Pressure Dependence of the Magnetic Transitions in Dysprosium and Erbium*

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The effect of hydrostatic pressure on the magnetic transitions of polycrystalline samples of dysprosium and erbium has been studied to 7 kbar. Pressure was generated using a helium-gas system and the transitions were detected by measuring, with a precision ratio-transformer bridge, the self-inductance of a coil containing the samples. For the antiferromagnetic transition of dysprosium we find that dT_N/dP increases in magnitude with pressure, having an initial value of -0.44 ± 0.02°K/kbar and an average of about -0.5°K/kbar. The Néel transition of erbium shows a constant slope of -0.26 ± 0.01°K/kbar. Determination of the ferromagnetic transitions was complicated by a hysteresis effect between warming and cooling data for dysprosium and a rather complicated variation of inductance with temperature for erbium; but with the exercise of systematic experimental procedure, including temperature cycling over a wide range and slow rates of temperature change, it is believed that reliable values for the pressure dependence of the Curie transition were obtained. For dysprosium, an inflection point in the inductance-temperature curve coincided at atmospheric pressure with the reported value of the transition temperature and was taken, therefore, to indicate the transition under high pressure as well, yielding $dT_c/dP=-1.24\pm0.10$°K/kbar. For erbium, between 4.2 and 60°K, two peaks were observed on cooling curves and three on warming curves. The low-temperature peak on warming coincided with the reported Curie transition at 20°K and was found to have a pressure dependence of -0.8 ± 0.2°K/kbar. A high-temperature peak coincided on warming curves with a 53.5°K peak that has been reported in specific-heat and magnetic measurements and is also associated with a transition reported at 52°K from neutron-diffraction experiments in which the magnetization transverse to the c axis changes. This peak shows a pressure dependence of -1.3 ± 0.2°K/kbar. A strong peak observed at about 25°K on cooling was pressure-independent, but on warming curves, was located at a slightly higher temperature and was pressure-dependent. The results are compared with other measurements on the rare earths, and with theory.

INTRODUCTION

THE dependence of magnetism upon interatomic distance provides information which should lead to a deeper understanding of this remarkable phenomenon. One of the simplest and most direct ways of obtaining experimental data related to this question for ferromagnetism and antiferromagnetism is to measure the pressure dependence of magnetic transition temperatures. The heavy rare earths, which have complex magnetic properties and in most cases show both antiferromagnetic and ferromagnetic ordering transitions, have recently been the subject of several such experimental studies, and of theoretical analysis. Bloch and Pauthenet[1,2] working with a helium gas system have measured the pressure dependence up to 4 to 6 kbar of the Néel transition T_N of terbium, dysprosium, and holmium, and of the Curie transition T_c of gadolinium. McWhan and Stevens[3] have studied the same transitions to 85 kbar with belt-anvil apparatus. Landry and Stevenson[4] have measured the shift of T_N of dysprosium to 8.5 kbar in piston-cylinder apparatus. Belov, *et al.*,[5] using the ice-bomb technique, measured the 1.8-kbar pressure shift of T_c of dysprosium. Robinson, *et al.*[6] using piston-cylinder apparatus have measured pressure dependences to 25 kbar of Néel and Curie temperatures of terbium and dysprosium. Swenson[7] has obtained unpublished data on the Curie transition of dysprosium. Of these studies, only those by Bloch and Pauthenet, and by Swenson were performed under hydrostatic conditions. Slightly different values have been obtained by the different investigators for the pressure coefficients of the Néel transitions and a marked discrepancy exists among the values reported for the pressure dependence of the Curie transition of dysprosium.

In the present study the magnetic transitions of erbium and dysprosium have been investigated as a function of hydrostatic pressure to 7 kbars using a helium-gas-pressure facility. To our knowledge, these are the first such measurements on erbium. For dysprosium the major purpose was to obtain an accurate hydrostatic pressure dependence for the Curie temperature in order to settle the existing discrepancy, but the Néel transition was also examined for comparison with other work.

