

Effect of Pressure on the Magnetic Properties and Crystal Structure of Gd, Tb, Dy, and Ho

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X-ray diffraction powder patterns taken at high pressure suggest by analogy to Gd that Tb, Dy, and Ho have first-order transitions from a hcp to a Sm-type structure at high pressure. The c/a ratio of the hcp phases increases with pressure toward the ideal value. The change of the Curie or Néel temperature with pressure of Gd, Tb, Dy, and Ho has been measured up to 85 kbar by an ac method in which the sample forms the core of a transformer. The first-order transitions are observed in changes in the magnetic properties. The initial susceptibility shows two new peaks in isobaric temperature cycles made above the transitions. The difference between the ordering temperature of the low- and high-pressure phases near the transition are -37 , -21 , -12 , and -9°K for Gd, Tb, Dy, and Ho, respectively. The change in the Curie point of Gd(I) is $-1.72 \pm 0.7^\circ\text{K/kbar}$. The changes in Néel temperature are: Gd(II) -1.46 ± 0.11 , Tb(I) -1.07 ± 0.03 , Tb(II) -0.83 ± 0.08 , Dy(I) -0.66 ± 0.04 , Dy(II) -0.67 ± 0.07 , Ho(I) $-0.48 \pm 0.01^\circ\text{K/kbar}$. The results are compared with other measurements on rare-earth metals.

THE crystallographic and magnetic properties of the lanthanide elements exhibit striking differences as the number of $4f$ electrons increases. The heavy rare earths from Gd to Lu with the exception of Yb crystallize in the hexagonal close-packed (hcp) structure with a c/a ratio of approximately 1.58. The lighter rare earths with the exception of Eu crystallize in structures having more complicated stacking sequences of the hexagonal layers. The c/a ratios of the lighter sequence, when corrected for the increased stacking, are approximately 1.62 which is close to the ideal value of 1.633.¹ The magnetic properties of the rare-earth metals are also complex. The metals which contain a partially filled $4f$ shell have ordering transitions as a function of decreasing temperature from a paramagnetic to an antiferromagnetic and/or a ferromagnetic state. From neutron-diffraction studies, a wide variety of oscillatory magnetic structures have been proposed for the different rare-earth metals, and these have been reviewed by Koehler.²

The effect of pressure on the physical properties of the lanthanides has been studied in several laboratories. The change in the electrical resistance with pressure was first investigated by Bridgman. He found irregularities (cusps) in almost all the rare earths. For the elements discussed in the present paper there were anomalies in Gd, Dy, and Ho. (Tb was not studied.) There were cusps in the electrical resistivity of Gd at 20–25 kbar, Dy at 70–80 kbar, and of Ho at 30–40 kbar.^{3,4} The pressure at which the cusp in Dy occurs is probably about 30% too high as a result of pressure gradients in Bridgman's opposed anvil apparatus. More recently electrical resistivity measurements to higher pressures have been reported by Stager and Drickamer⁵

and Stromberg and Stephens.⁶ The former group confirm Bridgman's results on Dy at 60–80 kbar. The latter workers failed to find the transition in Gd and reported a transition pressure of 52 kbar for Dy. They also found a cusp in Tb at 27 kbar. Thus anomalies have been reported for Gd, Tb, Dy, and Ho at 20–25, 27, 52, and 30–40 kbar, respectively.

Recently, Jayaraman and Sherwood have been able to establish the structure of Gd above 35 kbar by quenching experiments.⁷ They found that the high-pressure phase had the Sm-type structure. Similar experiments by the same authors on Sm metal indicated that at high pressures Sm transforms to the double hexagonal close-packed La structure (dhcp).⁸ On the basis of these experiments and the transition from dhcp to fcc that has been reported in La,^{9–11} Pr,¹¹ and Nd,¹¹ Jayaraman proposed that the polymorphic transitions under pressure in the trivalent rare-earth metals is in the order hcp \rightarrow Sm-type \rightarrow dhcp \rightarrow fcc.

An extensive study of the electrical resistance of Dy as a function of temperature and pressure has been made by Souers and Jura.¹² They proposed a phase diagram for Dy and were able to determine the change in the Néel temperature with pressure up to 45 kbar. Their value of $dT_N/dp = -0.62 \pm 0.04^\circ\text{K/kbar}$ is in fair agreement with the similar measurement of Landry and Stevenson of $-0.56 \pm 0.02 \times 10^3^\circ\text{K/kbar}$.¹³ Jamieson has made x-ray diffraction measurements on Dy up to ~ 160 kbar but has been unable to establish the nature of the transition unambiguously.¹⁴

⁶ H. D. Stromberg and D. R. Stephens, *J. Phys. Chem. Solids* **25**, 1015 (1964).

⁷ A. Jayaraman and R. C. Sherwood, *Phys. Rev. Letters* **12**, 22 (1964).

⁸ A. Jayaraman and R. C. Sherwood, *Phys. Rev.* **134**, A691 (1964).

⁹ D. B. McWhan and W. L. Bond, *Rev. Sci. Instr.* **35**, 626 (1964).

¹⁰ D. McWhan, P. W. Montgomery, H. D. Stromberg, and G. Jura, *J. Phys. Chem.* **67**, 2308 (1963).

¹¹ G. J. Piermarini and C. E. Weir, *Science* **144**, 69 (1964).

¹² P. C. Souers and G. Jura, *Science* **145**, 575 (1964).

¹³ P. Landry and R. Stevenson, *Can. J. Phys.* **41**, 1273 (1963).

¹⁴ J. C. Jamieson, *Science* **145**, 572 (1964).

¹ K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand Company, Princeton, New Jersey, 1961).

