Magnetic Properties of Thulium Metal

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(Received January 21, 1960)

Measurements made from 1.3 to 300°K, in fields up to 12 000 oe, show that thulium becomes antiferromagnetic on cooling to 60°K and is ferromagnetic below 22°K. In agreement with earlier work the susceptibility between 70 and 300°K obeys the Curie-Weiss law and the effective Bohr magneton number is 7.6, equal to the theoretical value for the trivalent ion core having two holes in the $4f$ shell. The highest observed ferromagnetic moment is only 0.5 Bohr magneton whereas the theoretical value is $gJ=7$. Large hysteresis and crystal anisotropy are observed at the lowest temperatures. It is suggested that the anisotropy is so large that the magnetization cannot be deviated appreciably from the hexagonal axis even in the higher fields (70 000 oe) used by Henry; he observed 3.4 Bohr magnetons whereas the highest expected for polycrystalline material on this assumption is 3.5.

INTRODUCTION

KLEMM and Bommer[1] found thulium to obey the Curie-Weiss law from 90 to 300°K with $\mu_{\text{eff}}=7.6$ Bohr magnetons per atom, the theoretical value for $Tm^{3+}(J=6,\ g=7/6)$. This was confirmed by Rhodes, Legvold, and Spedding,[2] whose measurements to lower temperatures indicated also an antiferromagnetic transition at 51°K and an additional transition at some temperature between 20 and 4°K, where ferromagnetic behavior was indicated. The present work was undertaken especially to clarify the behavior between 4 and 20°K.

MATERIALS AND PROCEDURE

The material used in these experiments was described by the supplier, Research Chemicals Incorporated, as containing 0.3% Ta, 0.2% O, 0.1% Ca, and 0.1% Mg, and to be spectroscopically free from other rare earths.

Measurements were made with the pendulum magnetometer previously described.[3] For measurement of temperature a copper-constantan couple was used above 80°K, a carbon resistor from 4 to 80°K, and vapor pressure from 1.3 to 4.2° when the specimen was immersed in liquid helium. The carbon resistor was calibrated at the boiling points of He, H_2, and N_2, and the triple points of H_2 and N_2.

The magnetic field was produced with a Varian 12-in. magnet. Hysteresis loops were measured after careful calibration of the magnet with a Hall-effect gaussmeter, taking account of the hysteresis and nonlinearity of the magnet in low and high fields. The sensitivity of the method reduces to zero in zero field, but measurements could be made with sufficient accuracy in fields of 50 to 100 oersteds. The sensitivity in fields of 12 000 oe was about 0.004 cgs unit.

In view of the hysteresis of the specimen at low temperatures, measurements of moment were made at a given field strength when the previously applied field had been alternatively +12 000 or −12 000 oe.

RESULTS

Figure 1 shows the reciprocal susceptibility per gram measured in fields of 8000 oe. The straight line is drawn with the slope corresponding to the theoretical value of $\mu_{\text{eff}}=7.56$ for a $4f^{12}$ core ($J=6$, $g=7/6$). The intercept at $T=20$ agrees with previous measurements[2] and corresponds to the Curie-Weiss expression for susceptibility per gram atom: $\chi_A=C_A/(T\text{-}20)$, the theoretical value of C_A being 7.14.

A maximum in the susceptibility vs temperature curve occurs at 60°K (see Fig. 2), whereas Rhodes *et al.*[2] observed it at 51° in their specimen. (It should be noted that 60° is near the triple point of N_2, 63.2°K, at which the resistor was calibrated.) There seems to be little doubt that this is the Néel temperature of antiferromagnetic ordering, since a similar point in erbium has been investigated by Koehler and Wollan[4] with neutron diffraction, and superlattice reflections have been found below the critical temperature.

Below 20°K the existence of ferromagnetism has

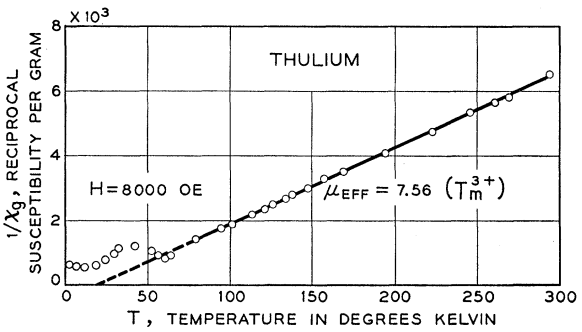

FIG. 1. Reciprocal susceptibility per gram vs temperature. Straight line has theoretical slope for Tm^{3+} ion core.

