

## Effect of Pressure on the Curie Temperature of Rare-Earth Metals. I. Gadolinium<sup>†</sup>

LAWRENCE BAYLOR ROBINSON AND FREDERICK MILSTEIN\*

*Department of Engineering, University of California, Los Angeles, California*

AND

A. JAYARAMAN<sup>‡</sup>

*Institute of Geophysics, University of California, Los Angeles, California*

(Received 30 September 1963; revised manuscript received 18 November 1963)

An experimental investigation has been undertaken for the purpose of learning the effect of interatomic distance on the magnetic exchange interaction in ferromagnetic rare-earth metals. The first material which has been studied is gadolinium. The equipment used was the high-pressure apparatus of Professor G. C. Kennedy of the Institute of Geophysics (UCLA). A toroidal-shaped specimen of gadolinium was subjected to pressures up to about 40 kilobars (kbar). The gadolinium toroid served as a transformer core. A constant input voltage was applied and the output voltage was studied as a function of pressure and temperature. The Curie temperature, obtained from the output voltage, was found to be depressed linearly with pressure at a rate of  $-1.60^{\circ}\text{C}/(\text{kbar})$  up to 21.5 kbar. Between 21.5 and 26.7 kbar a phase transition to a nonferromagnetic state occurred.

### I. INTRODUCTION

IT is known that ferromagnetism is exhibited by only a small number of elements, viz., iron, cobalt, nickel, and the rare earths, gadolinium, terbium, dysprosium, holmium, erbium, and thulium. This is largely because the exchange interaction, which is responsible for the ferromagnetic alignment of the electron spins, depends critically upon the interatomic distance in the crystal. A physical measure of this interaction is the Curie temperature, the temperature at which the random thermal energy and the exchange energy become equal. As the material is heated through the Curie point, the electron spins lose their net spontaneous alignment, and a transition from the ferromagnetic to the paramagnetic state occurs. By subjecting a ferromagnetic material to large pressures and observing the change in the Curie point, information may be obtained about the dependence of the exchange interaction upon interatomic distance.

The purpose of this article is to report on the experimental determination of the effect of high pressure, up to about 40 000 bar (40 kbar), on the Curie point of gadolinium (Gd). The effect of pressure on the Curie point of Gd was first measured by Patrick<sup>1</sup> and later by Bloch and Pauthenet.<sup>2</sup> Patrick's investigation was in the pressure range 0 to 8 kbar. He found the Curie point to vary linearly with pressure at the rate  $-1.2^{\circ}\text{C}/\text{kbar}$ . Bloch and Pauthenet's work was in the pressure range 0 to 6 kbar. They also found the Curie point to be linearly depressed with pressure, but at a slightly

greater rate,  $-1.53^{\circ}\text{C}/\text{kbar}$ . Neither Patrick nor Bloch and Pauthenet have presented a theoretical basis for the observed decrease of the Curie temperature of Gd with pressure.

The work reported on herein is different from the above-mentioned work in that in the present experimental work a considerably greater range of pressures was investigated. This was made possible by the greater utility of the high-pressure press kindly made available by Professor G. C. Kennedy (Institute of Geophysics, University of California, Los Angeles, California).

### II. EXPERIMENTAL WORK

#### A. Procedure

The method used for the detection of the ferromagnetic Curie point of the Gd specimen was similar to that used by Patrick, and (in earlier work) by Adams and Green.<sup>3</sup> The sample was used as the core of a small transformer. An alternating current of about  $\frac{1}{4}$  A rms at 1000 cps was fed to the primary windings. The output voltage across the secondary windings was recorded. As the sample changes from the paramagnetic to the ferromagnetic state, it undergoes a great increase in permeability and a large increase in secondary voltage occurs. A schematic diagram of the experimental setup is given in Fig. 1.

Pressures up to about 40 kbar were obtained by use of the apparatus of Professor Kennedy. The system is a piston-cylinder device which depends upon a  $\frac{1}{2}$ -in.-diam tungsten carbide piston, within a tungsten carbide pressure vessel, to generate the pressure. The apparatus has been described by Kennedy and La Mori.<sup>4</sup>

The gadolinium was purchased from the Jarrell-Ash

<sup>†</sup> Based on a thesis submitted by F. Milstein in partial satisfaction of the requirements for the degree of Master of Science in Engineering at the University of California, Los Angeles.