² W. C. Koehler, *J. Appl. Phys.* **36**, 1078 (1965).

³ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **82**, 83 (1953).

⁴ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **83**, 3 (1954).

⁵ R. A. Stager and H. G. Drickamer, *Phys. Rev.* **133**, A830 (1964).

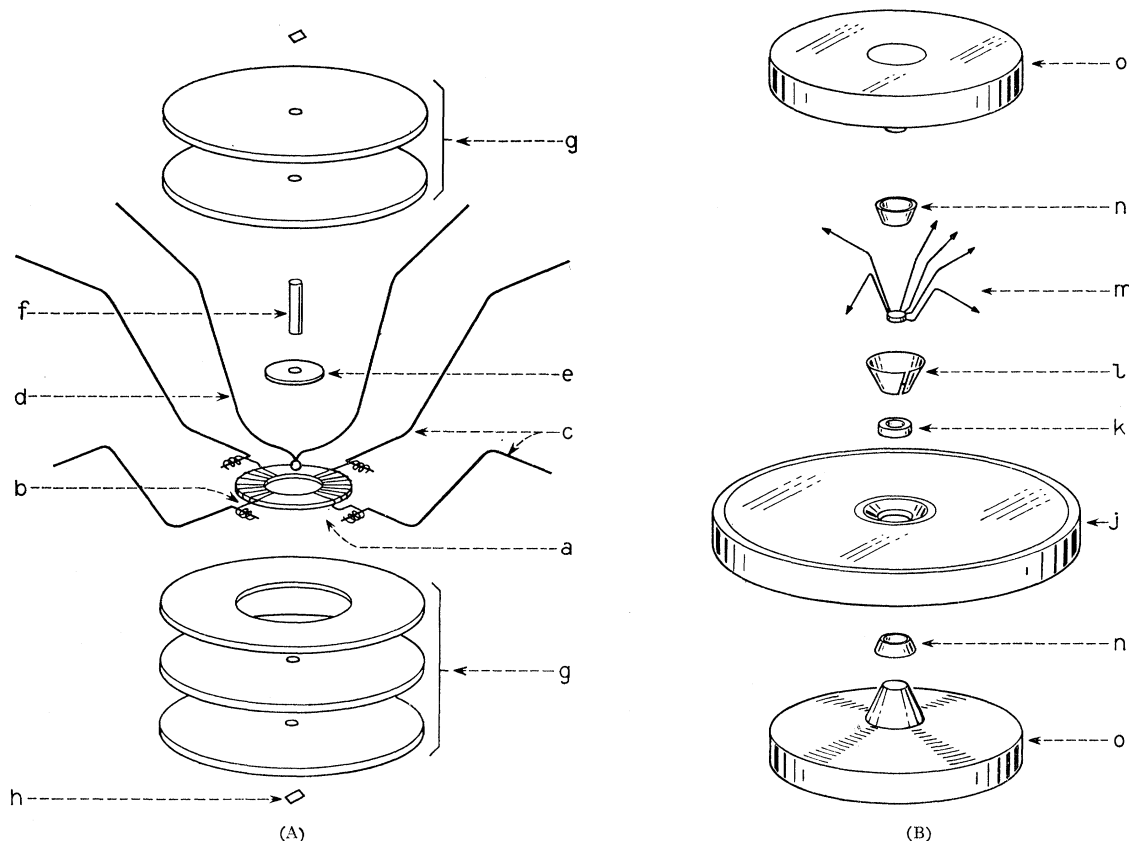


FIG. 1. (A) Sample cell assembly: (a) sample, (b) No. 44 Cu wire primary and secondary coils, (c) 0.005-in. Mo leads, (d) Chromel-Alumel thermocouple, (e,g) AgCl disks, (f) 0.010-in. Bi wire, (h) Pt contacts. (B) Girdle die assembly: (j) girdle-tungsten carbide supported by maraging steel jacket, (k,n) pyrophyllite gaskets, (l) 0.001-in. mica, (m) sample cell, (o) anvils-tungsten carbide with maraging steel jacket.

The change in the Curie point of Gd with pressure has been determined by several workers: Patrick ($-1.2^{\circ}\text{K}/\text{kbar}$),¹⁵ Block and Pauthenet ($-1.53^{\circ}\text{K}/\text{kbar}$),¹⁶ and Robinson, Milstein, and Jayaraman ($-1.60^{\circ}\text{K}/\text{kbar}$).¹⁷ The last study was made up to 40 kbar. At the transition to the Sm-type structure they observed a transition to an apparently nonferromagnetic state. Above the transition, isobaric temperature cycles showed two new peaks in the initial permeability, but no explanation for these peaks was given.

In order to tie these phenomena together a study of the crystal structure and magnetic properties of Gd, Tb, Dy, and Ho was undertaken. Some of the questions to be answered are: (1) Is the trend in crystal structure suggested by Jayaraman continued from Gd to Ho? (2) What is the effect of these first-order phase changes on the magnetic properties? (3) What information about the volume dependence of the exchange interaction in the rare-earth metals can be obtained?

¹⁵ L. Patrick, *Phys. Rev.* **93**, 384 (1954); L. D. Adams and J. W. Green, *Phil. Mag.* **12**, 361 (1931).

¹⁶ D. Bloch and R. Pauthenet, *Compt. Rend.* **254**, 1222 (1962).

¹⁷ L. B. Robinson, F. Milstein, and A. Jayaraman, *Phys. Rev.* **134**, A187 (1964).