EXPERIMENTAL PROCEDURE

A schematic diagram of the 14-kbar helium-gas-pressure system is shown in Fig. 1. The system consists of three stages separated by check valves and operating in series. The last two stages consist of model SA10

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[1] D. Bloch and R. Pauthenet, Compt. Rend. **254**, 1222 (1962).
[2] D. Bloch, Ann. Phys. (Paris) **14**, 93 (1966).
[3] D. B. McWhan and A. L. Stevens, Phys. Rev. **139**, A682 (1965).
[4] P. Landry and R. Stevenson, Can. J. Phys. **41**, 1273 (1963).
[5] K. P. Belov, S. A. Nikitin, and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. **45**, 26 (1963) [English transl.: Soviet Phys.—JETP **18**, 20 (1964)].
[6] L. B. Robinson, Swie-In Tan, and K. F. Sterrett, Phys. Rev. **141**, 548 (1966).
[7] C. Swenson (private communication).

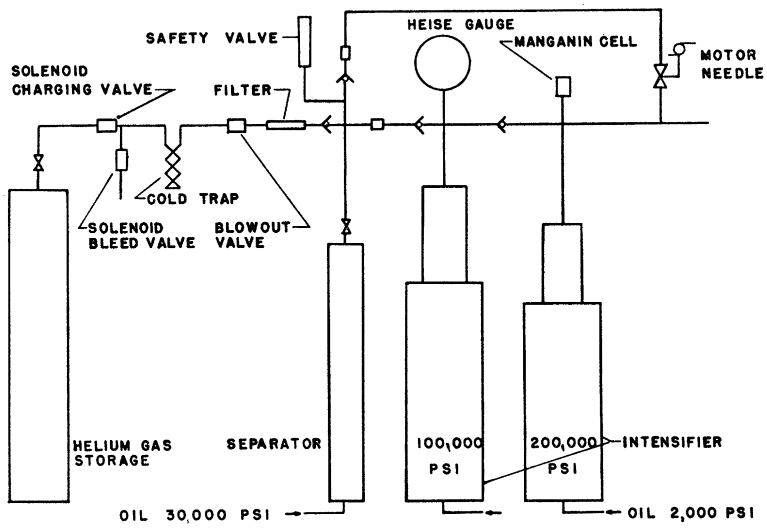

FIG. 1. The 14-kbar helium gas pressure system. Check valves separate the stages which are pressurized in series.

intensifiers manufactured by Harwood Engineering Company. For safety, all high-pressure components are housed in a specially constructed room below ground level and operated by remote control. Other equipment which must be placed in the room is operated remotely also. Helium gas pressure was measured by means of a manganin resistance cell calibrated to 14 kbar against a dead-weight balance at Harwood. The cell resistance was read on a Carey-Foster bridge and the pressure measurements are considered accurate to within 1%.

The pressure bomb was constructed of nonmagnetic beryllium copper. The bomb and pressure seals are described in separate publications.[8,9] Data were taken only if the bomb seals were absolutely tight since even a slight gas leak at the bomb will cause cooling of the sample and create temperature uncertainties.

The basic cryostat, which is shown in Fig. 2, consists of the pressure bomb surrounded by an evacuated can and inserted in a double Dewar system. The inner Dewar was filled with either liquid nitrogen or liquid helium depending on the temperature range to be covered. The bomb was cooled by admitting exchange gas into the can, thereby bringing it into thermal contact with the bath; then the can was evacuated and the heater was used to raise the temperature of the bomb and hold it at any desired value. The heater was wound noninductively with resistance wire. Aluminum foil, which has low emissivity, was used to wrap the bomb and line the inner wall of the can to reduce radiation. The inlet pressure line was $\frac{3}{16}$-in stainless steel and did not present a serious heat-conduction problem. The temperature was measured with three copper-constantan thermocouples which were wrapped twice around the bomb at different levels as shown and cemented to it. These thermocouples were calibrated in position periodically against a platinum resistance thermometer which could be inserted into a hole drilled into the band shown on the bomb. Absolute temperature accuracy was judged to be better than ± 0.25°K; reproducibility was better than ± 0.1°K.