\* Supported in part by aid provided by the UCLA Space Science Center (Grant NSG 237-62 Libby) and UCLA Educational Development Program (Ford Foundation Fellowship).

<sup>‡</sup> Present address: Bell Laboratories, Murray Hill, New Jersey.

<sup>1</sup> L. Patrick, *Phys. Rev.* **93**, 384 (1954).

<sup>2</sup> D. Bloch and R. Pauthenet, *Compt. Rend.* **254**, 1222 (1962).

<sup>3</sup> L. H. Adams and J. W. Green, *Phil. Mag.* **12**, 361 (1931).

<sup>4</sup> G. C. Kennedy and P. N. La Mori, *Progress in Very High Pressure Research, Proceedings*, edited by F. P. Bundy, W. R. Hibbard, Jr., and H. M. Strong (John Wiley & Sons, Inc., New York, 1960), p. 304 ff.

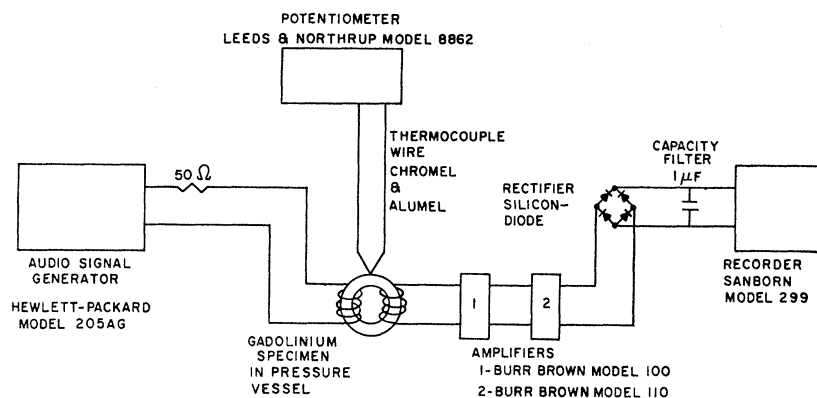


FIG. 1. Schematic diagram of experimental setup.

Company, in Newtonville, Massachusetts, whose suppliers are Johnson, Matthey and Company, Ltd., in London. It was specified by the vendor to contain less than 0.1% rare-earth metal impurities.

The gadolinium specimens were machined to the form of toroidal rings whose dimensions were nominally 0.75 cm outer diameter by 0.48 cm inner diameter by 0.1 cm thick. A 0.028-cm-thick saw cut, about 0.13 cm deep, was made in the specimen to serve as a thermocouple well. A chromel-alumel thermocouple junction was placed in this slot and the outer walls of the slot were squeezed in a vise so that the specimen would grip the thermocouple junction. Thus, the thermocouple, which was used to detect the temperature of the sample, was permanently embedded within the specimen.

To avoid shorting the windings to the specimen considerable care was taken in insulating the specimen. The gadolinium rings were first epoxy coated and then covered with a layer of masking tape. After this, the primary and secondary coils were wound snugly around the specimen, nine turns each of 0.03-cm-diam copper wire.

A cross section of the pressure capsule assembly containing the sample is shown in Fig. 2. The solid silver chloride (AgCl) serves as a quasihydrostatic pressure medium. The six leads, four for the specimen windings and two for the thermocouple, were led out through a six-hole ceramic insulating tube.

Cooling of the specimen was accomplished by bringing liquid nitrogen in contact with the tungsten carbide high-pressure plate.

Each run was made at constant pressure. The sample was cooled to the desired temperature during which time the secondary voltage was recorded. The sample was then allowed to warm up, usually to a temperature such that, at the following pressure to be applied, the sample would be in the paramagnetic state. The pressure would then be increased and the measurement of the secondary voltage would be repeated. Data were also taken upon warming for several runs to determine if there was any hysteresis between cooling and warming. The cooling was accomplished quite rapidly, but the warm-up period was rather lengthy (often several hours) as it depended upon ambient conditions to supply the necessary thermal gradient.

## B. Results

The salient results of the experimental investigation may be summarized as follows:

(a) In the range of pressures from atmospheric pressure to 21.5 kbar the Curie point of the Gd specimen was depressed linearly with pressure at a slope of  $d\theta_c/dP = -1.60$ , to  $\pm 0.05^\circ\text{C/kbar}$ .

