for the trapped state. For the present, therefore, we do not have a reasonable way to determine the constant α. We tentatively take $1/\alpha=7$ a.u. and the thermal ionization energy $\hbar\omega_i=0.85$ ev.[15] μ appearing in the expression of Δ is determined as follows. If one neglects long range forces, the relation between the compressibility β and the energy change produced by a volume change gives[16]

$$\mu/a=3\beta=C_{11}+2C_{12},$$

where a is the nearest neighbor distance and C_{11} and C_{12} the elastic constants, the observed values of which are 1.674×10^{12} dyne/cm^2 and 0.6523×10^{12} dyne/cm^2 respectively.

Using these numerical values, we got $\sigma^{(\mathrm{I})}\approx10^{-23}$ cm^2 and $\sigma^{(\mathrm{II})}\approx10^{-20}$ cm^2 at 300°K. This result shows that the distortion of the lattice vibration due to a lattice vacancy can enlarge the cross section by three orders of magnitude. Although the influence of the distortion of lattice vibration for the capture cross section is rather strong, it is not enough to explain the magnitudes of observed cross sections, which are of order 10^{-15} cm^2 to 10^{-17} cm^2. It thus appears that it may be possible to explain observed capture cross sections only by attributing to the deep traps a more complex structure than an isolated vacancy.

ACKNOWLEDGMENT

The present author wishes to express his cordial thanks to the late Professor K. Lark-Horovitz and Professor H. M. James for their hospitality at the Department of Physics, Purdue University. Thanks are also due to Professor James for many stimulating discussions and to Dr. B. V. Paranjape for his reading of the original manuscript. He also gratefully acknowledges the assistance of the Fulbright Commission during 1958–1959.

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[15] This value is equal to the energy gap between the bottom of the conduction band and the trap level located at 0.27 ev above the valence band.

[16] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

PHYSICAL REVIEW VOLUME 117, NUMBER 1 JANUARY 1, 1960

Low-Temperature Magnetic Remanence, Molecular Field, and Approach to Saturation of Holmium Metal

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(Received July 31, 1959)

Magnetization approaching absolute magnetic saturation has been achieved for polycrystalline holmium metal. At 1.3°K and 70 000 gauss, the magnetic moment is approaching 4.0 Bohr magnetons per atom of holmium in contrast to the 10 Bohr magnetons per atom expected on the basis of the spectroscopically determined quantum numbers. The actual results are explained on the basis of crystalline electric field splitting of the ground term of holmium and application of the Pauli exclusion principle. In the liquid helium range, there is a pronounced hysteresis; i.e., the moment at 10 000 gauss is 50% higher in decreasing fields than in increasing fields. The remanence is 0.22 Bohr magneton per atom of holmium at 4.2°K and 0.42 Bohr magneton per atom at 1.3°K. A sample motion technique was used to measure the magnetic moment of the 5-gram sample. The equipment was calibrated with iron and nickel.

INTRODUCTION

PREVIOUS magnetic studies on holmium metal have been carried out by Bommer[1] and by Rhodes, Legvold, and Spedding.[2] Bommer found that if he used the Curie-Weiss law

$$\chi=C/(T-\Delta),\tag{1}$$

with two adjustable parameters, C and Δ, he could fit his susceptibility data for 5 points (195°K, 294°K, 364°K, 428°K, and 515°K), but his 90°K point did not fit. Néel[3] had been able to calculate the predicted Curie temperatures of the rare-earth elements from the formula

$$\theta=16WS^2(J+1)/kJ,\tag{2}$$

where W is an interaction energy term, characteristic of rare earths, S the spin, J the total magnetic quantum number, and k the Boltzmann constant. This predicted value of θ is 86°K for holmium. Bommer found that if he took the Néel value for θ [Δ in Eq. (1)], he could fit his 5 points with a Curie constant, $C=14.3$. When Bommer used the formula

$$\mu=A[\chi(T-\Delta)]^{\frac{1}{2}},\tag{3}$$

where A is $(3k)^{\frac{1}{2}}$, he calculated a moment of 10.6 Bohr magnetons. Rhodes, Legvold, and Spedding, applying Eq. (3) to low field susceptibility data in the high-temperature range, got μ_{eff} of 10.9 Bohr magnetons

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[1] H. Bommer, Z. anorg. u. allgem. Chem. **242**, 277 (1939).