[1] W. Klemm and H. Bommer, Z. anorg. u. allgem. Chem. **231**, 138 (1937).
[2] B. L. Rhodes, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1547 (1958).
[3] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).
[4] W. Koehler and E. O. Wollan, Phys. Rev. **97**, 1177 (1955).

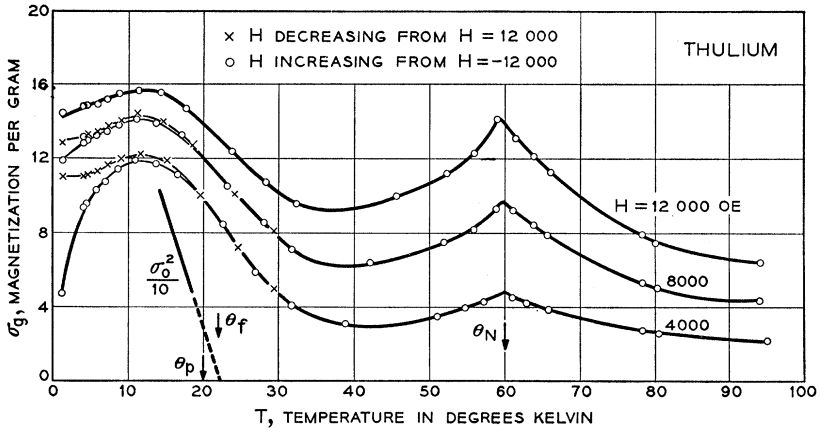

FIG. 2. Magnetization vs temperature for field strengths of 4, 8, and 12 kilo-oersteds. At low temperatures crosses indicate σ_g when previous value of H was +12 koe, circles when it was −12 koe.

been confirmed by the existence of hysteresis, which is readily detected by measuring the moment σ_g at a given field strength when this has been approached from +12 000 or −12 000 oersteds, as shown in Fig. 2. We have used the standard Weiss-Forrer method of determining the ferromagnetic Curie point, θ_f; this consists in extrapolating H vs T at constant σ_g to $H=0$ to obtain σ_0, and plotting σ_0^2 vs T to give $T=\theta_f$ at $\sigma_0=0$. The Curie point so determined was 22°K, as shown in Fig. 2. This is close to the paramagnetic Curie point, $\theta_p=20°$, and is just that predicted by Néel[5] using a molecular field model in which the exchange interaction is proportional to the spin moment (see Appendix).

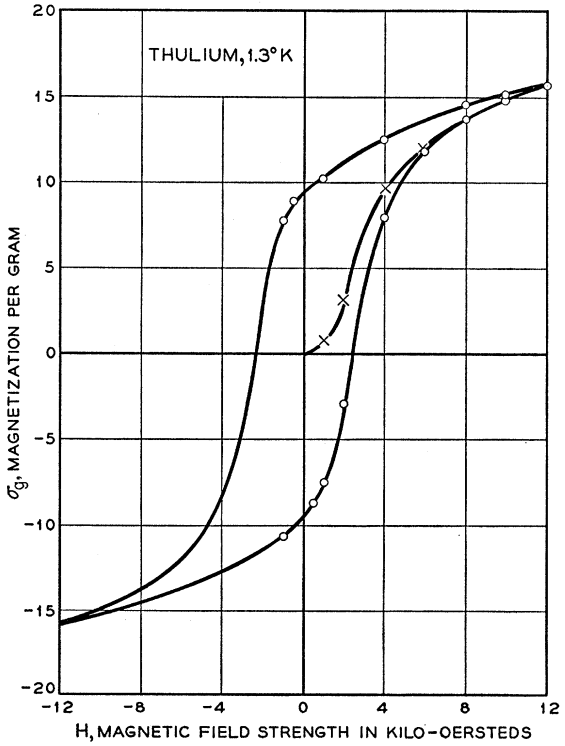

FIG. 3. Hysteresis loop of thulium.

A hysteresis loop for a second specimen of the same material is shown in Fig. 3. Evidence for the existence of ferromagnetism at low temperatures has also been reported by Joos.[6]

Our highest observed moment corresponds to about 0.5 Bohr magneton per atom. Using the much higher field of 70 000 oe, Henry[7] has observed 3.4 Bohr magnetons, whereas the saturation for the $4f^{12}$ state is $Jg=7$. Such a discrepancy may readily be explained if we assume the hexagonal axis to be a direction of easy magnetization, and the crystal anisotropy to be so large that the highest fields used do not make the magnetization deviate very much from the axis. In that case the magnetization in a randomly oriented polycrystalline material will be half of true saturation, or 3.5, in good agreement with Henry's measurements. Such difficulty in the saturation has already been observed[8] in dysprosium, in which, however, the direction of easy magnetization is perpendicular to the hexagonal axis.