(b) In the range of pressures 21.5 to 26.7 kbar a phase change occurred; the resulting state appeared to be non-ferromagnetic. This state was temporarily retained after the pressure was released.

(c) In addition to the initial increase in secondary voltage at the Curie point, at a lower temperature the secondary voltage increased again, went through a peak, and then began to drop off. Both the height of the peak and the temperature at which it occurred were depressed with increasing pressure.

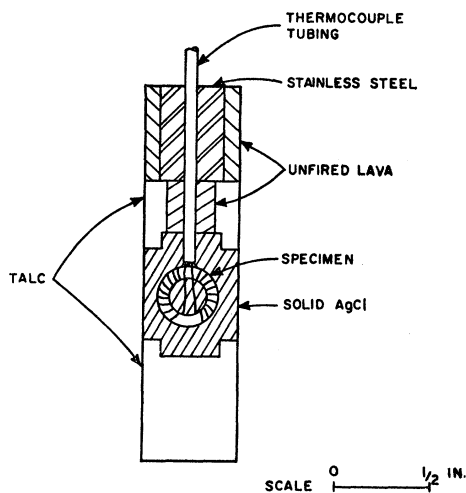


FIG. 2. Cross section of pressure capsule assembly.

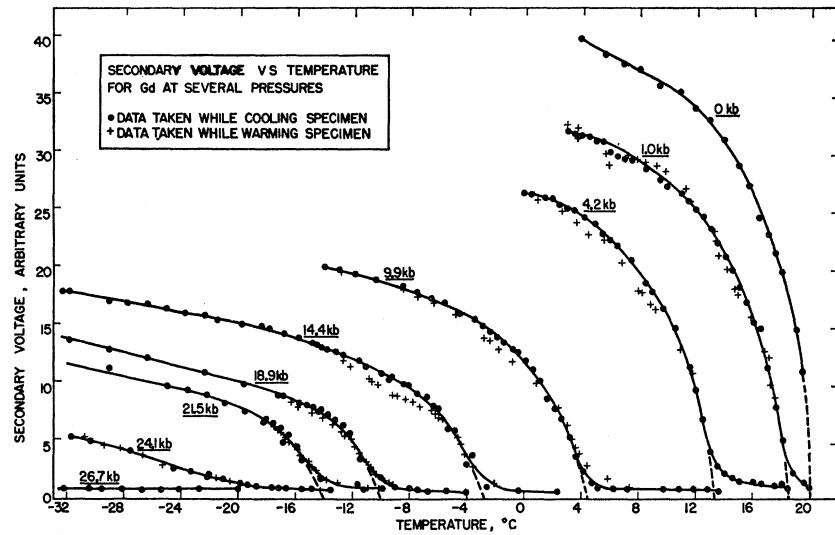


FIG. 3. Data within the range of temperature necessary to determine the shift in the Curie point with pressure (in kbar).

Two different successful runs, each with a separate specimen, were made. The first, or preliminary, run was made in order to get an indication of the expected shift in the Curie point within the range of pressures available (about 40 kbar, with a single stage run) and to determine if there were any interesting anomalies which could be more thoroughly investigated in a succeeding run. Although the data taken in the first run were rather sketchy, it was found that between 3 and 18.4 kbar, the shift in the Curie point was about  $-1.6^{\circ}\text{C}/\text{kbar}$ . The pressures investigated in this run were 3, 8, 12.6, 18.4, 23, 33, and 37.5 kbar. At 23 kbar the secondary voltage did not increase as rapidly as the expected Curie point as it had at the lower pressures. The data at 33 and 37.5 kbar showed essentially no increase in secondary voltage at the points where the respective Curie temperatures were expected, indicating that a transformation to a nonferromagnetic state had occurred.

The data taken in the second run were more thorough and precise than that of the first, and the result of the second run confirmed everything that was indicated by the first run. The secondary voltage versus temperature curves for the second run, in the range of temperatures necessary to show the shift of the Curie point with pressure, are shown in Fig. 3. The ordinate of Fig. 3 is such that one unit corresponds to about  $8\ \mu\text{V}$ .