[2] Rhodes, Legvold, and Spedding, Phys. Rev. **109**, 1547 (1958).

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

per atom for a sample 1 mm×1 mm×1 cm using the technique of Elliott, Legvold, and Spedding.[4] It must be pointed out that by using Eq. (3) there is danger in estimating the saturation magnetization, especially if there are exchange interaction and crystalline electric field effects. The true magnetic atomic constants should be determined by the direct measurement of the saturation magnetization, if possible. Rhodes, Legvold, and Spedding[2] have measured the magnetization of a wire of holmium 1 mm×1 mm×1 cm in fields up to 16 000 gauss at 4.2°K. Their graphs indicate that although saturation was not reached, they obtained a very high magnetization—8.6 Bohr magnetons per atom if the recorded results are the direct measurements and 6.7 Bohr magnetons per atom if the $4/\pi$ factor is used as by Behrendt *et al.*[5] for dysprosium. In the formation of the holmium wire, it is possible to have a preferential crystalline orientation, such that the easy direction of magnetization in an anisotropic crystal is measured.

The experimentally determined magnetic atomic constants are related to the positions (order) and relative spacing of the lower energy levels,[6] which can be checked by means of application of the quantum theory to spectra, including hyperfine spectra data. Although some work has been done on the spectra of holmium metal,[7] very little has been done on the exact splitting of the ground term of holmium. Recently, Belianin[8] has calculated the energy spacing of the four lowest energy levels from the accurate hyperfine structure spectral lines of solid metallic holmium.[9] From these large spacings, it is not to be expected that the full 10 Bohr magnetons which would characterize a fully degenerate ground term, $^5I_8$, nor the 9 Bohr magnetons for a fully degenerate $^4I_{15/2}$ ground term, for holmium, would be observed.

In this investigation, magnetization as near as possible to absolute magnetic saturation was measured and an attempt is made here to explain the measured saturation magnetization on the basis of the crystalline electric field splitting of the ground state of holmium metal.

EXPERIMENTAL METHOD

The average magnetization of holium metal has been measured by moving a 5-gram sample with respect to a coil system previously described.[10] A balistic galvanometer, in series with the oppositely wound coils, yields a deflection which is proportional to the magnetization of the sample. The constant of proportionality for the moment measuring system is determined with iron and nickel.

The fixed magnetic fields, up to 70 000 gauss, are produced by a modified Bitter[11] type solenoid. The low temperatures are maintained in a metal Dewar[12] for liquid helium. The holmium metal was obtained from City Chemical Company, the stated purity being better than 99.8%. A spectroscopic analysis by Mr. S. H. Kress of the Metallurgy Division of the Naval Research Laboratory, showed a favorable comparison with a 99.9% sample from Spex. The method of casting the holmium metal made a compact, polycrystalline (randomly oriented) sample highly probable.

DISCUSSION OF RESULTS

Figure 1 shows a plot of average magnetization against magnetic field for holmium metal. It is seen that an average magnetization of 4.0 Bohr magnetons per atom of holmium is being approached at the low temperatures and high magnetic fields. It has been established by spectral analysis that metallic holmium has a $^4I_{15/2}$ ground state, although high-temperature susceptibility data and Eq. (3) suggest a $^5I_8$ ground state, the same as for the tripositive holmium ion[2], with the implied values: $J=8$ and $g=1.25$. This leads to an expected saturation magnetization, gJ, of 10 Bohr magnetons per atom of holmium for an aggregate of simple atomic dipoles. The average magnetization on this assumption should be

$$\bar{\mu}=\frac{g\mu_B}{2}\left[(2J+1)\coth\frac{(2J+1)g\mu_B H}{2kT}-\coth\frac{g\mu_B H}{2kT}\right], \quad (4)$$

where g is the Landé splitting factor, J the total magnetic quantum number, H the effective magnetic field, T the absolute temperature, μ_B the Bohr magneton