EXPERIMENTAL

A. X-Ray Measurements

The Debye-Scherrer, high-pressure, x-ray powder camera used in this study has been described.⁹ The diluted sample fills a 0.25-mm-diam hole in a disk of amorphous boron dispersed in epoxy resin. The samples were prepared by placing a thin layer of metal filings on a glass slide and then by covering them with a drop of GE 7031 varnish. A strip of the metal-impregnated varnish was then loaded into the boron-epoxy disk. The disk is pressed between tungsten carbide anvils to the desired pressure. MoK_{α} radiation is used. The pressure calibration of this camera cannot be determined accurately without the use of an internal standard.¹⁸ In the present study the x-ray measurements were designed to establish the structural nature of the anomalies which had been observed in studies of the variation of the electrical resistance with pressure. Therefore, no attempt was made to establish an accurate pressure calibration. The estimated maximum pressure was

¹⁸ D. B. McWhan, Paper 64-WA/Pt-22 ASME, New York, 1964 (to be published).

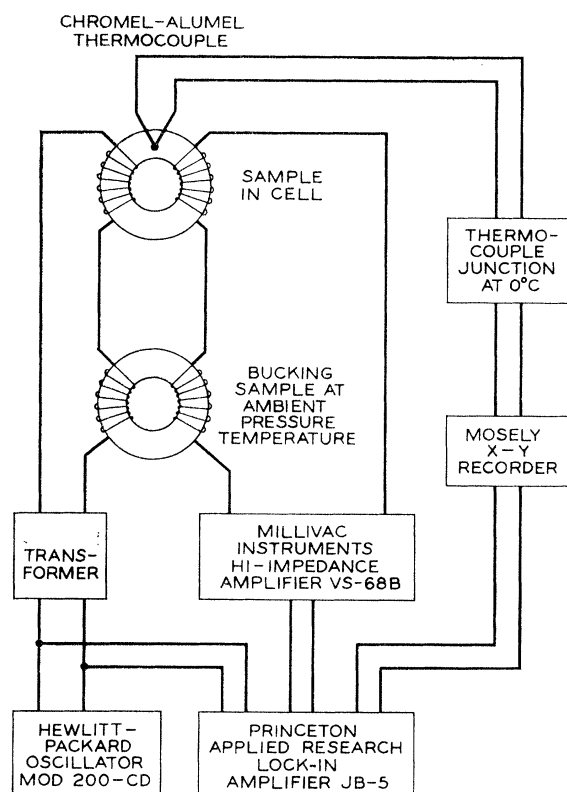


FIG. 2. Schematic drawing of electronics used in Curie and Néel point determination.

~ 85 kbar. The total error, both systematic and measurement, in the observed diffraction angles is estimated to be $\pm 0.03^\circ$ in θ .¹⁸ In order to minimize the error resulting from eccentricity and absorption, a correction curve was made by comparing the zero-load (1-atm) diffraction angles with the angles calculated from the lattice parameters reported by Spedding *et al.*¹⁹ The data obtained at pressure were then corrected on the assumption that the physical errors do not change appreciably with pressure. This procedure probably increases the precision by about a factor of 2.

B. Magnetic Measurements

A small girdle die of the type described by Stromberg and Stephens was used to attain pressures from 5 to 90 kbar in a cylindrical cavity 14.3 mm in diameter and ~ 2.5 mm high.⁶ The gasketing system is based on one described by Montgomery.²⁰ The die and sample cell assembly are shown in Fig. 1. The die is placed in a thermally insulated pot, and the load is transmitted through insulating stacks each composed of 100 alternate stainless-steel and mica disks 0.4 mm thick. The

load from a 300-ton press is measured with a strain-gauge instrumented load cell²¹ which is in series with the die. This avoids errors resulting from friction in the seals of the hydraulic ram. The pressure is calibrated by observing the known transitions in the electrical resistance of a bismuth wire mounted axially in the center of the sample cell. The room-temperature transition pressures used in the calibration were Bi I-II 25.4 kbar, Bi II-III 26.9 kbar, and Bi III-V 82 kbar.^{20,22,23} A linear calibration curve of applied load versus pressure passing through the origin was usually obtained. The precision in the pressure relative to the bismuth transitions is estimated to be ± 1 kbar at low pressures and ± 3 kbar at the highest pressures. It was assumed that at constant load the pressure in the cell did not change with temperature. The temperature was monitored by a Chromel-Alumel thermocouple in intimate contact with the sample in the cell. The temperature was calculated using liquid nitrogen as the reference. The estimated error in the temperature varies with the size and shape of the signal change at the transition but the average error is $\pm 3^\circ\text{K}$. No correction was made for the effect of pressure on the thermocouple, and all measurements were made by isobaric temperature cycles. As the AgCl pressure transmitting medium is probably much less plastic at low temperature, pressure was changed only when the temperature was near 0°C . The temperature was cycled between room temperature and 77°K by filling and draining the pot with liquid nitrogen. By controlling the nitrogen flow a cooling rate of $\sim 5^\circ\text{K}/\text{min}$ is obtained. A warming rate of $\sim 1.5^\circ\text{K}/\text{min}$ is obtained by wrapping a heating tape around the die. The ordering temperature measured on cooling and warming never differed by more than $1-2^\circ\text{K}$.

The change in the Curie or Néel temperature with pressure is measured by an ac method in which the sample forms the core of a transformer.¹⁵ The samples are washers 4.75 mm o.d., 2.36 mm i.d., and 0.25 mm thick. The samples are coated with GE 7031 varnish for insulation. The primary and secondary coils consist of 30 turns each of polyurethane-coated No. 44 copper wire. A schematic drawing of the associated electronics is shown in Fig. 2. A frequency of 10 kc/sec was used, and a field of ~ 1 Oe was produced by the primary.