Liquid or solid nitrogen could be used as coolant for studying all the transitions except the ferromagnetic transition in erbium which occurs at about 20°K and requires liquid helium. At this temperature high pressures can not be achieved with fluid helium before encountering the fusion curve. High hydrostatic pressures were obtained by freezing the helium at constant pressure, being careful to freeze from the bottom of the bomb upward and finally plugging the inlet line with solid after all the helium in the bomb was solid. This was achieved by slight modification of the cryostat in Fig. 2. Two heavy copper straps were soldered con-

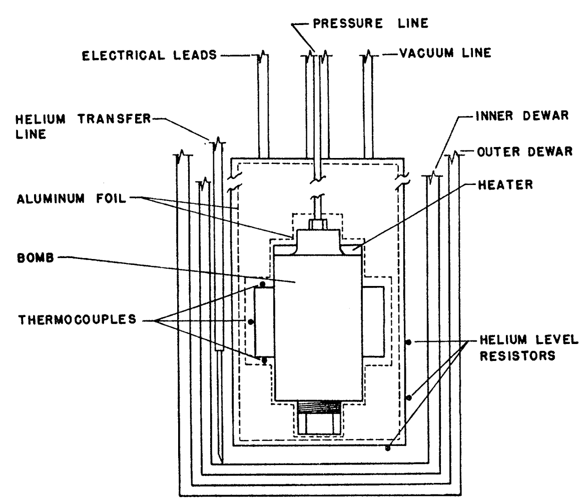

FIG. 2. Schematic of cryostat with pressure bomb in position.

[8] W. S. Goree, B. McDowell, and T. A. Scott, Rev. Sci. Instr. **36**, 99 (1965).

[9] J. E. Milton, Ph.D. dissertation, University of Florida, 1966 (unpublished).

necting the bottom of the bomb and the can. A second heater was wrapped around the inlet pressure line so that it could be kept warmer than the bomb. By slowly transferring cold helium vapor through the transfer tube shown and employing the heaters, a substantial temperature gradient could be maintained across the bomb insuring that the pressurized helium froze from the bottom.

The magnetic transitions were detected by measuring the change in inductance of a coil containing the sample. The single-coil technique seems to be an entirely satisfactory method of measuring shifts in transition temperatures, and for high-pressure work it has the considerable advantage of simplicity. Similar conclusions have been reached independently by Samara and Giardini.[10] The coils typically contained about 14 000 turns with a length of $\frac{13}{16}$ in., an i.d. of $\frac{1}{8}$ in., an o.d. of $\frac{7}{16}$ in. and had an inductance of 0.4 H. The coil inductance was read on a sensitive ratio-transformer inductance bridge, which was built following a design by Hillhouse and Kline.[11] This bridge was operated at a frequency of 2 kHz and is capable of detecting changes of inductance of one part per million.

Polycrystalline samples of dysprosium and erbium having a specified purity of 99.9% were obtained from Leytess Metal and Chemical Corporation. The samples were machined to a final size of $\frac{1}{8}$-in. diam by $\frac{13}{16}$ in. long. The samples were not annealed after purchase.

RESULTS AND DISCUSSION

Néel Transitions

The Néel transitions characteristically produce a susceptibility maximum and, therefore, a peak in the inductance of the coil containing the sample. This peak was found to be sharp, reversible with temperature sweep direction and rate, and measurable with an

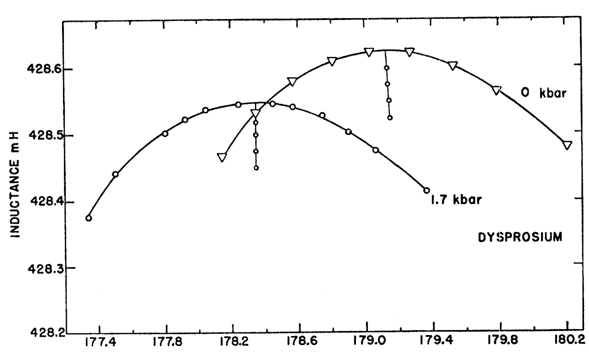

FIG. 3. Peak regions in bridge inductance readings for a dysprosium sample at two pressures.

[10] G. A. Samara and A. A. Giardini, Rev. Sci. Instr. **36**, 108 (1965).

[11] D. L. Hillhouse and H. W. Kline, Trans. AIEE Instr. Measr. **9**, 251 (1960).