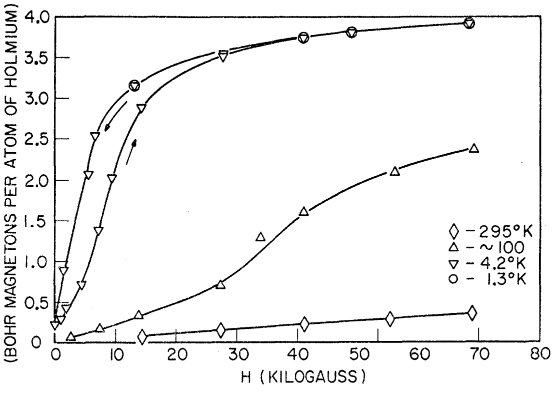

FIG. 1. Plot of average magnetization ($\bar{\mu}$) against magnetic field (H) for 295°K, 100°K, 4.2°K, and 1.3°K.

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

[5] Behrendt, Legvold, and Spedding, Phys. Rev. **109**, 1544 (1958).

[6] J. H. Van Vleck, J. Chem. Phys. **3**, 807 (1935); and private communication.

[7] M. H. L. Pryce (private communication).

[8] V. B. Belianin, Optika i Spectroskopiya **5**, 236 (1958); See also references in Belianin's article including P. F. A. Klinkenberg, Physica **13**, 1 (1947).

[9] V. B. Belianin, Optika i Spectroskopiya **3**, 322 (1957).

[10] W. E. Henry, Phys. Rev. **88**, 559 (1952); U. S. Bureau of Standards Circular No. 519 (U. S. Government Printing Office, Washington, D. C., 1952), p. 237.

[11] F. M. Bitter, Rev. Sci. Instr. **10**, 373 (1939).

[12] W. E. Henry and R. L. Dolecek, Rev. Sci. Instr. **21**, 496 (1950); W. E. Henry, J. Appl. Phys. **22**, 489 (1951).

and k the Boltzmann constant. The effective field, H, is compounded from the applied field and the projection of the molecular field on the Z axis. If this were a simple case, the Néel[3] formula for the molecular field of the rare earth could be applied and the magnetization could be calculated as a function of the temperature and the applied field.

The simplicity vanishes with the combined effect of spin-orbit coupling and the crystalline electric field splitting of the ground state. This splitting forces the application of the Pauli exclusion principle. That is, it has been shown[8] by solid-state spectroscopic studies that the lowest 4 levels in the split holmium ground state are: $J_{15/2}=0$ cm^{-1}; $J_{13/2}=4664$ cm^{-1}; $J_{11/2}=8758$ cm^{-1}; and $J_{9/2}=12\,541$ cm^{-1}. Use of the interval rule of the quantum theory predicts that the next two energy level spacings should be of the order of 2800 cm^{-1} and 2200 cm^{-1}, respectively. Thus, even if we use 11 electrons instead of 3 holes, the pertinent energy level separations are all large compared with kT, even at room temperatures. It follows that the Boltzmann factors for occupation ratios will tend to exclude high-level occupation, except through limitation of low-level occupation by the Pauli principle. Now, if a series of $(n+1)$ low-lying levels are separated energy-wise by ΔE_1, ΔE_2, $\cdots$ $\Delta E_{(n-1)}$, ΔE_n, and if each level retains only a Kramers-type magnetic twofold degeneracy and if the ΔE's are large compared with kT, then as long as the number of electrons is less than $2n$, an odd number of electrons at magnetic saturation will yield only one Bohr magneton per atom. This has been experimentally illustrated by a comparison of the saturation magnetization of iron ammonium alum[10] with that of potassium ferricyanide,[13] in which the saturation magnetization is one Bohr magneton per atom of iron instead of 5 Bohr magnetons per atom of iron as in iron ammonium alum.

