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Influence of Hydrostatic Pressure on Magnetic Transitions in Terbium and Dysprosium

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The effect of hydrostatic pressure on the magnetic tiansitions in terbium and dysprosium has been investigated. The transformer method is used, in which the toroidal core of the miniature transformer is the rare-earth metal itself. Results are obtained as curves of secondary voltage versus temperature. A cusp in the secondary voltage indicates the occurrence of a Néel temperature, at which a transformation takes place from a paramagnetic to an antiferromagnetic state, while a sharp rise in the secondary voltage indicates the passage through a Curie temperature, where a transformation from an antiferromagnetic to a ferromagnetic state occurs. The pressures, up to 25 kbar, are obtained by the piston-cylinder technique, using silver chloride as the pressure-transmitting medium. The temperature range is from 40°K to room temperature. This has been achieved with the use of a new 4-wall cryogenic Dewar and liquid helium as coolant. The pressure coefficient of the transition temperature of terbium is found to be -1.0°K/kbar. Under pressure, the atmospheric Néel temperature either disappears or, because of the narrowness of the antiferromagnetic region, is difficult to separate from the Curie temperature. The pressure coefficient of the Néel temperature for dysprosium is -0.4°K/kbar. In the range of from zero to about 7 kbar, the Curie temperature appears to increase with increasing pressure; beyond 7 kbar, the Curie temperature appears to decrease with increasing pressure. In the low-pressure range, the pressure coefficient of the Curie temperature appears to be positive, and in the high-pressure range it is -0.8°K/kbar. The above results involving measurements on dysprosium must be taken as tentative. The shape of the secondary-voltage-versus-temperature curves is such that one cannot assign the coefficients in an unambiguous manner.

I. INTRODUCTION

THIS article is the second in a series of articles relating to the effect of pressure on magnetic properties of rare-earth metals. The first article in this series reported the results of investigations with gadolinium[1]; the present article pertains primarily to terbium with some reference to dysprosium.

The experimental procedure was to a large extent, similar to that given in Robinson, Milstein and Jayaraman,[1] except that a new high-pressure four-wall Dewar assembly was used, which will be described in a forthcoming article. The specimens were machined in the form of small rings which were used as transformers, coupling input and output coils. A constant voltage was supplied and the output voltage was measured as a function of temperature, while the specimen was under pressure. The Curie temperature is identified by the method given in Ref. 1; the characteristic kink in the output-voltage-versus-temperature curve identifies the Néel temperature.

The magnetic properties of the pressurized rare-earth samples were correlated with the secondary voltage from a small toroidal transformer, the core of which was the rare-earth metal itself. As the sample changed from a nonferromagnetic to an antiferromagnetic or to a ferromagnetic state, an increase in permeability and hence in secondary voltage was observed.

Pressures up to about 40 kbar were obtained with a piston-cylinder high-pressure press equipped with a four-wall stainless steel Dewar which was designed and constructed by one of us (K. F. S.) and made available at Northrop Space Laboratories by Dr. J. T. Thomas. This Dewar has been described previously.[2,3] Temperatures down to 77°K were obtained by filling the Dewar slowly with liquid nitrogen. Heating was provided by a Constantan resistance heater wound around the periphery of the supported tungsten carbide pressure vessel. The rates of heating and cooling were carefully controlled in each experiment not to exceed 2.5° per minute. Near the transition temperature these rates were usually maintained at about 1.5° per minute.

Figure 1 shows a cross section of the sample capsule assembly. The metals used were certified by the manufacturer to be 99.9% pure. The specimens were machined in the form of small toroids which were coated with epoxy cement and covered with a layer of masking tape to prevent the windings from shorting and the sample from reacting with the silver chloride.

A summary of the atmospheric-pressure values of the transition temperatures in terbium and dysprosium is given in Table I. The methods by which the tempera-

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* Based on experiments performed by Swie-In Tan in partial fulfillment of the requirements for the Ph.D. degree.

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[1] L. B. Robinson, F. Milstein, and A. Jayaraman, Phys. Rev. **134**, A187 (1964).

