Specific Heat of Dysprosium Metal between 0.4 and 4°K*

O. V. LOUNASMAA† AND R. A. GUENTHER‡
Argonne National Laboratory, Argonne, Illinois
(Received January 8, 1962)

The heat capacity of dysprosium has been measured between 0.4 and 4°K in a He^3 cryostat. In this temperature range the specific heat of the metal can be written $C_p=AT^3+BT+CT^{\frac{3}{2}}+DT^{-2}-ET^{-3}-FT^{-4}$. The first term is the lattice specific heat, the second the electronic specific heat, the third the magnetic specific heat caused by exchange interaction between the electronic spins, and the remaining terms are the nuclear specific heat due to splitting of the nuclear energy levels by the strong magnetic field of the $4f$ electrons and by quadrupole coupling. An anomalous contribution to the heat capacity, probably due to the 0.08% oxygen impurity in the sample, was observed between 1.2 and 3.5°K. By excluding the measurements in this temperature region the following values were obtained for the constants in the above equation (for specific heat in millijoules/mole °K): $B=9.5\pm10\%$, $C=9.7\pm10\%$, $D=26.4\pm2\%$. The result $A=0.22$ by Dreyfus *et al.* was adopted and constants $E=1.32$ and $F=0.12$ were calculated from the available electron-paramagnetic resonance data.

Considerable disagreement exists in the temperature range from 2 to 4°K between measurements of the specific heat of dysprosium by different investigators. It is shown, however, that the discrepancies appear to be in the magnetic specific heat only, C varying between 0 and 24. The various values of B are all in good agreement. Our result for D is in excellent accord with the value 26.6 obtained from electron paramagnetic resonance experiments on dilute salts. The magnetic field at the dysprosium nucleus as calculated from the value of D after the effect of quadrupole coupling had been subtracted is 7.1×10^6 gauss, in good agreement with $H_{\mathrm{eff}}=7.3\times10^6$ gauss determined for Dy^{161} by Mössbauer techniques.

I. INTRODUCTION

IN addition to the usual lattice and electronic contributions, $C_L=AT^3$ and $C_E=BT$, respectively, the specific heat of most rare earth metals at low temperatures has two other terms which are caused by electrons in the incompleted $4f$ shell. These are the magnetic specific heat C_M, due to interatomic exchange interaction between electronic spins, and the nuclear specific heat C_N, caused mainly by the interaction of the nuclear magnetic moment with the intense magnetic field produced by the $4f$ electrons at the site of the nucleus.

Measurements of the heat capacity of dysprosium metal between 0.4 and 4°K are reported in this paper. The experiments were undertaken with the aim of providing accurate data for evaluating the nuclear term and, if possible, for deducing the electronic specific heat as well. The experiments were carried out in a He^3 cryostat which is described in Sec. II of our paper.

The first specific heat measurements of dysprosium in the liquid helium range and below were made by Dash, Taylor, and Craig.[1] They covered the temperature interval from 0.25° to 2°K, but the data showed a very large apparently anomalous specific heat above 0.5°K. At the recent Second Rare Earth Conference (Glenwood Springs, September, 1961), besides the present results, new measurements of the heat capacity of dysprosium were described by Parks.[2] At about the same time data by Dreyfus, Goodman, Trolliet, and Weil[3] were published. However, after this sudden wealth of information the situation is still very confusing: At the lowest temperatures the various measurements agree reasonably well, but at 4°K the discrepancies are 100%.

The electronic structure of rare earth atoms outside a xenon core is ($4f^n$, $5s^2$, $5p^6$, $6s^2$, $5d^1$) where the value of n increases from 0 for lanthanum to 14 for lutetium. The outer electron configuration of these metals is thus the same; the atoms are normally trivalent with the $6s$ and $5d$ electrons in the conduction band. It is interesting to compare the electronic specific heats of the rare earth metals with each other.

Below 85°K, dysprosium metal is ferromagnetic. In the liquid helium region the spin moments of the $4f$ electrons are thus parallel to each other within a given domain and the number of spins pointing in a different direction is very small. These spin deviations do not stay localized in the crystal but because of exchange interaction with neighboring atoms they will travel through the lattice as spin waves. If the number of spin deviations is sufficiently small so that their mutual interaction may be neglected the magnetic specific heat can be calculated by the simple spin wave theory.[4] In this theory it is assumed that the magnetism is entirely caused by electronic spins regularly spaced in the crystal. The exchange energy is $-2K\sum\mathbf{S}_i\cdot\mathbf{S}_j$, where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spin vectors of atoms i and j, respectively, and the summation is extended over nearest neighbors only. K is the exchange integral. The spin wave theory predicts

$$C_M=cR(kT/2KS)^{\frac{3}{2}}, \tag{1}$$

i.e., $C_M=\mathrm{const}\times T^{\frac{3}{2}}$. Here k is the Boltzmann constant, R the gas constant, and c a numerical factor which depends on the crystal structure.