An increase in magnetization of about 10%, measured at 4.2°K, was effected by cooling Tm from 78° in a magnetic field of 8000 oe.

ACKNOWLEDGMENT

We are indebted to Mr. A. J. Williams for assistance with the measurements.

APPENDIX

Néel's formula for the Curie point,

$$\theta=4\beta^2S^2(J+1)J^{-1}n/3k$$

in which n is the molecular field constant, applies to the rare earths Gd to Lu. A more general formula, applying

[5] L. Néel, Z. Elektrochem. **45**, 379 (1939).

[6] G. Joos, *Proceedings of the Fifth Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 581.

[7] W. Henry, *Fifth Conference on Magnetism and Magnetic Materials, Detroit, November 19, 1959* [J. Appl. Phys. (1960) (to be published)].

[8] D. R. Behrendt, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1544 (1958).

to all the rare earths, has been derived by de Gennes[9] and by Brout and Suhl[10]:

$$\theta=4\beta^2J(J+1)(g-1)^2n/3k;$$

this reduces to Néel's formula when $J=L+S$, appropriate to the elements Gd to Lu, and to the formula

$$\theta=4\beta^2S^2J(J+1)^{-1}n/3k,$$

when $J=L-S$, appropriate to the rare earths La to Gd.

[9] P. G. de Gennes, Compt. rend. **247**, 1836 (1958).
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PHYSICAL REVIEW VOLUME 118, NUMBER 6 JUNE 15, 1960

Elastic Constants of Palladium from 4.2–300°K

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(Received January 20, 1960)

Elastic constant measurements have been made on a single crystal of palladium in the temperature range 4.2–300°K. Extrapolation of the data to absolute zero gives

$$c_{11}=2.341\pm0.027\times10^{12}\text{ dyne cm}^{-2},$$
$$c_{12}=1.761\pm0.027\times10^{12}\text{ dyne cm}^{-2},$$
$$c_{44}=0.712\pm0.003\times10^{12}\text{ dyne cm}^{-2}.$$

The corresponding value of Debye temperature is $\theta_0=275\pm8$°K, which compares well with the calorimetric figure of $\theta_0=274\pm3$°K. Both shear constants show an anomalous temperature dependence. This dependence can be correlated with the temperature variation of the contribution to $C=c_{44}$ and $C'=\frac{1}{2}(c_{11}-c_{12})$, resulting from the presence of holes in the d band of palladium.

I. INTRODUCTION

THE elastic properties of the transition metals are of considerable interest. If there is a contribution to the bulk modulus of a metal arising from the conduction electrons, as has been suggested by DeLaunay,[1] the effect should be most pronounced in the transition elements, which have narrow unfilled d bands containing a considerable number of electrons. Again from the work of Leigh,[2] it might be anticipated that the holes in the d bands should contribute to the shear constants. For those metals having almost filled d bands, and hence a low degeneracy temperature, this hole contribution would vary significantly with temperature, thereby causing an anomalous temperature dependence of the shear constants.

Thus far, the only transition metal to be studied in detail has been nickel,[3] which has the added complication of being ferromagnetic. Of the nonferromagnetic cubic transition metals, palladium is especially well suited to an investigation of the above effects, since it has an almost filled d band and the grosser features of its band structure are reasonably well understood from susceptibility and specific heat measurements[4,5] on silver-palladium alloys. In addition, elastic data would be of use in providing a reliable value for the Debye temperature of palladium, since the accuracy of that obtained from calorimetric data[5,6] is quite low owing to the high electronic heat capacity of the metal. In this paper the results of elastic constant measurements on palladium from 4.2–300°K will be presented.

II. EXPERIMENTAL

The specimen of palladium used in these experiments was prepared from a single crystal ingot having a purity of 99.8%, the principal contaminants being iron and platinum. This ingot was prepared, using the Czochralski technique, by Dr. James Kirn of the Virginia Institute for Scientific Research. When etched electrolytically in solution of sulfuric acid and glycerin, it revealed no appreciable mosaic structure. The ingot was oriented by the usual Laue back reflection technique and a cylinder, approximately $\frac{5}{8}$ in. in length and $\frac{5}{8}$ in. in diameter with its axis along the [110] direction, was then cut from it. The cylinder ends were lapped for parallelism to within 0.0001 in., after which they were lightly etched using the same solution as used previously.

The ultrasonic measurements were made using an Arenberg[7] ultrasonic pulse generator and wide band amplifier together with a Tektronix type 545 oscillograph. Details of the measuring techniques have been

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