[2] S. I. Tan, Ph.D. thesis, University of California, Los Angeles, Dept. of Engineering, 1965 (unpublished).

[3] L. B. Robinson, F. Milstein, S. I. Tan, and K. F. Sterrett, *Physics of Solids at High Pressures*, edited by K. Tomizuka and R. Emrick (Academic Press Inc., New York, 1966, to be published).

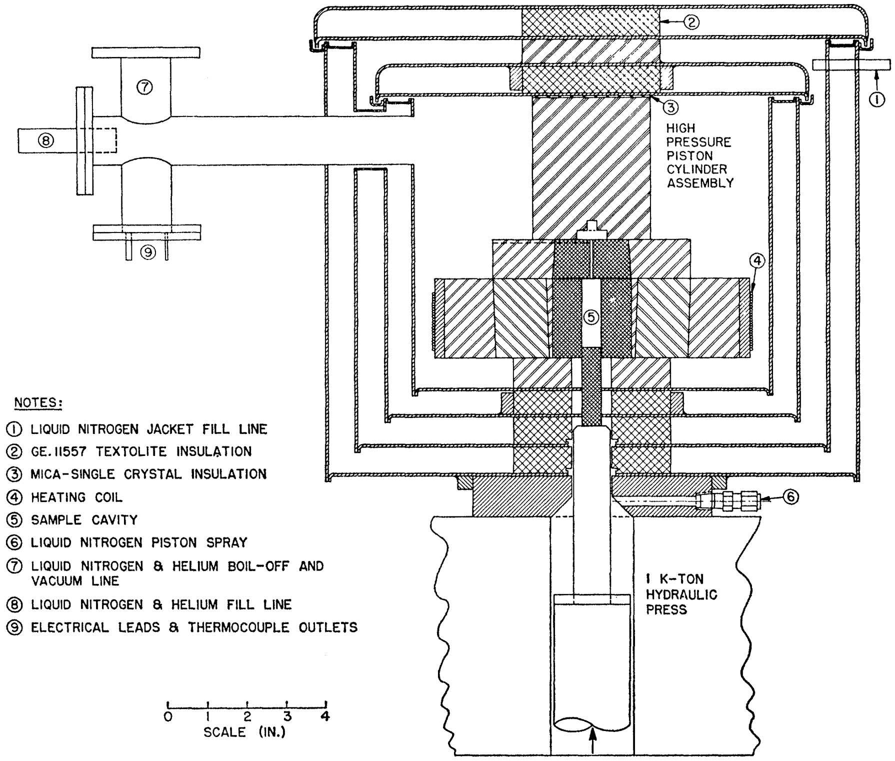

FIG. 1. High-pressure Dewar and piston-cylinder assembly.