* Work performed under the auspices of the U. S. Atomic Energy Commission.
† On leave from the Wihuri Physical Laboratory, University of Turku, Turku, Finland.
‡ Now at the Illinois Institute of Technology, Chicago, Illinois.
[1] J. G. Dash, R. D. Taylor, and P. P. Craig, *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1961), p. 705.
[2] R. D. Parks, "Proceedings of the Second Rare Earth Conference", Glenwood Springs, September, 1961 (to be published).
[3] B. Dreyfus, B. B. Goodman, G. Trolliet, and L. Weil, Compt. rend. **253**, 1085 (1961).
[4] J. van Krandendonk and J. H. van Vleck, Revs. Modern Phys. **30**, 1 (1958).

Marshall[5] has shown that at low enough temperatures where the electron spins are oriented the nucleus is in a temperature-independent effective magnetic field H_{eff}. This field is the sum of the local magnetic field at the nucleus, the effective magnetic field arising from contact interaction with the polarized conduction electrons, and the effective field due to the $4f$ electrons of the same atom. In this field the nucleus with a spin I will have, relative to H_{eff}, $2I+1$ spin orientations. At absolute zero only the lowest nuclear energy level is populated; at 1°K the levels are already approximately equally occupied. Below 1°K a redistribution among the spin orientations takes place and a Schottky type anomaly is observed in the specific heat. The maximum of the anomaly is below 0.1°K but its high temperature "tail" is clearly visible because C_L, C_E, and C_M are small below 2°K. This nuclear specific heat has recently been observed for a number of rare earths.[1–3,6–12]

Bleaney and Hill[13] and Bleaney[14] have shown that in many cases effects due to the nuclear-electric quadrupole interactions are important for calculating C_N. They write the Hamiltonian for the nuclei in the form

$$\mathcal{H}=a'I_z+P[I_z^2-\tfrac{1}{3}I(I+1)], \quad (2)$$

where the magnetic field is assumed in the z direction. The magnetic hyperfine constant a' should vary $\langle J_z\rangle$, which measures the electronic magnetization, and the quadrupole coupling constant P as $\langle J_z^2-\frac{1}{3}J(J+1)\rangle$, which is a measure of the average value of the electronic quadrupole moment. Here J corresponds to the ground state of the trivalent lanthanide ion. At temperatures well below the Curie point, $\langle J_z\rangle$ can be replaced by J and $\langle J_z^2-\frac{1}{3}J(J+1)\rangle$ by $J^2-\frac{1}{3}J(J+1)$. By calculating the specific heat from the partition function in the usual way and by expanding it in inverse powers of T, we obtain[14]

$$C_N=DT^{-2}-ET^{-3}-FT^{-4}+\cdots, \quad (3)$$

where

$$D/R=\frac{1}{3}a'^2I(I+1)+\frac{1}{45}P^2I(I+1)(2I-1)(2I+3), \quad (4)$$

$$E/R=\frac{1}{15}a'^2PI(I+1)(2I-1)(2I+3), \quad (5)$$

$$F/R=\frac{1}{30}a'^4I(I+1)(2I^2+2I+1). \quad (6)$$

According to the preceding discussion the low temperature specific heat of ferromagnetic rare earths becomes

$$C_p=AT^3+BT+CT^{\frac{3}{2}}+DT^{-2}-ET^{-3}-FT^{-4}. \quad (7)$$

Coefficients D, E, and F are interdependent through (4), (5), and (6).

II. EXPERIMENTAL[15]

1. The Cryostat

The inner parts of our He^3 cryostat are shown in Fig. 1. The sample is surrounded by the inner vacuum case which, in turn, is soldered to the He^3 pot with Wood's metal. The whole assembly is separated from the He^4 bath by the outer vacuum case.

A magnetic thermometer, with its superconducting niobium primary coil, copper secondary coils, and salt sphere is situated inside the He^3 pot. The 1.3-cm salt sphere was made of powered chromium methylamine alum. In order to eliminate the effect of harmful eddy currents the inside of the He^3 pot was tinned with 50/50 solder; the magnetic thermometer is thus enclosed in a superconducting cavity which reduces its sensitivity somewhat. The thermometer leads are brought out through the center pumping tube and are thermally bonded to the He^4 bath as they pass through a radiation shield at the top of the outer vacuum case.