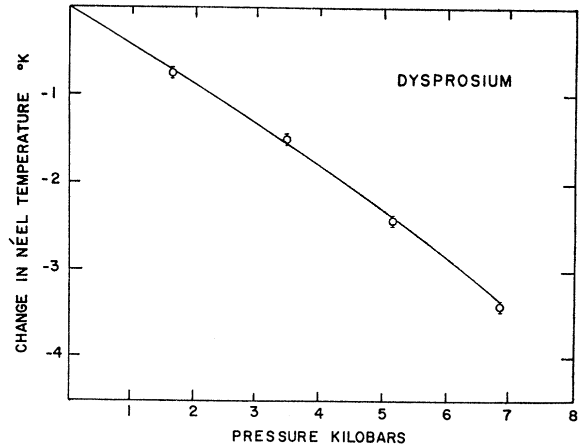

FIG. 4. Pressure dependence of the Néel temperature of dysprosium.

accuracy of ±0.02°K for a given experimental setup; however, if the sample system was taken apart and reassembled, somewhat larger displacements of the peak were noted, presumably because of some slight redistribution of temperature gradients or perhaps of bridge balance conditions. The pressure data were taken without disturbing the assembly, or if this was necessary, the measurements were overlapped and normalized by rerunning the zero-pressure curve. The zero-pressure point was also usually checked after pressure runs. At least two separate runs were made at each pressure and in most cases more, and the resultant data are self-consistent and reproducible. The peak in the inductance curve was taken to be at the Néel temperature. Whether or not this point is precisely the transition[12] it seems likely that it will have the same pressure dependence. To locate this peak accurately it was necessary to sweep through only about one degree in temperature.

The peak regions for dysprosium at 0 and 25 000 ψ are shown in Fig. 3 as typical examples of the data. The peaks were located by selecting pairs of temperatures corresponding to the same inductance and averaging to obtain the vertical curve that is the locus of these points on Fig. 3. The peak was shifted to lower temperature and also depressed by application of pressure. The pressure dependence of the Néel transition of dysprosium thus obtained is shown in Fig. 4. The dependence shows some curvature with an initial slope $dT_N/dP = -0.44 \pm 0.02$°K/kbar, and an average slope over the pressure range covered of about -0.5°K/kbar. This curvature may be an explanation of the slightly different values reported for this coefficient by different experimentors.

The Néel transition in erbium occurs at about 85°K and is qualitatively very similar to that of dysprosium. The pressure dependence of the transition temperature

[12] M. E. Fisher, Phil. Mag. **7**, 1731 (1962).

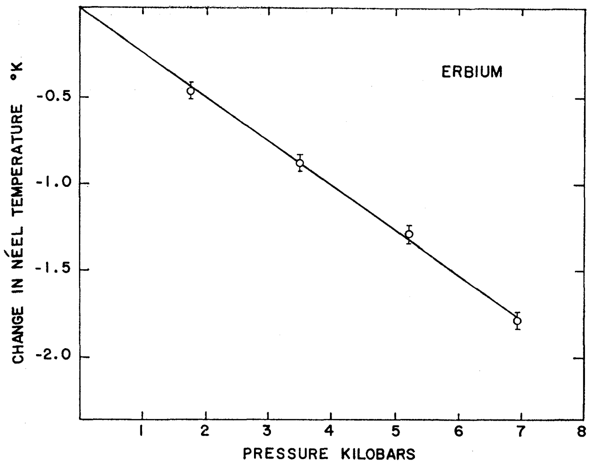

FIG. 5. Pressure dependence of the Néel temperature of erbium.

is shown in Fig. 5. No curvature was detected and the slope is $dT_N/dP = -0.26 \pm 0.01$°K/kbar to our highest pressure at 7 kbar.

It seems well established that the magnetic properties of the rare earths are governed by the indirect exchange interaction.[13–15] Based on the theory of de Gennes,[13] McWhan[3] has given an interaction curve for the heavy rare earths in which he plots the Néel transition temperatures in units of the de Gennes function $(g-1)^2J(J+1)$ versus interatomic distance in units of the diameter of the $4f$ shell. This curve is shown in Fig. 6 with the point for erbium added and reveals a remarkably consistent ordering of the transition temperatures. The curve also accounts satisfactorily for observed pressure dependences and predicts a negative pressure coefficient. For dysprosium and erbium we have added points on Fig. 6 corresponding to the transition temperature at the highest pressure reached in our experiments. The change in interatomic distance was computed assuming an isotropic compressibility and using the compressibility measured at room temperature by Bridgman, and assuming that the diameter of the $4f$ shell was unchanged by pressure. The two points fall very closely on the interaction curve; the agreement, in fact, is better than one might expect from the rough approximation made for compressibility.