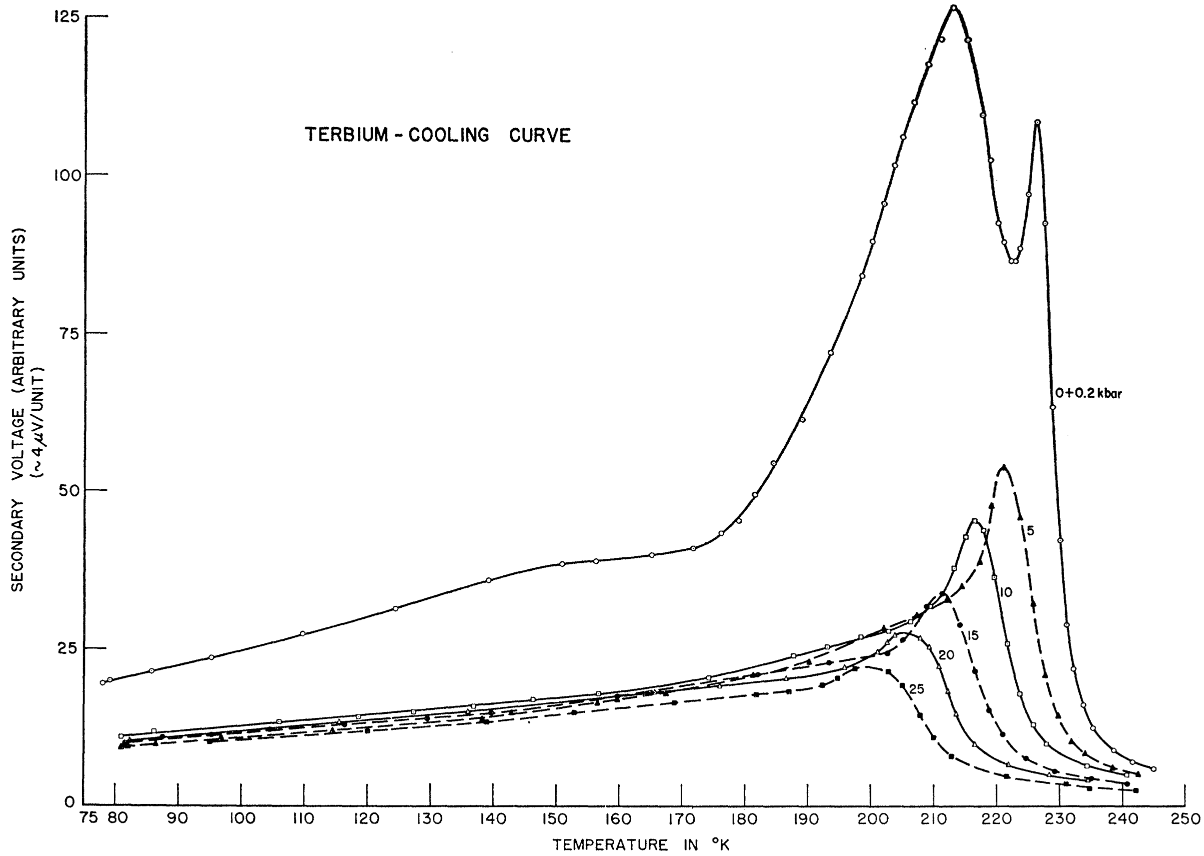

FIG. 2. Effect of pressure on the output voltage for terbium (cooling).