The calorimeter consists of two copper caps which are screwed into the sample. In order to increase the heat contact between the dysprosium sample and the caps a small amount of stopcock grease was used between the two metals. A non-inductively wound manganin heater was attached to the top cap. To the bottom cap an indicator wire was soldered for determining electrically whether the calorimeter is resting on the platform or not.

A carbon thermometer for use in the specific heat measurements was made in the following manner: A thin layer of General Electric No. 7031 adhesive was first baked on the cylindrical surface of the bottom cap and two copper wires, approximately 2 mm apart and 5 cm long, were then fixed on the surface. The insulation

[5] W. Marshall, Phys. Rev. **110**, 1280 (1958).
[6] B. Dreyfus, B. B. Goodman, G. Trolliet, and L. Weil, Compt. rend. **252**, 1743 (1961).
[7] O. V. Lounasmaa, preceding paper [Phys. Rev. **126**, 1352 (1962)].
[8] N. Kurti and R. S. Safrata, Phil. Mag. **3**, 780 (1958).
[9] R. M. Stanton, L. D. Jennings, and F. H. Spedding, J. Chem. Phys. **32**, 630 (1960).
[10] E. C. Heltemes and C. A. Swenson, J. Chem. Phys. **35**, 1264 (1961).
[11] J. E. Gordon, C. W. Dempesy, and T. Soller, Phys. Rev. **124**, 724 (1961); "Proceedings of the Second Rare Earth Conference," Glenwood Springs, September, 1961 (to be published).
[12] B. Dreyfus, B. B. Goodman, A. Lacaze, and G. Trolliet, Compt. rend. **253**, 1764 (1961).
[13] B. Bleaney and R. W. Hill, Proc. Phys. Soc. (London) **78**, 313 (1961).
[14] B. Bleaney, "Proceedings of the International Conference on Magnetism and Crystallography," Kyoto, September, 1961 (to be published).

[15] For a more detailed description, see R. A. Guenther, MS thesis, Illinois Institute of Technology, 1962 (unpublished); Argonne National Laboratory Technical Report (to be published).

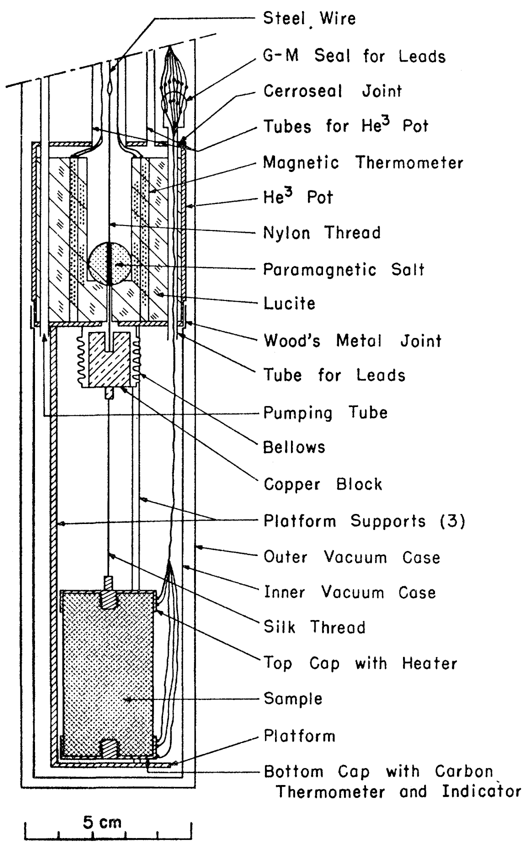

FIG. 1. The inner parts of the He^3 cryostat.

from the top of these wires was filed off and a narrow strip of Du Pont No. 4817 silver paint applied to both of them. A thin layer of Acheson Colloids Co. Aquadag (colloidal graphite in water) was then painted between and on the wires for a length of 2 cm. This thermometer is very reliable; its response time is extremely short, its heat capacity low, and its resistance stays within convenient limits (140 ohms at 4°K, 820 ohms at 0.4°K). Overheating of the thermometer is effectively prevented by separating it from the heater. All leads between the calorimeter and the top of the outer vacuum case are tinned constantan and thus stay superconducting below 4°K.