The Curie temperature of the Gd specimen as a function of pressure, as determined by the displacement of the constant pressure curves of Fig. 3, is shown in Fig. 4. Two techniques were used to determine the shift in Curie temperature with pressure. (The results of both of these determinations are shown in Fig. 4.) First, the inflection point of the curves of Fig. 3 was taken as the Curie temperature; thus the shift in the inflection point was taken as the change in the Curie point. The second method was to extrapolate the curves of Fig. 3 so that they would intersect the temperature

axis, and to equate the change of this intersection with pressure to the change in the Curie temperature as a function of pressure. The method by which this extrapolation was made is shown by the dashed-line extensions of the curves of Fig. 3. It was found that the Curie temperature varied linearly with pressure in the range 0 to 21.5 kbar, such that the slope calculated by the first and the second above-mentioned techniques was  $-1.62$  and  $-1.58^{\circ}\text{C}/\text{kbar}$ , respectively.

Patrick<sup>1</sup> has been very careful to point out that the technique used in these experiments (i.e., monitoring the secondary voltage of a specimen which is in the form of a transformer) is quite suitable for the determination of the shift in the Curie point, by noting the shift in the secondary voltage versus temperature curves; however, it is not an accurate means of determining the Curie point itself. The Curie temperature

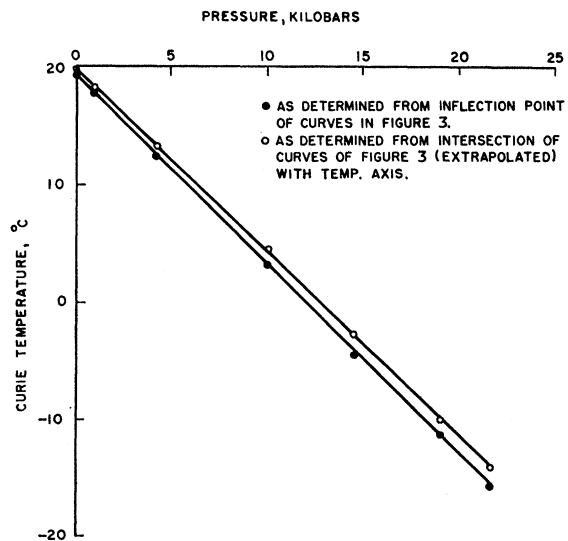


FIG. 4. Curie point versus pressure for gadolinium.

for Gd is usually listed in the literature at from 16 to 18°C. By the techniques employed herein, it would appear to be at about 19.5 to 20°C.

The data taken for the secondary voltage of the Gd specimen at the pressures investigated, over the complete temperature range which was examined, is shown in Fig. 5. The curves of Fig. 3 are also drawn in Fig. 5, but the data points have not been drawn. A logarithmic scale has been used for the secondary voltage in this figure so that both the high-temperature (over  $-32^{\circ}\text{C}$ ) and the low-temperature behavior could be drawn conveniently on one chart. The arbitrary units of the ordinate are the same as those of Fig. 3.

It is of interest to discuss the curves of Fig. 5 in chronological order. In the first day of experimentation, runs were made to determine the shift in the Curie temperature versus pressure at pressures well below that at which the phase transformation to a nonferromagnetic state had occurred in the preliminary run. Thus, the curves at 1.0, 4.2, 9.9, and 14.4 kbar were recorded during the first day. The sample was left overnight in the press at 14.4 kbar.

In the morning of the following day, the pressure was released and the run at 0 kbar was made. The behavior of this run indicates that there were essentially no irreversible effects due to pressure up to 14.4 kbar. Following the run at 0 kbar, the runs at 8.0, 13.1, 18.9, 21.5, and 24.1 kbar were made. These runs, which include the lower temperature region, show the behavior of the additional climb and the peak of the secondary voltage.

The sample was left in the press overnight at 24.1 kbar, and on the next day, the runs at 26.7, 30.0, 34.0, and 38.8 kbar were made. Figure 5 clearly shows the transition which was underway at 24.1 kbar and which

was apparently completed at 26.7 kbar. The secondary voltage, when the pressure was 26.7 kbar and the temperature was near the expected Curie point, was an order of magnitude lower than what would be predicted for the sample to be ferromagnetic. Thus, it is concluded that between 21.5 and 26.7 kbar the Gd specimen transformed to a nonferromagnetic state. Two anomalous peaks were observed in the secondary voltage curves of the higher pressure phase. The cause of these peaks is not known.