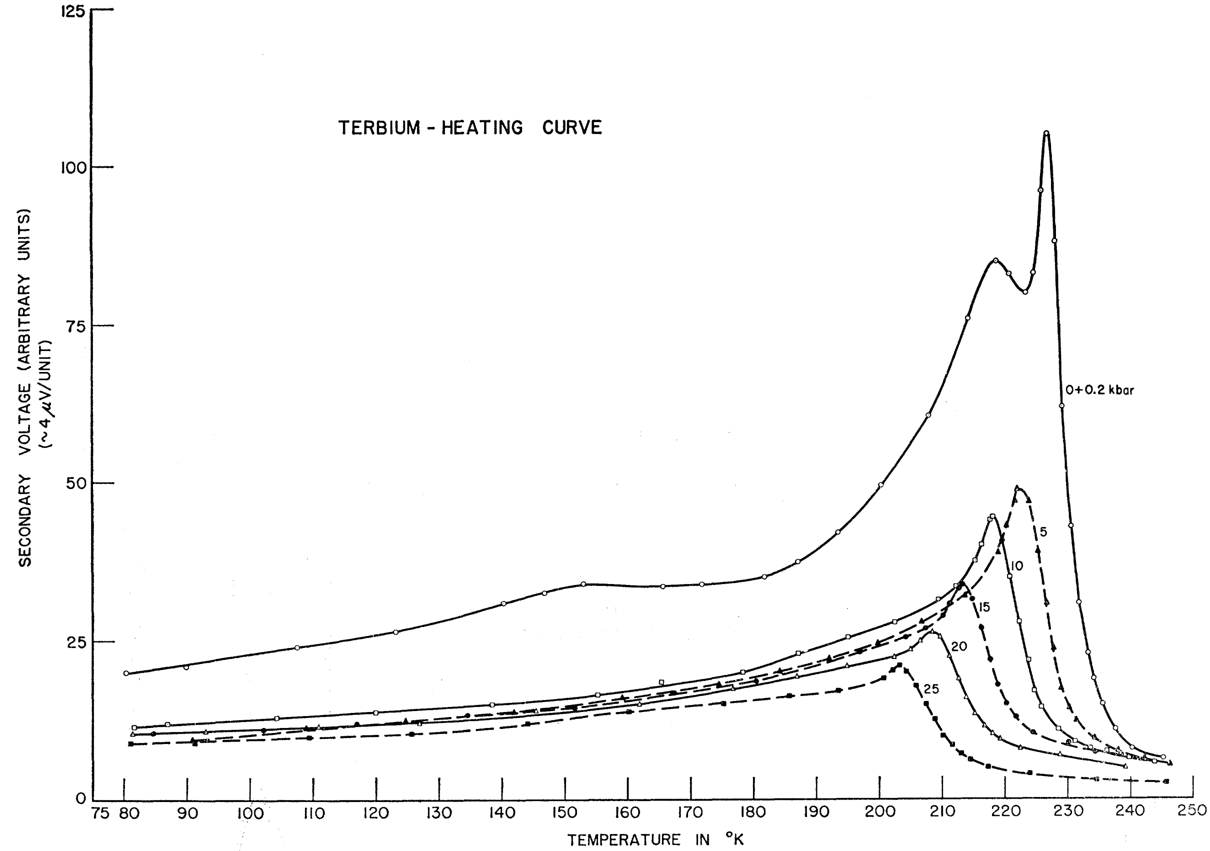

FIG. 3. Effect of pressure on the output voltage for terbium (heating).

tures are determined, as well as references, are also given.

TABLE I. Curie and Néel temperatures of terbium and dysprosium.

Element	T_{Curie}	$T_{\text{Néel}}$	Notes and references
Terbium	224°K	230°K	Neutron diffraction. See Ref. 6.
	218°K	230°K	Magnetic measurements. See Ref. 5.
Dysprosium	87°K	179°K	Neutron diffraction. See Ref. 9.
	85°K	178°K	Magnetic measurements. See Ref. 8.

II. TERBIUM

Under atmospheric pressure, terbium exhibits both a Curie temperature and a Néel temperature, as may be seen in Fig. 2. On the curve labeled 0+0.2 kbar, the peak near 230°K represents the Néel temperature, whereas the peak near 210°K is characteristic of the Curie temperature. When additional pressure was applied, only one transition temperature persisted. It could be that one or the other disappears under pressure or that the one masks the other. It is now difficult to say unequivocally whether it is the Néel or the Curie temperature which remains. Henceforth, the transition temperature which remains, upon the application of pressure, shall be referred to only as the *transition temperature*, even though the shape of the curves appears to be more characteristic of the Curie temperature.

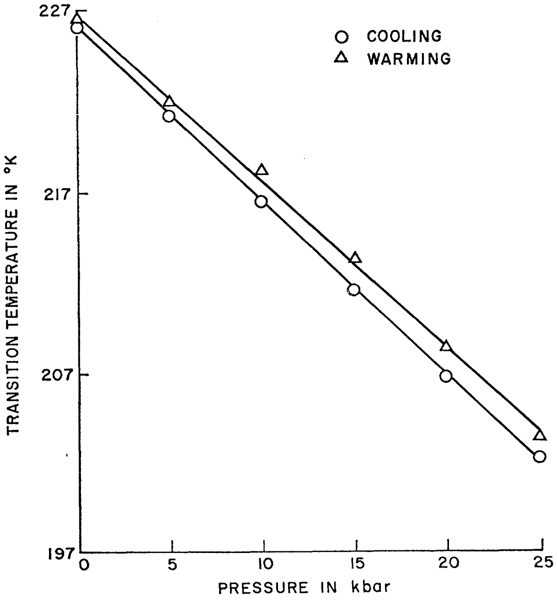

FIG. 4. The shift of transition temperature of terbium as a function of pressure.