When it is desired to break the heat contact between the sample and the platform, the calorimeter is lifted by means of a motor and screw assembly at the top of the cryostat; this assembly is connected to the calorimeter through a silk thread, bellows, nylon thread, and steel wire. For improving the heat transfer the surfaces in contact between the platform and the bottom cap were polished flat and gold plated.

As the previous description indicates, our apparatus has many similar features with the He^3 cryostat of Seidel and Keesom.[16]

[16] G. M. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).

2. Experimental Procedure

Exchange gas was used for cooling the sample down to 4.2°K; the space surrounding the calorimeter was then evacuated by pumping for at least twelve hours until a mass spectrometer type leak detector indicated a very small helium reading. After the He^4 bath had been pumped down to 1.15°K, five liters of He^3 gas was condensed to the pot. By pumping on this liquid with a diffusion pump through the 12-mm center tube a temperature of 0.33°K could be reached and maintained for 48 hr without recondensing.

During all this time the sample was resting on the platform and was cooled by contact. Because of the large heat capacity of the sample at the lowest temperatures about 18 hr were needed to reach 0.4°K. The He^4 Dewar had to be warmed up to 4.2°K every twelve hours for adding more liquid; this affected the temperature of the He^3 pot only very slightly. In order to refill the pot the sample was lifted and He^3 gas condensed in.

When the lowest experimental temperature was reached the sample was lifted from the platform. At this time no heating effects due to vibrations were observed. During measurements the He^3 pot was kept at 0.33°K. The temperature drift, which was about 10 μdeg/min at 1°K and about 200 μdeg/min at 4°K and thus hardly noticeable, was first recorded and heat then supplied for about 60 sec. The heating time was measured to 0.01 sec with an electronic timer which automatically switched the heat on and off. For calculating the energy input the heater resistance was determined in advance ($R_H=361.91+0.03T$ ohms) and the heating current was measured with a Rubicon No. 2781 potentiometer. Since the leads between the He^4 bath and the calorimeter were superconducting, no energy which could flow to the sample was created outside the heater. A suitable heating current (0.3–1.5 ma) was chosen for spacing the experimental points about $0.1T$ apart. After a heating period the sample came to equilibrium in less than 10 sec.

The voltage across the carbon thermometer and the current (2 μa) through it were measured with a Rubicon No. 2773 double potentiometer. A suitable galvanometer amplifier and a recorder were used to achieve a sensitivity of about 30 mm/μv.

3. Thermometer Calibrations

The precision in calorimetry below 4°K is almost invariably determined by the accuracy which can be achieved in calibrating the thermometer. Our carbon thermometer was calibrated after every group of experiments before the cryostat was warmed above 6°K in the following sequence:

1. Between 2.0° and 0.75°K the vapor pressure of He^3, measured through the large tube from the pot, was employed as primary thermometer. The smaller tube was used for balancing the heat leak by pumping and

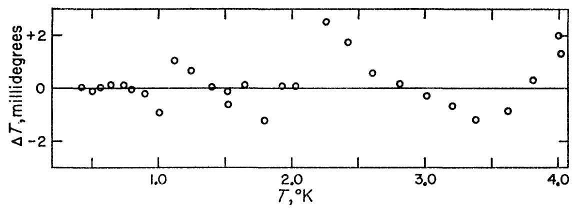

FIG. 2. Deviation plot for the calibration curve $\Delta T = T(\text{calc.}) - T(\text{exp.})$.

thus for keeping the temperature constant. At the same time readings from the magnetic thermometer were also taken. To ensure equilibrium He^3 exchange gas was admitted to the inner vacuum space. The temperature scale of Sydoriak and Roberts[17] was used for evaluating the temperatures (recalculated to the T_{58} scale[18]) and a correction was applied for the 0.6% of He^4 in our He^3 gas.

2. Between 0.75 and 0.4°K the susceptibility of the chromium methylamine alum was employed as a primary thermometer. Temperatures were calculated from the equation[19]

$$M = A + \frac{B}{T + 0.0028/T + \beta}, \tag{8}$$

where M is the mutual inductance reading of the bridge and the constants were determined by the method of least squares from calibration points between 2.2° and 0.75°K. The sensitivity of the measuring system is 0.1 mdeg at 1°K. By using a magnetic thermometer, vapor pressure measurements below 0.75°K were not necessary and large corrections due to the thermomolecular pressure difference were avoided.