At a paramagnetic to ferromagnetic transition, there is a sharp rise in the secondary voltage which is proportional to the change in the initial permeability. The Curie temperature was obtained by extrapolating the curve to the temperature at which it intersects an extrapolation of the background. At a paramagnetic to antiferromagnetic transition, the secondary voltage rises sharply to a peak and then drops off again almost

²¹ Supplied by H. D. Stromberg, Oakland, California.

²² G. C. Kennedy and P. N. Lamori, *J. Geophys. Res.* **67**, 851 (1962).

²³ A. A. Giardini and G. A. Samara, Paper 64-WA/Pt-10, and W. A. Stark, Jr., and G. Jura, Paper 64-WA-Pt-28 ASME, New York, 1964 (unpublished).

¹⁹ F. H. Spedding, A. H. Daane, and K. W. Herrmann, *Acta Cryst.* **9**, 559 (1956).

²⁰ P. W. Montgomery, Paper 64-WA/Pt-18 ASME, New York, 1964 (unpublished).

to background. The Néel temperature was taken as the peak in the curve.

The rare-earth metals were purchased from Research Chemicals, Burbank, California, and the stated purity was 99.9%. The samples were not annealed after machining or filing.

RESULTS

A. X-Ray Measurements

Obtaining good high-pressure x-ray powder patterns of hexagonal metals is severely complicated by preferred orientation effects. These result from the quasi-hydrostatic nature of the applied pressure in our x-ray camera. There is a uniaxial component perpendicular to the plane of the x-ray measurements. As a result of the preferred orientation the reflections with l greater than 1 are very weak and are not observable at the higher pressures. It is known that a phase of Gd having the samarium-type structure can be retained metastably by quenching from high temperature and pressure.⁷ By observing the change in the x-ray pattern of gadolinium at the transition and then by comparing it with the results obtained on other rare earths, one can infer by analogy that a similar transition occurs. The x-ray measurements on Gd are shown diagrammatically in Fig. 3. In order to compare the different patterns ($\log d + C$) has been plotted and C chosen to normalize the patterns to the 11.0 reflection which is common to both structures. The length of the bars is proportional to the visually estimated intensity. As can be seen, the 10.1 reflection of the hcp structure broadens and splits into the 10.4 and 01.5 reflections of the Sm-type structure at the transition. On releasing the pressure the relative pattern remains unchanged. If the sample is removed from the camera, powdered, and a pattern obtained in a 114.6-mm Norelco powder camera using filtered Cr radiation, the top pattern is obtained. This pattern agrees well with that calculated for the Sm-type structure. As a further check a pattern of Sm metal at 10 kbar was obtained and found to agree qualitatively with the patterns obtained from Gd above the transition. To compare these results with those obtained from at least two independent samples of the other rare-earth metals (Tb, Dy, and Ho) a plot of the first line versus the second has been made (Fig. 4). As the two lines are in a similar angular range the physical

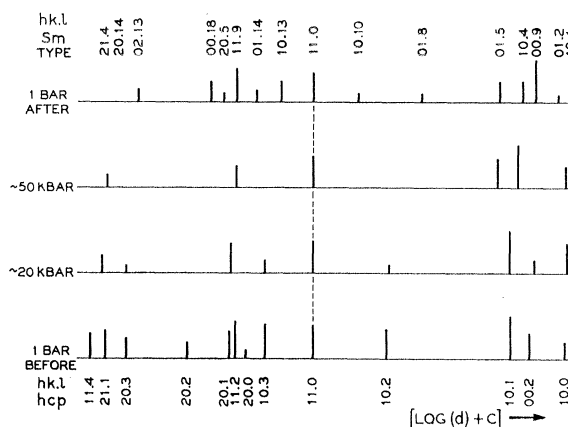


FIG. 3. Diagram of powder patterns of Gd before and after transition from hcp to Sm-type structure.

errors resulting, for example, from eccentricity and absorption are minimized. In the hcp phase these lines correspond to the 10.0 and 10.1 reflections and in the Sm-type structure to the 10.1 and 10.4 reflections. As can be seen in Fig. 4, all four metals show a similar transition which, by analogy to Gd, is from the hcp to the Sm-type structure [space group $R\bar{3}m$ with atoms in $1a(000)$ and $2c \pm (uuu)$].²⁴ The available data are not sufficient to determine the positional parameter, but presumably it is similar to that observed in Sm metal ($u=0.222$).²⁴ The lattice parameters for the hexagonal cell above the transition are given in Table I.

The change in the c/a ratio of the low-pressure phase with pressure can be calculated from the ratio $d_{10.1}/d_{10.0}$. As no pressure calibration was made, only the change in the ratio from 1 atm to the transition can be given. The percentage change is given in Table I.

B. Magnetic Measurements

The structural transitions observed in the x-ray studies are also seen in the magnetic measurements. At pressures above the transition, isobaric temperature cycles show two new peaks at lower temperatures in the initial permeability. A set of curves for Dy is shown in Fig. 5. The transitions are very sluggish so that the peak resulting from the low-pressure phase is still observable as high as 30 kbar above the transition pressure. On releasing pressure the reverse transformation is also sluggish, and, for example, in Dy traces of the peaks from the high-pressure phase are still observable as low as 10 kbar. In all the materials studied with the exception of Ho, the forward transition was completed below 85 kbar. In the case of holmium the occurrence of a second peak in the high-pressure phase can only be inferred. The initial permeability is rising sharply at 77°K, but the peak has not been passed. At 5 kbar the

TABLE I. X-ray data for Gd-Ho at high pressure.

	hcp phase		Sm-type structure		
	$\Delta(c/a)\%$ 1 atm to trans	(c/a) atm trans	Lattice $a\text{\AA}$	Parameters $c\text{\AA}$	P kbar
Gd	$+2.5 \pm 0.7$	1.63	3.49 ± 0.01	25.6 ± 0.1	35 ± 5
Tb	$+2.3 \pm 0.7$	1.62	3.41 ± 0.01	24.5 ± 0.1	60 ± 10
Dy	$+1.2 \pm 0.7$	1.59	3.34 ± 0.01	24.5 ± 0.1	75 ± 10
Ho	$+1.0 \pm 0.7$	1.59	3.34 ± 0.01	24.1 ± 0.1	85 ± 10

²⁴ F. H. Ellinger and W. H. Zachariasen, J. Am. Chem. Soc. 75, 5650 (1953). A. H. Daane, R. E. Rundle, H. S. Smith, and F. H. Spedding, Acta Cryst. 7, 532 (1954).