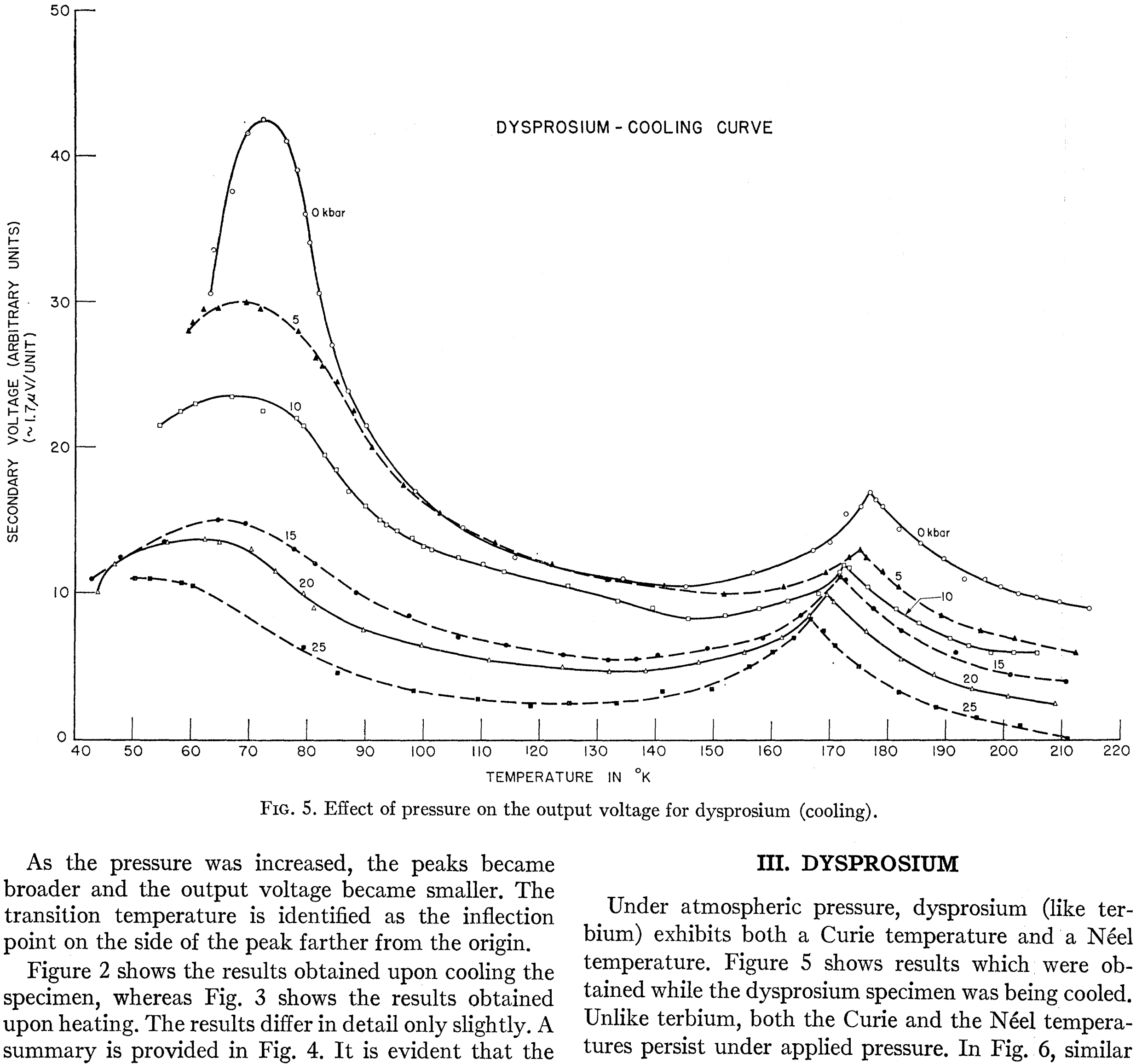

FIG. 5. Effect of pressure on the output voltage for dysprosium (cooling).

As the pressure was increased, the peaks became broader and the output voltage became smaller. The transition temperature is identified as the inflection point on the side of the peak farther from the origin.

Figure 2 shows the results obtained upon cooling the specimen, whereas Fig. 3 shows the results obtained upon heating. The results differ in detail only slightly. A summary is provided in Fig. 4. It is evident that the transition temperature has a pressure coefficient of approximately −1.0°K/kbar.