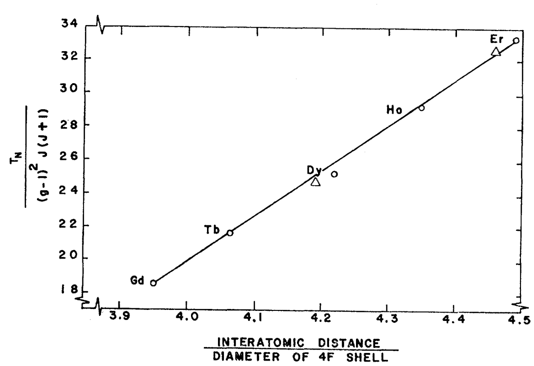

FIG. 6. The Néel temperature in units of the de Gennes function $(g-1)^2J(J+1)$ versus interatomic distance in units of the diameter of the $4f$ shell for several heavy rare earths at atmospheric pressure. The triangular points for Dy and Er correspond to a pressure of 6.8 kbar.

[13] P. G. de Gennes, Compt. Rend. **247**, 1836 (1958).

[14] R. J. Elliott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., 1965), Vol. IIA, p. 389.

[15] K. Yosida, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1964), Vol. 4, p. 265.

Curie Transitions

The ferromagnetic transitions were much more difficult to work with than the Néel transitions. A considerably wider temperature range had to be covered due to a complex behavior of the sample inductance, and the lack of any sharp effect that could be associated with the transition. In addition, there was a complicated hysteresis effect between warming and cooling curves. Dysprosium was simpler and better behaved than erbium and will be discussed first.

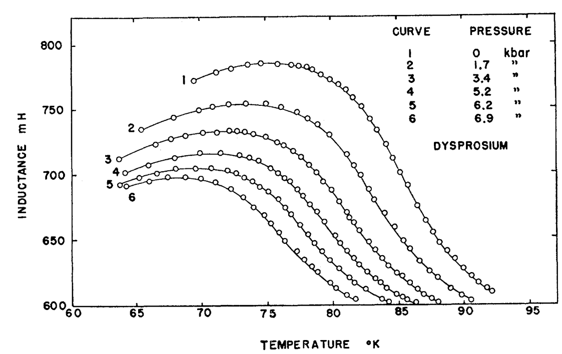

FIG. 7. Inductance readings versus temperature in the region of the Curie transition for a dysprosium sample at six pressures.

Cooling curves for dysprosium did not show appreciable increase of inductance until the sample was about 10 deg below the expected Curie temperature. Furthermore, the result depended on the cooling rate and if one stopped the cooling at a temperature near the transition the inductance would continue to increase for many hours. It was found that if one cooled the sample well below its Curie temperature at 85°K, viz. to about 60°K, held it there for a couple of hours and then took data while warming, these were reproducible, independent of warming rate, and an inflection point in the inductance-versus-temperature curve occurred at 85°K at zero pressure. Since this is in good agreement with other measurements, the inflection point was accepted as the location of the Curie temperature for the determination of the pressure shift. Thermal hysteresis for the ferromagnetic transition of dysprosium as well as other rare earths has previously been observed