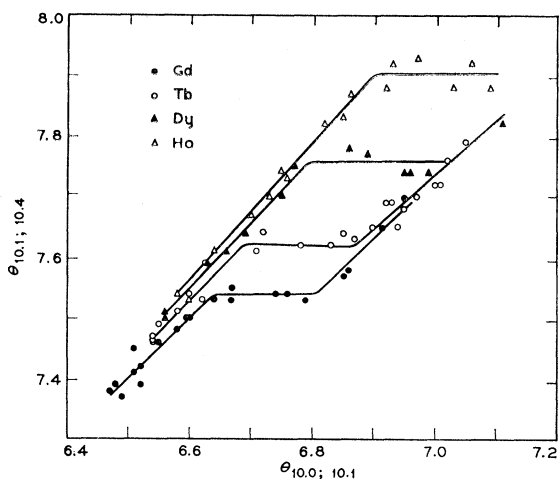


FIG. 4. Comparison of x-ray data for Gd through Ho.

Curie temperature in Dy is observed above 77°K but is too low to measure at 10 and 15 kbar. The Curie point in Tb cannot be distinguished from the Néel point because of the small difference between the two ordering temperatures.

Gd exhibits more complex behavior than the other rare-earth metals studied. Even at 1 atm, weak-field magnetization measurements show a complex behavior.²⁵ It is the only material studied which goes ferromagnetic without first passing through an antiferromagnetic state. A set of curves for Gd is shown in Fig. 6. As the pressure is increased a second broad hump appears. Between 20 and 25 kbar three peaks grow in, and the anomalies from the low-pressure phase decrease in amplitude. Between 5 and 30 kbar the signal at the ordering temperature decreases by a factor of 25. The first of the three peaks is much smaller than the other two and disappears by 38 kbar. Holding a Gd sample at 34 kbar for 15 h caused the peaks from the low-pressure phase to disappear leaving only the two larger peaks. Around 50 kbar the first of these peaks decreases in amplitude and another peak grows in at a still lower temperature. Between 50 and 85 kbar, isobaric temperature cycles show two peaks. The results are further complicated by the differences in dT/dP of each peak. In all there are four peaks, the first two change at one rate and the last two at another. However, in the high-pressure phases of Tb and Dy, dT/dP is the same for both peaks in the high-pressure phase. It is difficult on the basis of the available data to unambiguously assign which peaks belong to which phase or whether they represent equilibrium conditions.

At least three independent samples of each metal were run, and all the data for the low-pressure phase and the first peak of the high-pressure phase are shown in Fig. 7. The data for the temperature variation of

²⁵ K. P. Belov and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. 42, 87 (1962) [English transl.: Soviet Phys.—JETP 15, 62 (1962)].

TABLE II. Change in ordering temperatures with pressures.

	T_λ	$T_0^\circ\text{K}$	$(dT/dP)^\circ\text{K/kbar}$	P range kbar
Gd (I)	291.8 ^a	292±2	-1.72±0.07	5-52
		(255)	(-1.4)	(25-38)
		247±4	-1.46±0.11	25-52
		218±2	-1.19±0.04	25-84
Tb (I)	227.7 ^b	227±1	-1.07±0.03	4-71
		196±5	-0.83±0.08	35-85
Dy (I)	174 ^c	167±4	-0.85±0.06	35-85
		179±2	-0.66±0.04	5-77
Ho (I)	131.6 ^d	166±5	-0.67±0.07	49-85
		145±6	-0.74±0.08	49-85
		133±1	-0.48±0.01	5-82
		(126±14)	(-0.5±0.2)	70-82

^a M. Griffel, R. E. Skochdopole, and F. H. Spedding, Phys. Rev. 93, 657 (1954).

^b L. D. Jennings, R. M. Stanton, and F. H. Spedding, J. Chem. Phys. 27, 909 (1957).

^c M. Griffel, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. 25, 75 (1956).

^d B. C. Gerstein, M. Griffel, L. O. Jennings, R. E. Miller, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. 27, 394 (1957).

each peak with pressure were fitted to a straight line by the method of least squares. The constants with their standard deviations and the applicable pressure range are tabulated in Table II.