The results obtained here, at atmospheric pressure, agree well with recently reported measurements made using different techniques. Heat-capacity[4] and magnetic[5] measurements on terbium have shown the existence of two anomalies, at 228 and 220°K, corresponding to a transition from a para- to an antiferromagnetic state and from an anti- to a ferromagnetic state, respectively. Koehler *et al.*[6] have confirmed, by neutron diffraction, the existence of a helical spin structure in the 230°K region, which corresponds to the Néel temperature.

III. DYSPROSIUM

Under atmospheric pressure, dysprosium (like terbium) exhibits both a Curie temperature and a Néel temperature. Figure 5 shows results which were obtained while the dysprosium specimen was being cooled. Unlike terbium, both the Curie and the Néel temperatures persist under applied pressure. In Fig. 6, similar results are obtained for the case in which the specimen was heated.

One may summarize as follows. The result for one atmosphere agrees well with heat-capacity,[7] magnetic,[8] and neutron-diffraction[7] measurements. Such measurements show the existence of a Néel temperature between 175 and 179°K and a ferromagnetic Curie temperature at 85°K. Figures 5 and 6 show that the one-atmosphere isobar gives a Néel temperature of 177°K. It is interesting to note that the minimum of the *one-atmosphere* isobar exhibits a minimum at approximately 145°K. The minimum corresponds closely to the temperature (140°K) at which the onset of a minor

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[4] L. D. Jennings, R. M. Stanton, and F. H. Spedding, J. Chem. Phys. **27**, 909 (1957).

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[6] W. C. Koehler, H. R. Child, E. O. Wohlan, and J. W. Cable, J. Appl. Phys. **34**, 1335 (1963).

[7] M. Griffel, R. E. Shockdopole, and F. H. Spedding, J. Chem. Phys. **25**, 75 (1956).