The sample was then left in the press overnight at 38.8 kbar. On the following morning, the pressure was released and a run was begun about 10 min later (run labeled "0 kbar, next to final run" in Fig. 5). The secondary voltage of this run had some of the characteristics of the higher pressure phase, which indicated that the Gd specimen had not completely transformed to its 0 kbar equilibrium phase. Upon going to lower temperatures during this run, it was noticed that the secondary voltage continued to increase, in discord with what was observed in prior runs. This indicated that the specimen was still approaching its 0 kbar equilibrium state. The specimen was then allowed to warm up, which required about 3 h, and a final run at 0 kbar was made. In this run, the usual type of ferromagnetic transition had occurred, but the permeability of the specimen at the peak value was down by almost two orders of magnitude from what it was at the initial 0 kbar run. Thus the specimen still had not transformed back to its equilibrium phase. That this loss in permeability was caused by the higher pressure phase transformation, rather than any possible permanent deformation of the specimen, is shown by the behavior of the initial 0 kbar run. That is, the initial 0 kbar run was made after subjecting the specimen to

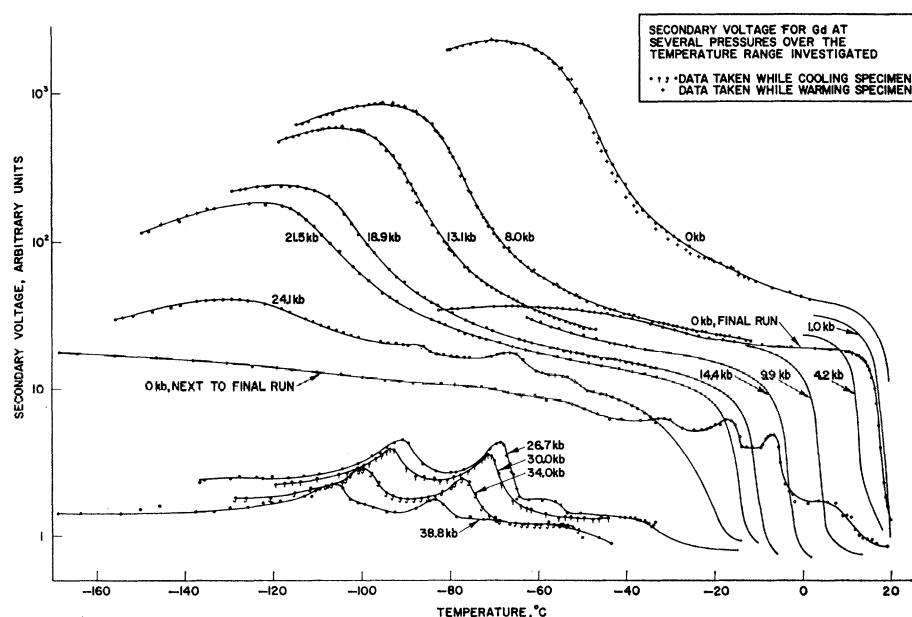
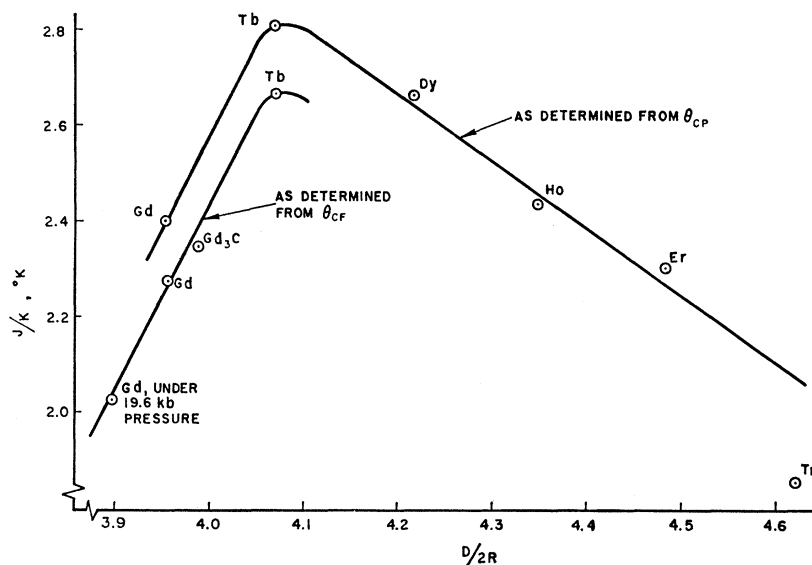


FIG. 5. Data throughout the temperature range investigated. (Pressure in kbar.)