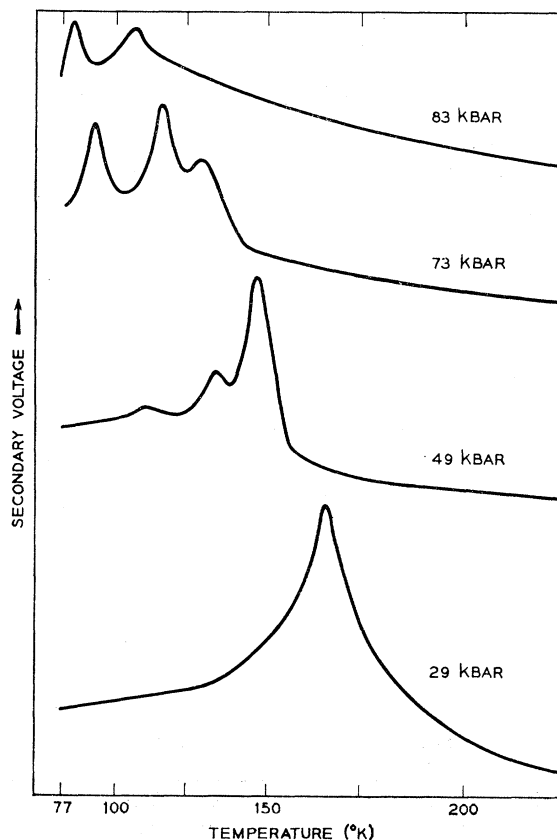


FIG. 5. Relative secondary voltage as a function of temperature for Dy at different pressures.

This method is reliable for determining changes in the Curie temperature but is not an accurate measure of the Curie temperature itself.¹⁵ The ordering temperatures at 1 atm obtained by extrapolation agree fairly well with values reported in the literature. The ordering temperatures observed in heat-capacity studies are listed in Table II for comparison.

The differences in the ordering temperature of the two phases at the lowest pressure at which the high-pressure phase is observed in the magnetic measurements are: Gd 37°K at 25.4 kbar, Tb 21°K at 35 kbar, Dy 12°K at 49 kbar, and Ho 9°K at 76 kbar. In each case the ordering temperature of the high-pressure phase is lower than that of the low-pressure phase.

The temperature difference of the two peaks of the high-pressure phase is independent of pressure within experimental error. The differences are: Gd 20°K at 25.4 kbar, Tb 29°K at 35 kbar, Dy 23°K at 49 kbar, Ho (estimated) 15–20°K at 76 kbar. The figures quoted for Gd are based on the larger two of the three peaks that appear around 20–25 kbar.

DISCUSSION

A definite sequence of crystal structures as a function of pressure and atomic number seems to exist for the trivalent rare-earth metals.⁸ This trend from hcp \rightarrow Sm type \rightarrow dhcp \rightarrow fcc can be viewed as a step-wise progression from hexagonal to cubic nearest-neighbor symmetry. If each structure is considered as stacking sequences of close-packed layers with *ABA* being hexagonal (*H*) and *ABC* cubic (*C*), then the sequence becomes *H* \rightarrow *CH*₂ \rightarrow *2CH* \rightarrow *C*.²⁶ In the limited pressure range studied, Tb, Dy, and Ho, by analogy to Gd, transform to the Sm-type structure. The magnetic changes observed in Gd around 50 kbar may indicate

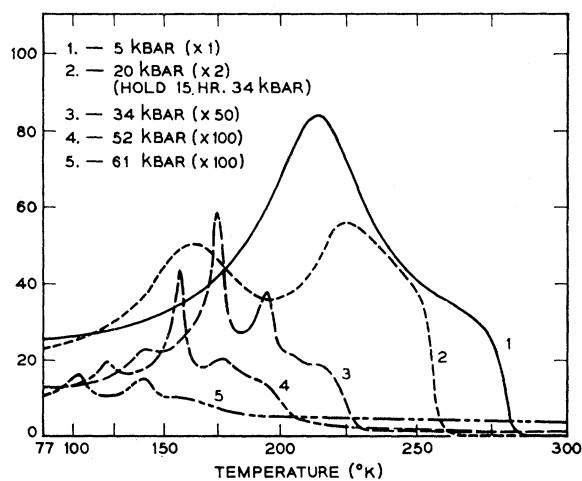


FIG. 6. Secondary voltage versus temperature for Gd at different pressures.

²⁶ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 407.

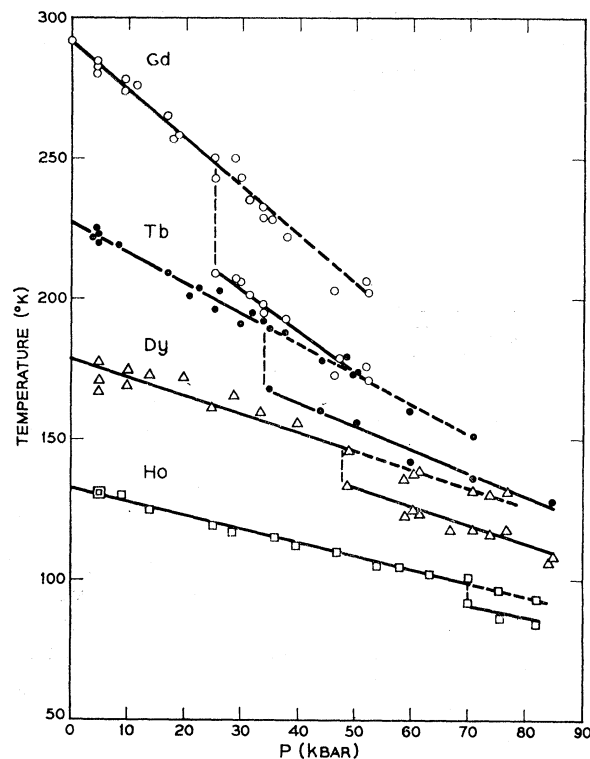


FIG. 7. Change in ordering temperature with pressure.

a second transition. If the trend is continued Gd may go to the dhcp structure but no evidence for this was found in the x-ray studies. It would be of interest to extend the x-ray studies to higher pressures to see if other transitions would occur.