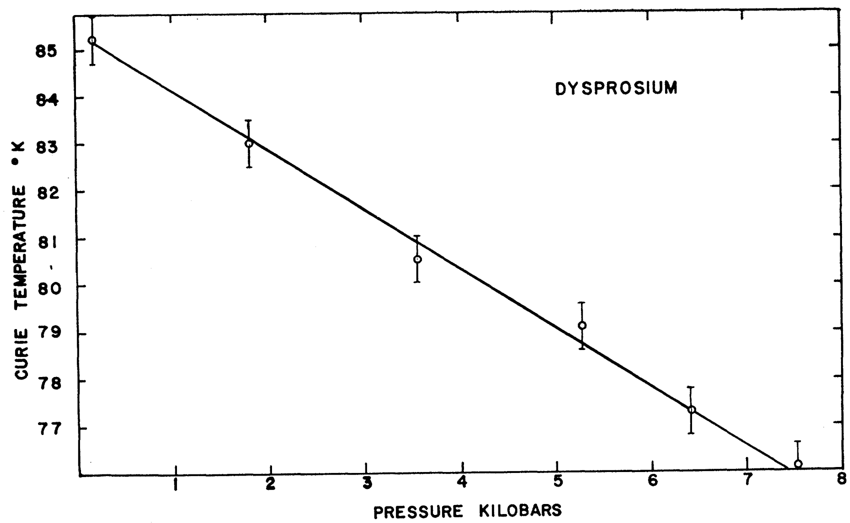

FIG. 8. Pressure dependence of the Curie transition of dysprosium.

by Jelinek *et al.*[16] while studying magnetic susceptibility of polycrystalline samples. They observed a 13°K thermal hysteresis between warming and cooling data on the susceptibility of dysprosium and found that the warming data were reproducible and in close agreement with specific-heat measurements[17] of the transition temperature if the sample was first cooled to 4.2°K and held there for an hour. Our observations are in accord with these. Swenson[7] noted the same hysteresis in his study.

The family of inductance curves thus obtained at six different pressures is shown in Fig. 7. These were all run at a constant warming rate of about 6°K/h. Again, as with the Néel temperature, the transition temperature and value of the inductance are both depressed by pressure. Many more experimental points were taken than are shown in Fig. 7 and when these were plotted on large graph paper the inflection point was distinct and easily located. A plot of the Curie temperature versus pressure is given in Fig. 8, and from it one deduces $dT_c/dP = -1.24 \pm 0.10$°K/kbar. It is worthy of note that for comparison the pressure dependence of the peak in the inductance curve, occurring at about 76°K at atmospheric pressure, was also computed and within experimental error the same coefficient was obtained as for the inflection point.

As mentioned in the introduction, the pressure dependence of the Curie temperature of dysprosium has been measured previously by Swenson,[7] by Belov,[5] and by Robinson, *et al.*[6] Our results agree well with Swenson, who obtained $dT_c/dP = -1.0$°K/kbar, but do not agree well with Belov's larger value of $dT_c/dP = -3.9$°K/kbar, and disagree even in sign with Robinson, *et al.*, who found a positive coefficient of about 1°K/kbar up to about 5 kbar. The ice-bomb technique used by Belov does not usually give a good hydrostatic pressure; it has been demonstrated,[18] for example, that the agreement between hydrostatic measurements of pressure coefficients of electrical resistivity and similar ice-bomb measurements is also poor. The anisotropic thermal expansion of a hexagonal metal relative to ice is certain to cause difficulties. Possibly the initial positive coefficient found by Robinson, *et al.* is also due to nonhydrostatic pressure distribution at low pressures in

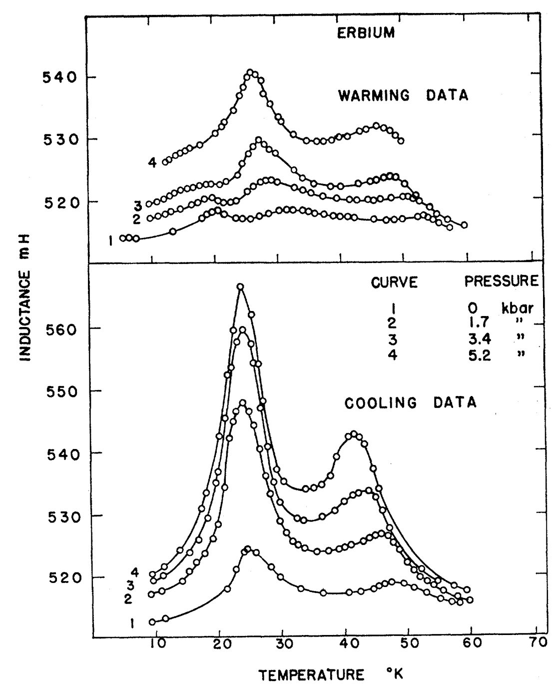

FIG. 9. Inductance readings versus temperature for an erbium sample at four different values of pressure. Both warming and cooling curves are shown.

[16] F. J. Jelinek, E. D. Hill, and B. C. Gerstein, J. Phys. Chem. Solids **26**, 1475 (1965).