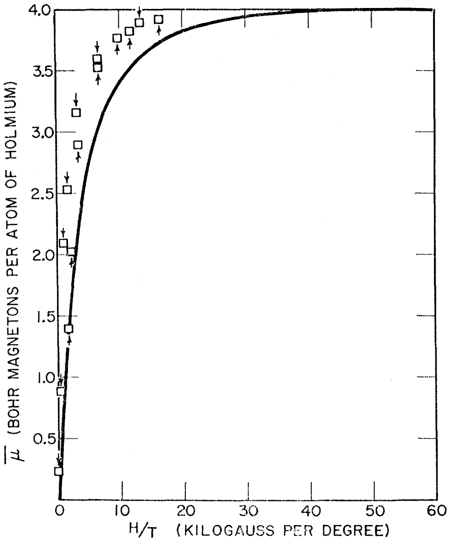

FIG. 2. Plot of average magnetization against H/T. The heavy curve is for magnetization as calculated from Eq. (6). The experimental points are for 4.2°K.

Magnetic anisotropy has been demonstrated for the rare earth element, dysprosium.[5] Hexagonal close-packed structures[14] can induce structure dependent ferromagnetic anisotropy and are usually characterized by three cyrstalline axes, two of which are equivalent. Holmium is hexagonal close-packed. If it is assumed that in some "easy" direction of magnetization in space, such as along the hexagonal axis, the crystalline electric field splits the ground state such that the ΔE's are small, the magnetization would proceed in accordance with a Brillouin function [Eq. (4)] in which $J=8$ and $g=1.25$. On the other hand, if it is assumed that in directions perpendicular to the above axis, the splitting takes place as shown from spectral analysis, as carried out by Belianin,[8] then it follows that $J'=\frac{1}{2}$ and $g'=2$. The average magnetization for a polycrystalline sample is

$$\bar{\mu}=\tfrac{1}{3}(\mu_{11}+2\mu_{\perp}), \tag{5}$$

or

$$\bar{\mu}=\frac{1}{3}\left\{0.625\mu_B\left[17\coth\left(\frac{17\times0.625\mu_B H}{kT}\right)-\coth\left(\frac{0.625\mu_B H}{kT}\right)\right]+2\tanh\frac{\mu_B H}{kT}\right\}, \tag{6}$$

which, for high values of H/T, approaches 4.0 Bohr magnetons per atom, as shown in the heavy curve of Fig. 2. It is seen from Fig. 1 that there is agreement between the measured magnetization which approaches saturation and the calculated saturation magnetization. In Fig. 2, some experimental points for $T=4.2$°K are given for $\bar{\mu}$ *versus* H/T where H is taken as the applied field. It is seen that the points occur above the theoretical curve, suggesting an internal field characteristic of positive exchange or ferromagnetic interaction.

Using the agreement between the calculated and measured saturation magnetization as an indication of the plausibility of the proposed picture, we now attempt to calculate an apparent molecular field from the high-temperature magnetization of holmium. Figure 3 is an expanded plot of magnetization against H/T. The heavy curve represents Eq. (6). The experimental points (squares) are for 295°K. These experimental points are above the theoretical curve and suggest ferromagnetic interaction. The apparent molecular field is obtained by means of a technique previously used.[15] A constant, γ, is determined in the equation,

$$H_{\text{eff}}=H_0+\gamma M, \tag{7}$$

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[13] W. E. Henry, Phys. Rev. **106**, 465 (1957).

[14] K. D. Bowers and J. Owens, *Reports of Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304; J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937); F. Bloch and G. Gentile, Z. Physik **70**, 395 (1931).

[15] W. E. Henry, Phys. Rev. **94**, 1146 (1954).