This sequence may be explained by a decrease in the localization of the 4*f* electrons with increasing pressure. The degree of 4*f* localization decreases with decreasing atomic number as evidenced by the electronic transition in metallic Ce and the tendency to have multiple oxidation states in Ce and Pr. The 5*f* electrons in the actinide series are not substantially localized until americium which is similar to lanthanum in many ways.²⁷ Therefore, it is not unreasonable to expect that by decreasing the volume of a rare-earth or actinide metal the participation of the 4*f* or 5*f* electrons in metallic bonding will be increased. Admittedly this effect will be very small except at the beginning of the series, but it may be sufficient to cause the trend from hexagonal to cubic symmetry.

Polymorphic transitions in the rare-earth metals are very sensitive to the value of the *c/a* ratio. In studies of the crystal structure of the rare-earth metals at high temperature, Spedding, Hanak, and Daane found a limiting value of the *c/a* ratio at the hcp-bcc transition.²⁸

²⁷ D. B. McWhan, B. B. Cunningham, and J. C. Wallmann, *J. Inorgan. Nucl. Chem.* **24**, 1025 (1962).

²⁸ F. H. Spedding, J. J. Hanak, and A. H. Daane, *J. Less-Common Metals* **3**, 110 (1961).

TABLE III. Anomalies at second-order transition.

	Experimental	Calculated	
	ΔC_p cal/deg/mole	$\Delta\alpha \times 10^6$ $^{\circ}\text{K}^{-1}$	$\Delta\beta \times 10^{15}$ cm^2/dyn
Gd	6 ^a	-72	124
Tb	11 ^b	-110	118
Dy	8.5 ^c	-67	44
		-64 ^d	40 ^d
Ho	5.4 ^e	-42	20

^a Reference a of Table II.

^b Reference b of Table II.

^c Reference c of Table II.

^d Reference 12.

^e Reference d of Table II.

The c/a ratio at the transition in Y, Gd, Tb, Ho, and Lu was 1.601 ± 0.001 . The lighter rare earths La through Nd have a limiting ratio of 1.619 ± 0.002 . The high-pressure x-ray studies on Gd, Tb, Dy, and Ho are of limited accuracy, but they do indicate that the c/a ratio in the hcp phase increases with pressure toward the ideal value. For Gd and Tb the limiting value is around 1.62-1.63 which is the limiting ratio found for La through Nd in the high-temperature x-ray studies.

Below the observed ordering temperature, the high-pressure phases of Gd through Ho may be antiferromagnetic. This conclusion is based on the similarity in both shape and amplitude of the peaks in secondary voltage observed in Tb, Dy, and Ho at pressures below and above the first-order phase boundary. The peaks observed in Gd above 25 kbar are similar to those observed in the other three metals at high pressures, and by analogy to them the high-pressure phase of Gd is also probably antiferromagnetic below the ordering temperature.

The two peaks observed in isobaric temperature cycles above the first-order transition pressure suggest that two independent ordering transitions exist. The crystallographic evidence presented above indicates that there is a difference in the number of symmetry sites that are occupied in the low- and high-pressure phases. In the hcp phase all the atoms have hexagonal symmetry; whereas, in the Sm-type and dhcp structures varying proportions of atoms have hexagonal and cubic nearest-neighbor symmetry. From single-crystal neutron-diffraction studies on Nd, which has the dhcp structure, a model has been proposed in which the hexagonal sites order in an antiferromagnetic arrangement at 19°K and the cubic sites remain unordered until 7.2°K .²⁹ It is not unreasonable to suppose that a similar situation exists in the Sm-type high-pressure phases of Gd, Tb, Dy, and Ho and that the two types of crystallographic sites order at different temperatures.

In each of the four metals studied the transition to the high-pressure phase is accompanied by a decrease in the ordering temperature. As the high-pressure phase

must have a smaller volume, the change in magnetic energy with volume is positive. This is in agreement with the observed changes in ordering temperature with volume in any one phase. In fact there is a good correlation between the magnitude of the slope and the ΔT at the transition. By comparison samarium shows the opposite effect. The quenched high-pressure dhcp phase has a Néel temperature of 27°K as compared with 15°K for normal samarium.⁸ On the basis of the correlation between dT_c/dP or dT_N/dP and ΔT_c or ΔT_N for Gd through Ho, this implies that the Néel temperature in samarium will rise with increasing pressure.

There have been several determinations of dT_c/dP for Gd over various pressure ranges. These include -1.2 ,¹⁵ -1.53 ,¹⁶ and -1.60 $^{\circ}\text{K}/\text{kbar}$.¹⁷ The value of -1.72 ± 0.07 $^{\circ}\text{K}/\text{kbar}$ obtained in the present study agrees reasonably well with the later literature values. Reported values of dT_N/dP in Dy are¹³ -0.56 ± 0.02 and -0.62 ± 0.04 $^{\circ}\text{K}/\text{kbar}$.¹² Our value of -0.66 ± 0.05 $^{\circ}\text{K}/\text{kbar}$ is in reasonable agreement. In both Gd and Dy our values are high suggesting a systematic error, but the difference is not statistically significant.

On the assumption that the magnetic transitions are second order, dT/dP can be related by thermodynamic equations to the anomalies in the coefficient of thermal expansion ($\Delta\alpha$), compressibility ($\Delta\beta$), and heat capacity at constant pressure (ΔC_p). The relations are³⁰

$$\frac{dT}{dP} = \frac{TV\Delta\alpha}{\Delta C_p} = \frac{\Delta\beta}{\Delta\alpha}$$

Values for $\Delta\alpha$ and $\Delta\beta$ are calculated from experimental values of ΔC_p and dT/dP and are presented in Table III. The coefficient of thermal expansion of Gd, Tb, and Dy has been measured by Barson, Legvold, and Spedding.³¹ Their data confirm the sign and approximate magnitude of $\Delta\alpha$ at the ordering temperature.

