3
8.8	34.4	11.9	34.7
9.8	39.4	12.3	37.2
11.4	44.4	13.0	39.7
12.4	46.9	15.1	44.6
13.4	48.3	16.7	47.1
14.0	49.4	17.8	48.5
14.3	50.6	18.7	49.5
14.3	50.1	17.0	54.5
13.5	51.8	15.3	56.8
12.2	54.4	13.9	59.3
11.0	56.8	12.1	64.2
10.1	59.2	10.6	69.1
7.8	69.1	14.1	59.3
6.2	78.7	15.3	56.8
6.1	81.2	17.0	54.5
10.4	59.2	18.8	52.0
12.3	54.4	18.6	49.5
13.9	51.8	17.8	48.5
14.4	50.6	16.6	47.1
14.2	49.8	14.0	42.1
13.2	48.3	12.5	37.2
		12.1	34.7

H, T T°K
H=16,040

15.6	64.2
18.0	59.3
21.6	54.5
24.0	52.0
26.0	49.5
25.4	47.1
21.7	44.6
19.0	41.7
17.4	39.1
16.3	35.8
15.6	32.6
15.8	30.0
16.8	26.3
17.9	24.6
16.9	28.1
15.9	29.9
15.8	32.3
15.9	34.7
16.8	37.2
18.0	39.7
19.5	42.1
22.7	44.6
25.6	47.1
25.8	49.5
23.6	52.0
21.3	54.5
19.2	57.0
17.7	59.3
15.4	64.2
13.8	69.0
11.3	78.6
9.0	93.1
7.1	112.5
6.2	121.2
5.8	129.9
5.3	138.1
4.6	153.4
4.0	174.2

2. Isotherm data for thulium.

H, T	H
T=20.4°K	
(Run #1)	
1.9	1,010
4.2	2,690
5.8	4,010
8.2	5,950
10.1	7,470
12.8	10,190
13.0	10,480
14.7	12,080
15.2	12,990
16.2	13,950
17.4	14,970
20.4	16,030
23.9	16,760
26.0	17,070
28.5	17,440
31.2	17,780

H, T	H
T=20.4°K	
(Run #2)	
6.9	2,700
10.2	5,970
12.5	8,940
14.9	12,080
16.6	13,960
21.0	16,050
26.1	17,040
28.9	17,480
31.4	17,820

T=28.2°K	
2.3	1,330
3.4	2,980
4.5	4,240
6.4	6,290
7.7	7,750
9.0	9,160
10.4	10,630
11.8	12,210
12.7	13,110
13.7	14,080
14.9	15,070
16.6	16,080
18.6	16,790
19.6	17,070
21.5	17,510
23.2	17,810

T=31.8°K	
3.7	4,020
6.8	7,480
9.8	10,460
12.2	12,990
13.2	13,950
14.5	14,970
15.8	16,040
16.9	16,770
17.5	17,070
18.7	17,530
19.6	17,820
19.9	17,860

H,T
T=39.2°K

1.5	1,330
4.3	4,240
8.3	7,750
11.4	10,670
14.3	13,130
15.4	14,090
16.7	15,080
18.1	16,080
19.1	16,800
19.6	17,070
20.4	17,510
21.1	17,830

H,T
T=50.5°K

6.6	4,020
12.1	7,490
16.7	10,510
20.4	13,000
21.7	13,960
23.2	14,980
24.8	16,040
25.7	16,770
26.8	17,530
27.1	17,790

T=59.1°K

4.3	4,030
8.7	7,500
11.7	10,470
14.4	13,010
16.7	15,030
17.8	16,060
18.7	16,780
18.9	17,090
19.4	17,500
20.1	18,020

T=299.5°K

0.6	4,310
1.8	8,630
1.9	12,130
2.2	14,110
2.5	16,110
2.6	17,110
2.8	17,880

H,T H
T=30.0°K

5.0	4,890
9.6	9,000
11.4	12,120
15.7	16,030

H,T H
T=34.0°K

4.9	4,890
8.4	9,010
11.7	12,120
15.9	16,040

T=38.0°K

5.6	4,890
9.6	9,010
12.7	12,120
17.3	16,040

T=42.0°K

5.7	4,890
10.5	9,010
14.0	12,130
19.4	16,040

T=46.0°K

7.2	5,330
12.4	9,020
17.0	12,130
26.0	16,040

T=48.0°K

6.8	4,890
13.0	9,020
18.5	12,130
26.3	16,070

T=50.0°K

14.3	9,020
19.1	12,130
25.5	16,040

T=52.0°K

7.6	4,890
13.6	9,020
18.0	12,130
23.8	16,050

T=54.0°K

6.9	4,850
12.5	9,010
16.2	12,120
20.7	16,040

T=56.0°K

6.5	4,890
11.8	9,010
15.4	12,120
20.5	16,040

H,T H
T=60.0°K

5.7	4,890
10.2	9,010
13.3	12,120
17.8	16,040

T=85.0°K

3.9	4,890
5.9	9,010
7.8	12,120
10.6	16,040

T=140°K

1.9	4,890
3.3	9,000
4.3	12,120
5.7	16,020

T=260°K

0.9	4,890
1.6	9,000
2.2	12,120
3.0	16,020

H,T H
T=70.0°K

4.3	4,890
8.0	9,010
10.5	12,120
13.9	16,040

T=100°K

2.8	4,890
4.8	9,010
6.3	12,120
8.5	16,040

T=200°K

1.2	4,890
2.2	9,000
2.9	12,090
3.8	16,020

T=294°K

0.8	4,870
1.5	8,980
1.9	12,090
2.6	17,970

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