FIG. 6. Exchange interaction curve for the ferromagnetic rare-earth metals. Two curves are shown, one based on  $\theta_{CP}$ , the paramagnetic Curie temperature, and the other on  $\theta_{CF}$ , the ferromagnetic Curie temperature.



14.4 kbar, a pressure sufficiently high to produce permanent deformation of the specimen if it were to occur, and this run did not display the irreversible behavior of the final 0 kbar run.

The inside and the outside diameters of the specimen were measured before and after the run. The dimensions at three locations on the specimen,  $120^\circ$  apart, were, for the outer diameter and inner diameter, respectively, before the run, 0.785, 0.770, and 0.762 and 0.480, 0.482, and 0.477 cm. And after the run, these dimensions were, respectively, 0.785, 0.756, and 0.756, and 0.477, 0.462, and 0.457 cm. No deformation visible to the unaided eye had occurred.

The sample which was used in the preliminary run was annealed at  $775^\circ\text{C}$  for 17 min, after the pressure run. This anneal was found to restore the sample to its initial condition; i.e., before the anneal the secondary voltage did not pass through the characteristic high peak, but it did so after the anneal.

### C. Comparison with Results of Others

The shift in the Curie point of Gd found in the present work, viz.,  $-1.58$  and  $-1.62^\circ\text{C}/\text{kbar}$  as determined by the two techniques employed, is in good agreement with the value  $=1.53^\circ\text{C}/\text{kbar}$  reported by Bloch and Pauthenet. Neither Patrick nor Bloch and Pauthenet have published their curves of secondary voltage or permeability of Gd as a function of temperature.

The phase change that was observed in the present work could not, of course, have been noted in the work of Patrick or Bloch and Pauthenet, as their work was in a lower pressure range.

Bridgman<sup>5</sup> has investigated the effect of pressure on

the electrical resistivity of Gd, and has reported as follows:

“When exposed to 30 000 [ $\text{kg}/\text{cm}^2$ ] gadolinium exhibits an instability in resistance beginning at approximately 20 000. Below this, resistance is steady under constant pressure. Above 20 000 resistance at constant pressure drifts rapidly downward. This drift occurs in the entire region between 20 000 and 25 000. If there is any tendency to asymptotic cessation of drift at any pressure in this range it was too slow to be found in the course of ordinary manipulation. Between 25 000 and 30 000 readings are approximately constant at fixed pressure, but the slope of the curve of resistance against pressure is much greater than at lower pressures. On release of pressure reversal of drift does not occur, but readings are constant all the way back to atmospheric pressure, where the initial resistance is diminished by approximately 7%. At atmospheric pressure there appears to be a very slow drift of resistance back toward the initial value; on standing three days at atmospheric pressure there was a 1% recovery of resistance.”

This transition observed by Bridgman was apparently the same transition to a nonferromagnetic state found between 21.5 and 26.7 kbar in the present work. Bridgman also measured the volume change of Gd under pressure. He found no break in the compressibility curve between 20 000 and 25 000  $\text{kg}/\text{cm}^2$ . He did detect a small volume change of  $\Delta V/V_0 = -0.00432$ . Bridgman did not suggest the nature of the transition which had occurred.

With regard to the additional rise and the peak in secondary voltage observed in the present work, similar peaks were observed by Belov and Pedko<sup>6</sup> in magnetization versus temperature curves for Gd in the presence of weak magnetic fields (less than about 3 Oe). They explained this behavior by assuming Gd to possess a screw spin structure, with a very small screw angle, which is destroyed in the presence of all but a very weak

<sup>5</sup> P. W. Bridgman, Proc. Am. Acad. 82, 83 (1953).

<sup>6</sup> K. P. Belov and A. V. Pedko, Zh. Eksperim. i Teor. Fiz. 42, 87 (1962) [English transl.: Soviet Phys.—JETP 15, 62 (1962)].

magnetic field. Low-field magnetization measurements made by Graham<sup>7</sup> do not support the interpretation given by Belov and Pedko.