The logarithmic dependence of the ordering temperature with volume can be calculated using Bridgman's compressibilities (κ) on Gd, Dy, and Ho and interpolating to Tb.^{1,4} This quantity, which is approximately equal to minus the magnetic Grüneisen parameter (γ_m), has been calculated for the Néel temperature of cerium and the lower transition in neodymium by Andres.³² He measured the change in thermal expansion ($\Delta\alpha$) in La, Ce, and Nd at low temperatures. Assuming that the lattice and electronic contributions are the same in La, Ce, and Nd, the magnetic contribution could be calculated from

$$-\frac{d \ln T_N}{d \ln V} = \frac{V(\alpha_{Ce} - \alpha_{La})}{\kappa(C_{Ce} - C_{La})} = \gamma_m,$$

and a similar equation for Nd. His results are compared

³⁰ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), p. 434.

³¹ F. Barson, S. Legvold, and F. H. Spedding, *Phys. Rev.* **105**, 418 (1957).

³² K. Andres, *Phys. Kondensierten Materie* **2**, 294 (1964).

²⁹ R. M. Moon, J. W. Cable, and W. C. Koehler, *J. Appl. Phys.* **35**, 1041 (1964).

TABLE IV. Variation of $d \ln(T)/d \ln(V)$ in rare-earth metals.

R.E.	Ce	Nd	Sm	Gd	Tb	Dy	Ho
$\frac{d \ln(T)}{d \ln(V)}$	2.5	0.7	<0	2.2	1.8	1.4	1.4
				2.0		1.3	
				1.6		1.2	
Ref.	32	32	8 ^a	
				16 17		12	
				15		13	

^a See text.

with ours in Table IV. From ΔT_N between the two phases of Sm it was inferred above that $dT_N/dP > 0$ and therefore $d \ln T_N/d \ln V < 0$. The data in Table IV fall into two distinct families as a function of atomic number with a discontinuity at the middle of the rare-earth series. Recently a similar relation has been found by Jayaraman for the initial melting slopes of the rare earths.³³

In studying the exchange interaction in magnetic materials it is customary to construct a curve of exchange energy versus the ratio of the interatomic distance to the diameter of the unfilled shell. Robinson *et al.* have proposed that the transition elements and the ferromagnetic rare-earth elements should follow different interaction curves.¹⁷ They constructed such a curve for the ferromagnetic Curie points of the rare-earth metals based on experimental data. Their curve predicts a positive slope for dT_c/dP in Dy which is not in agreement with our results. It is of value to construct an interaction curve for the highest ordering temperature and to determine experimentally if a smooth curve of exchange energy versus interatomic distance is obtained. In order to eliminate the dependence of the ordering temperature on the quantum numbers, J , L , and S , the observed ordering temperatures are divided by the de Gennes function $(g-1)^2 J(J+1)$.³⁴ The ratio of the interatomic distance (R) to the diameter of the unfilled $4f$ shell (r) is estimated from (1) radii tabulated by Gschneidner,¹ (2) an extrapolation of Bridgman's volume compressibilities⁴ to 90 kbar and an interpolation for Tb, and (3) the Slater orbital method.³⁵ The resulting experimental exchange interaction curve is shown in Fig. 8. The data fall fairly well onto two curves representing the low- and high-pressure phases. Con-

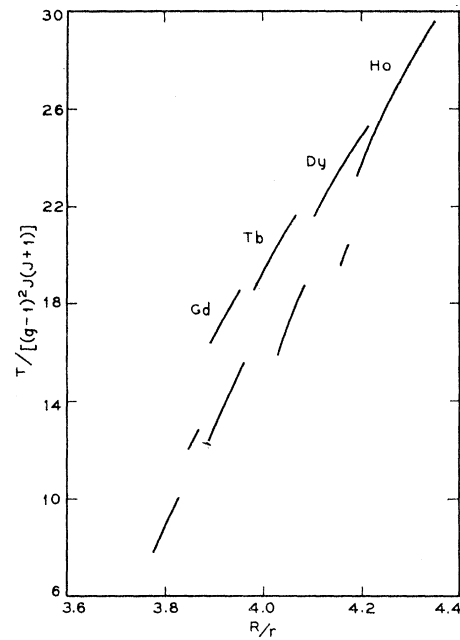


FIG. 8. Experimental exchange interaction curve for rare-earth metals Gd through Ho.

sidering the many assumptions and approximations involved, the fit to a smooth curve is reasonable. The curves indicate at least qualitatively that the exchange interaction increases smoothly on going from Gd to Ho, i.e., with increasing R/r .

In summary, the trend in crystal structure in the trivalent rare-earth metals (hcp \rightarrow Sm type \rightarrow dhcp \rightarrow fcc) is continued from Gd to Ho. This trend from hexagonal to cubic symmetry may reflect a slight decrease in the localization of the $4f$ electrons with decreasing volume. ΔT_c or ΔT_N at the transition is negative, and it is suggested that the hexagonal and cubic sites in the high-pressure phase order at different temperatures. Values of $(d \ln T)/(d \ln V)$ across the rare-earth series fall onto two curves with an apparent break in the middle of the series. For the heavy rare-earth metals a reasonably smooth curve of exchange energy $(T/[(g-1)^2 J(J+1)])$ versus interatomic distance (R/r) can be constructed.

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³³ A. Jayaraman, Phys. Rev. **139**, A690 (1965).

³⁴ P. G. deGennes, Compt. Rend. **247**, 1836 (1958).

³⁵ J. C. Slater, Phys. Rev. **36**, 57 (1930).