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

[18] W. S. Goree and T. A. Scott, J. Phys. Chem. Solids **27**, 835 (1966).

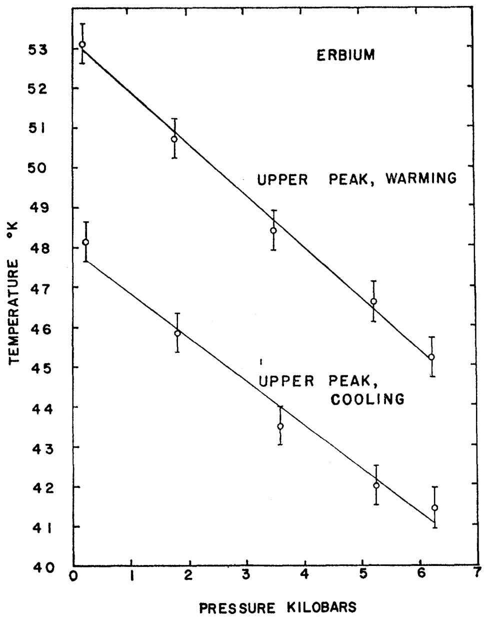

FIG. 10. Pressure dependence of the upper inductance peak on both cooling and warming curves for an erbium sample as shown in Fig. 9.

their piston-cylinder apparatus, or it may be due to difficulties in interpreting the experimental curves which these authors point out and which causes them to qualify their result as tentative. It should be noted that above about 5 kbar they obtain a negative coefficient of -0.8°K/kbar which is in fair agreement with our value. Our results were obtained with unquestionably hydrostatic pressure and the measurements were of a simplicity encouraging confidence in the measurements.

Erbium showed a much more complex inductance behavior than dysprosium. A thermal hysteresis effect was again noted. Both warming and cooling curves are shown in Fig. 9. These data were taken cooling slowly from 77 to 4.2°K and then warming slowly at a rate of about 6°K/h. Two peaks are observed on cooling and three on warming. The Curie temperature of erbium is reported from neutron-diffraction,[19] specific-heat,[20] and magnetic measurements[21] to be at about 19.6°K. Specific heat and magnetic data have also revealed a transition at 53.5°K, while neutron diffraction work shows that above 52°K only the c component of the magnetic moment is modulated, whereas at lower temperature the perpendicular component is also modulated. The low-temperature and high-temperature peaks on the warming curves in Fig. 9 correspond to these two temperatures, respectively. The middle peak occurring at about 30°K on warming and the huge peak at 25°K on cooling are not understood and do not seem to correlate with other work. The temperatures of all of the peaks are pressure dependent, except the cooling peak at 25°K whose temperature does not seem to depend on pressure up to at least 6 kbar. A blank run was made with the sample removed to check that we were not observing some extraneous effect and the inductance was found to vary smoothly and, of course, to be very much smaller. Thus there seems no doubt that all the peaks are characteristic of erbium. The peak at 20°K which we associate with the Curie transition is weak and washes out with pressure above about 3 kbar. At the lower pressures, however, we deduce a pressure shift of -0.8 ± 0.2°K/kbar, which we take as a rough value for dT_c/dP.

The pressure shift of the upper peak on both warming and cooling is shown in Fig. 10. The position of the warming peak is a linear function of pressure, but some curvature exists on the cooling data at the higher pressure. However, the average slopes are nearly the same. From the warming curve, which is accepted as the correct one to use, we deduce

$$dT/dP = -1.3\pm0.2\text{°K/kbar}.$$

Note added in proof. Since the completion of the manuscript an article by T. Okamoto, N. Iwata, S. Ishida, and E. Tatsumoto [J. Phys. Soc. Japan **21**, 2727 (1966)] has come to our attention. They have studied the pressure dependence of the magnetic transitions in dysprosium to about 6 kbar using a magnetoresistance technique. Their pressure coefficients are in fairly good agreement with ours.

[19] J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **140**, A1896 (1965).
[20] R. E. Skochdopole, M. Griffel, and F. H. Spedding, J. Chem. Phys. **23**, 2258 (1955).
[21] R. W. Green, S. Legvold, and F. H. Spedding, Phys. Rev. **122**, 827 (1961).