### III. CONCLUSIONS

The effect of pressure on the Curie points of ferromagnetic materials has often been interpreted in terms of exchange interaction curves. These curves always show gadolinium far to the right due to its large ratio of interatomic distance to unfilled electron-shell diameter. Thus, in terms of these curves, the Curie temperature of Gd would be expected to increase with pressure. The results presented in this paper, as well as those of Patrick and of Bloch and Pauthenet, have demonstrated that it is not proper to include the ferromagnetic rare earths on exchange interaction curves constructed for the first transition group ferromagnetic metals.

In view of this result it is of interest to speculate upon the construction of an interaction curve limited to the ferromagnetic rare earths. Néel<sup>8</sup> has derived an expression, for the exchange energy for the rare earths, of the form

$$J_e = \frac{3k\theta_C J}{2zS^2(J+1)}. \quad (1)$$

$k$  is the Boltzmann constant,  $\theta_C$  is the Curie temperature (Néel used the paramagnetic Curie temperature),  $J$  is the total angular momentum quantum number,  $S$  is the total spin quantum number, and  $z$  is the coordination number. Néel assumed  $J_e$  to be constant, and showed the paramagnetic Curie temperature of the elements Gd-Tm to be approximately proportional to the factor  $S^2(J+1)/J$ . In attempting to construct an interaction curve, it would be more fruitful to use the known values

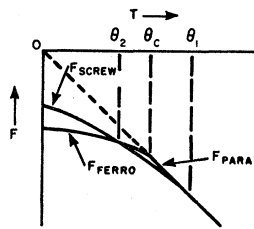


FIG. 7. Free energy versus temperature curves for the ferromagnetic, screw, and paramagnetic states (after Yosida and Miwa [K. Yosida and H. Miwa, *J. Appl. Phys.* **32**, Suppl. 3, 85 (1961)]). Between 0 and  $\theta_2$ , the material is ferromagnetic, between  $\theta_1$  and  $\theta_2$  the spin structure exists, and above  $\theta_1$  the substance is paramagnetic.

<sup>7</sup> C. D. Graham, Jr., *J. Appl. Phys.* **34**, 1341 (1963).

<sup>8</sup> L. Néel, *Compt. Rend.* **206**, 49 (1938).

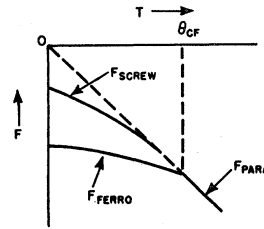


FIG. 8. Possible form (schematic) for the free energy versus temperature curves for the ferromagnetic, screw, and paramagnetic states for gadolinium.

of  $\theta_C$  to calculate  $J_e$ , and to consider  $J_e$  as an indication of the relative magnitude of the exchange energy in the rare earths. Figure 6 shows  $J_e/k$ , as determined from Eq. (1), versus the interatomic distance divided by the diameter of the  $4f$  electron shell (as calculated by the Slater orbital method<sup>9</sup>) for the ferromagnetic rare earths. Using the compressibility data of Bridgman,<sup>5</sup> a point for Gd under 19.6 kbar pressure is included. The effect of pressure on the Curie temperature of Gd is found to be consistent with this interaction curve.

On the basis of the experiments of Bridgman and of those presented herein, the nature of the phase transition, which was found to occur between 21.5 and 26.7 kbar, is not definitely known. A possible interpretation is presented herein.

Gadolinium apparently does not possess the screw spin structure (or helical magnetic structure) as the elements Tb-Tm (terbium through thulium) do. The free-energy curves of the paramagnetic, ferromagnetic, and screw states versus temperature for the elements Tb-Tm are schematically drawn in Fig. 7. As Gd exists only in the paramagnetic or the ferromagnetic state the free-energy curve of the screw state must lie higher than for the ferromagnetic state, as is illustrated in Fig. 8. From the experiments performed it is known that the free energy for the ferromagnetic state must increase with pressure, since  $\theta_{Cf}$  (the ferromagnetic Curie temperature) decreased. It is not known how the pressure affects the free-energy curve for the screw state. A possible explanation for the observed phase transition in the Gd specimen is that with increasing pressure the free energy of the screw state would become lower than that of the ferromagnetic state; thus the specimen would exist in the screw state rather than the ferromagnetic state at pressures above 26.7 kbar.

### ACKNOWLEDGMENT

The authors wish to thank Professor G. C. Kennedy for allowing them to use his high-pressure equipment, without which this work would not have been possible.

<sup>9</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).