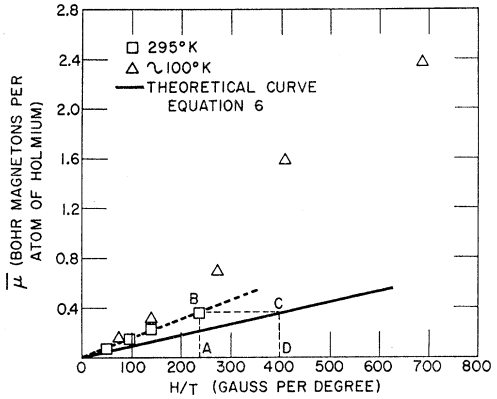

FIG. 3. Plot of average magnetization against H/T in expanded scale for small values of H/T. The heavy curve is calculated from Eq. (6). The squares are for 295°K and the triangles are for 100°K.

in which H_0 is the applied field and M the magnetization. In Fig. 3, an experimental point B (as an example) is chosen, corresponding to an actual applied field, $T(H/T)$, at point A. From point B, a constant moment line is followed to point C where the effective field is read off from point D. This is repeated for other points like B. Then from the value of γ thus determined, and the saturation magnetization, M_0, the apparent molecular field is determined from

$$H_m=\gamma M_0; \tag{8}$$

for holmium this amounts to about 550 000 gauss. Now, if we say that the magnetic energy is approximately equal to the thermal energy at the ferromagnetic Curie temperature; i.e.,

$$\mu H_m=kT_C, \tag{9}$$

then $T_C=37$°K. This value is closer to the experimental ferromagnetic Curie temperature of 20°K indicated from a specific heat maximum[16] than the 86°K predicted by the Néel formula and implied by the use of Eq. (1), with high temperature susceptibillty measurements.[1,2]

A substantial remanence (magnetization measured at $H=0$) in the liquid helium range is consistent with a ferromagnetic exchange interaction, with crystalline electric field anisotropy and with spin-orbit interaction. At 4.2°K the remanence is 0.22 Bohr magneton per atom of holmium and at 1.3°K it is 0.42 Bohr magneton per atom. This amounts, respectively, to 5% and 10% of the saturation magnetization. There is a pronounced hysteresis in the helium range. For example, at 4.2°K, the magnetization in decreasing field (shown by arrows pointing down in the figures) is 50% higher than in increasing fields at 10 000 gauss, and 100% higher at 5000 gauss.

SUMMARY

The magnetization experiments on holmium metal have shown an asymptotic approach to absolute saturation. The measured magnetization of a polycrystalline sample is 3.95 Bohr magnetons per atom of holmium at 1.3°K and 70 000 gauss. The absolute saturation magnetization experimentally approached seems to be 4.0 Bohr magnetons per atom of holmium instead of 10 Bohr magnetons per atom on the basis of a $^5I_8$ ground state or instead of 9 Bohr magnetons per atom on the basis of a $^4I_{15/2}$ ground state. This experimental value can be explained on the basis of the directional dependence of the gJ product suggested in this paper. That is, if gJ is 10 Bohr magnetons per atom in a direction parallel to an axis of "easy" magnetization and one Bohr magneton per atom in a plane perpendicular to the direction of "easy" magnetization, the limiting magnetization expected is 4.0 Bohr magnetons per atom of holmium. On the other hand, the value would be 3.7 Bohr magnetons per atom if the value of 9 is taken for the axis of easy magnetization, in which case a 5% preferential orientation would lead to the experimental results of this investigation.

The remanence goes from a barely perceptible value at 100°K to 10% of the saturation magnetization at 1.3°K. From the high-temperature magnetization measurements and an anisotropic Brillouin function, an apparent molecular field is calculated which leads to an estimated ferromagnetic Curie temperature of 37°K (the experimental Curie point, based on specific heats, is 20°K). The apparent molecular field of 550 000 gauss can also be calculated on the basis of a modified Néel ferromagnetic interaction energy, provided we put in linearly the anisotropy conditions which respect to the Pauli restriction. This restriction, which leads to an explanation of a saturation magnetization of 4.0 Bohr magnetons per atom of holmium, results from the energy level spacing induced by the combined effect of the spin-orbit coupling and the crystalline electric field which lifts the orbital degeneracy of the ground state of holmium. While there may be other ways of explaining the experimental results of this investigation of the saturation magnetization of holmium, the explanation here given is simple and fits the facts.

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[16] Gerstein, Griffel, Jennings, Miller, Skochdopole, and Spedding, J. Chem. Phys. 27, 394 (1957).