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

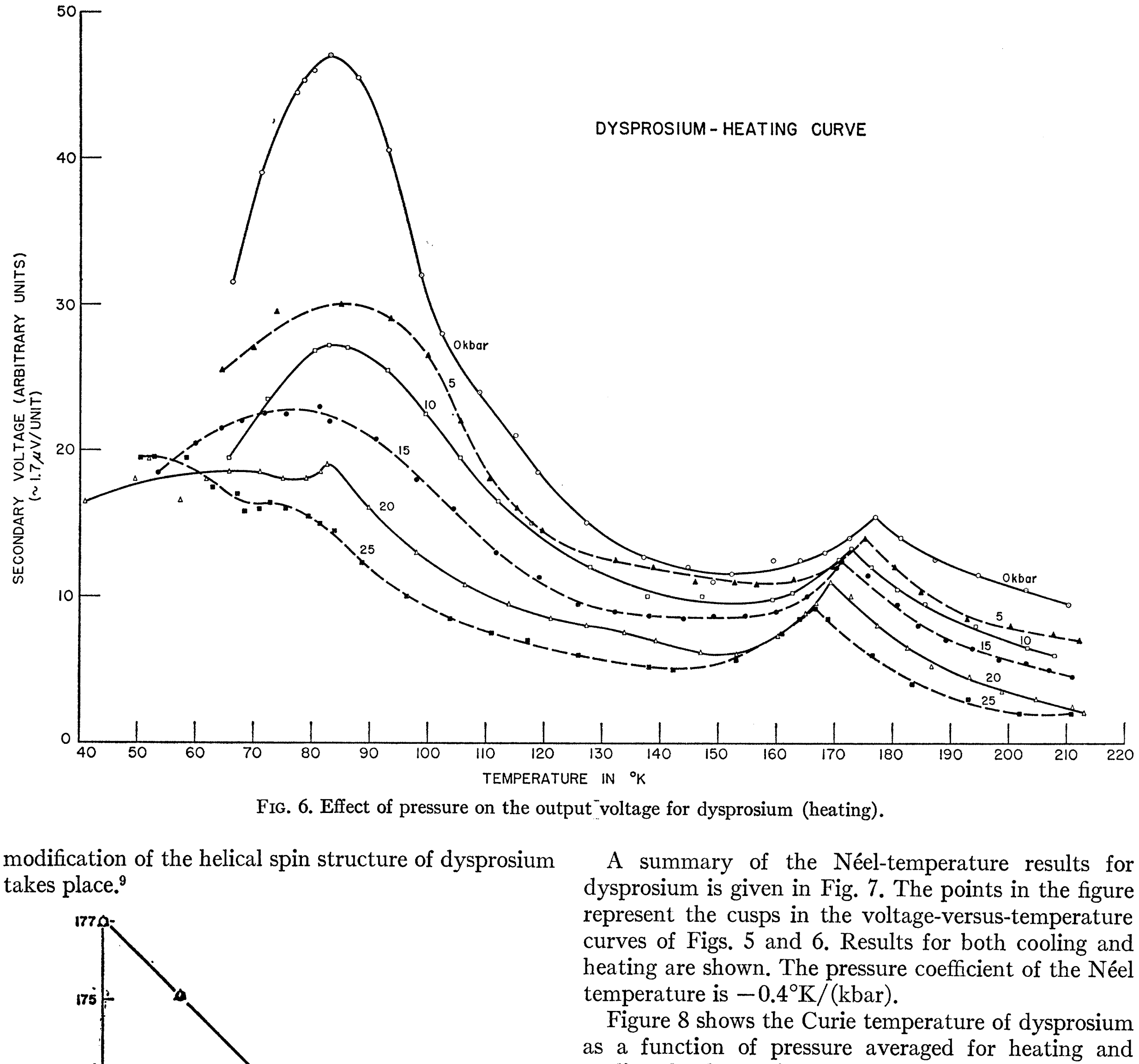

Fig. 6. Effect of pressure on the output voltage for dysprosium (heating).

modification of the helical spin structure of dysprosium takes place.[9]

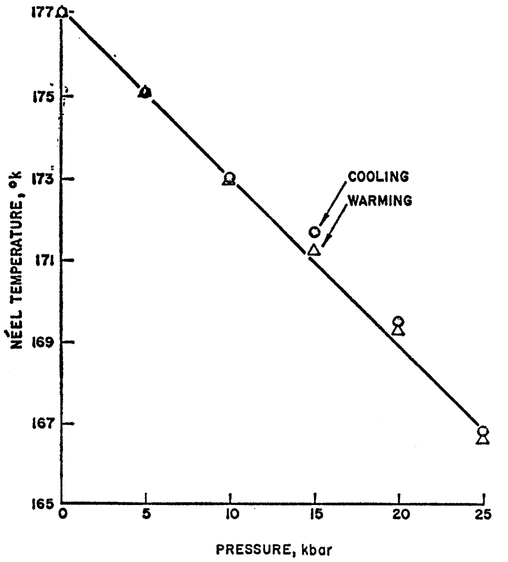

Fig. 7. The shift of Néel temperature of dysprosium as a function of pressure.

A summary of the Néel-temperature results for dysprosium is given in Fig. 7. The points in the figure represent the cusps in the voltage-versus-temperature curves of Figs. 5 and 6. Results for both cooling and heating are shown. The pressure coefficient of the Néel temperature is -0.4°K/(kbar).

Figure 8 shows the Curie temperature of dysprosium as a function of pressure averaged for heating and cooling the dysprosium specimen. Higher values of the Curie temperatures occurred when the specimen was

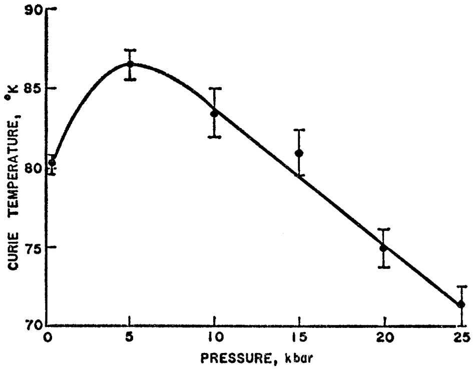

Fig. 8. The shift of Curie temperature of dysprosium as a function of pressure (averaged for heating and cooling).

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[9] M. K. Wilkinson, W. C. Koehler, E. O. Wohlan, and J. W. Cable, J. Appl. Phys. 32 (Suppl.) No. 3, 48 (1961).

undergoing heating. Evidently some rate effect accounts for the differences in the two curves. An indication of the uncertainty in the values is given by the length of the lines through the points. In the low-pressure range (i.e., from atmospheric pressure to about 7 kbar), the Curie temperature appears to increase with increasing pressure. The shapes of the curves in Figs. 5 and 6 make a more precise determination difficult to obtain. In the high-pressure range (beyond 7 kbar), the Curie temperature appears to decrease with increasing pressure, having a coefficient of -0.8°K/(kbar).

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de Haas–van Alphen Effect and the Fermi Surface of Dilute Alloys of Zinc*

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Torsion measurements have been made of the de Haas–van Alphen magnetic-susceptibility oscillations in dilute Zn-Cu (up to 0.2 at.%) and Zn-Al (0.1%) alloys in magnetic fields up to 33kG. Sizeable alloying effects occur in the two longest periods P_1 and P_2 (the two smallest orbits on the zinc Fermi surface). Both periods *decrease* by 30% with only 0.2% Cu. With 0.1% Al, P_2 *increases* substantially while P_1 is only slightly increased, by an amount comparable to the 4% uncertainty in period determination (the oscillation amplitude is very small in the alloys). Following an earlier suggestion of Harrison, these alloying changes have been interpreted using the nearly-free-electron construction. The model explains both the sign and the magnitude of the P_1 changes, in particular demonstrating that the dominant effect of the axial-ratio change can make a metal of *lower* electron concentration act to *increase* the size of an electron piece of the Fermi surface. The model accounts for the sign but not the magnitude of the P_2 changes, which are more than a factor of three larger than predicted by the model. No changes greater than 1% were observed in the third longest period P_3. An unexplained result is the observation of a period of order $400\times10^{-7}\mathrm{G}^{-1}$ for fields in the (0001) plane in crystals containing copper impurities, but not in pure zinc or Zn-Al.

INTRODUCTION

An explanation for the regularity observed by Hume-Rothery in phase diagrams of the noble metals was suggested by Jones more than 30 years ago.[1] His explanation considers the effect of anomalies in the density of states which occur in the regions of electron concentration where the Fermi surface (FS) contacts a Brillouin-zone boundary. This concept has been used by Jones and others to interpret phase boundaries, and, in hexagonal metals, axial-ratio changes on alloying.[2,3] The starting point for all of these interpretations was a postulated FS whose topology could not be well verified experimentally or theoretically. This situation has changed with the advent of experimental techniques such as the de Haas–van Alphen (dHvA) effect for the experimental measurement of the FS.[4] The dHvA oscillations in magnetic susceptibility are observed in pure metals in high magnetic fields ($\omega_c\tau>1$, where $\omega_c=eH/m^*c$) at low temperatures ($kT<\hbar\omega_c$). The oscillations are periodic in inverse magnetic field $1/H$, with period inversely proportional to the extremal cross-sectional area A of the FS perpendicular to the magnetic-field direction[5]:

$$P=\Delta 1/H=2\pi e/\hbar cA \quad (A \text{ in } k \text{ space}) . \tag{1}$$

With such measurements it has been found[6,7] that in the pure noble metals the FS contacts the (111) zone face. This is a major distortion of the free-electron sphere and throws into doubt the earlier explanation[1] that the α-phase boundary of the noble-metal alloys is due to (111) zone face contact at an electron/atom ratio of 1.4. Though attempts have been made to patch up the theory,[8] a more direct approach would be FS measure-

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† Part of a dissertation submitted to the Graduate School of Northwestern University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

‡ Present address: Department of Physics, University of Oregon, Eugene, Oregon. National Science Foundation predoctoral fellow while at Northwestern.

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[3] T. B. Massalski and H. W. King, Acta. Met. **10**, 1171 (1962).

[4] See, for example, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, New York, 1960).

[5] L. Onsager, Phil. Mag. **43**, 1006 (1952).

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[7] D. Shoenberg, Phil. Trans. Roy. Soc. **A255**, 85 (1962).

[8] W. Hume-Rothery and D. J. Roaf, Phil. Mag. **6**, 55 (1961). See also Ref. 1, p. 329.