3. From 4.2 to 2.0°K the carbon thermometer was calibrated against the vapor pressure of He^4; for this purpose about 40 cc of liquid He^4 were condensed to the inner vacuum case. Temperatures were determined according to the T_{58} scale.[18]

About 30 calibration points were measured for the carbon thermometer over the whole temperature range. The results were then fitted to an equation of the type

$$1/T = aR^{-2} + bR^{-1} + cR^{-\frac{1}{2}} + d + eR^{\frac{1}{2}} + fR, \tag{9}$$

where R is the thermometer resistance and $a, \cdots, f$ are constants. Figure 2 shows a typical deviation plot from the mathematical curve. The scatter is generally less than 2 mdeg and the He^3 and He^4 calibrations join smoothly together. The calculated temperature is thus probably within 1 mdeg of the temperature defined by the He^3 and He^4 scales. Uncertainties of about 2 mdeg can arise from the extrapolation of the magnetic thermometer calibration below 0.75°K.

III. RESULTS

Our dysprosium sample was prepared by Research Chemicals (Division of Nuclear Corporation of America). It was vacuum distilled, then remelted in a vacuum and cast into a tantalum crucible. Next the tantalum was machined off and the sample turned down to a cylinder 5.0 cm long and 3.2 cm in diameter; its weight was 256.66 g (=1.5794 moles). The following impurities were detected in our laboratory: tantalum, 0.03%; other metals not found in spectrochemical analysis; hydrogen, 0.03%; oxygen, 0.08%.

The experimental results are listed in Table I and most of the points are also plotted in Fig. 3. All the data, including calibrations, were calculated with an IBM 704 digital computer.[20] Figure 3 shows that the specific heat has an anomalous "hump" centered around 2.35°K.

Due to the rapid establishment of equilibrium after heating and because of the good thermal insulation of the calorimeter, the random scatter of experimental points is only about 0.1% within each run. Systematic errors in timing, heating current, and heater resistance total not more than 0.2% in the final results. The heat capacity of the empty calorimeter (i.e., the two caps) was measured in a separate experiment and was always less than 1% of the heat capacity of the sample. Since exchange gas was not used for cooling below 4.2°K, no errors could arise from desorption of helium during heating periods. The experimental accuracy is mainly limited by thermometer calibrations. Aside from possible errors in the He^3 temperature scale, which may be several mdeg off, the accuracy of the present results is estimated as 1% between 0.8° and 4°K and somewhat better than 2% at 0.4°K.

The separation of the measured specific heat into contributions according to (7) is difficult because of the anomaly, and it was decided to omit the points between 1.2 and 3.5°K from the analysis. Further, since the data by Dreyfus *et al.*[3] on one of their samples (sample A, cf. Fig. 3) showed neither anomaly nor magnetic specific heat, a fact which makes the determination of the lattice specific heat more certain, their value for $A = 0.22$ millijoules/mole °K^4 was adopted. The constants $E = 1.32$ millijoules °K^2/mole and $F = 0.12$ millijoules °K^3/mole were calculated according to (5) and (6) from the data given in Bleaney's[14] paper. A, E, and F were thus all treated as predetermined constants in the least squares analysis. For the remaining constants the results were (for specific heat in millijoules/mole °K): $B = 9.5 \pm 0.9$, $C = 9.7 \pm 0.5$, $D = 26.4 \pm 0.1$. The limits of error are statistical only.

The calculated specific heat curve is shown in Fig. 3. Below 1.2°K the experimental points fit to this curve within 1–2%. The temperature dependence of C_E and C_M is so similar that the two contributions cannot be

[17] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).
[18] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1 (1960).
[19] M. Durieux, thesis (Leiden, 1960).
[20] P. R. Roach, Argonne Natl. Laboratory Technical Report No. 6497 (1962).

TABLE I. Specific heat of dysprosium metal. Experimental results.

T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)
Run IA		Run IB		Run IC		Run IIA		Run IIB		Run III	
0.5822	81.89	0.4241	128.09	0.7075	62.12	1.3656	42.75	3.0658	94.62	2.2947	78.49
0.5942	79.52	0.4559	116.24	0.7738	55.28	1.4217	43.89	3.1885	99.07	2.4207	78.74
0.6107	76.38	0.4949	103.80	0.8476	49.73	1.4856	45.16	3.3131	103.43	2.5522	78.80
0.6279	73.47	0.5429	90.77	0.9287	45.59	1.5555	47.18	3.4417	108.05	2.6872	81.83
0.6459	69.92	0.5928	79.83	1.0159	42.88	1.6292	49.47	3.5750	112.54	2.8227	85.68
0.7104	61.74	0.6504	69.68	1.1075	41.44	1.7055	52.33			2.9577	89.74
0.7317	59.19	0.7220	60.27	1.2009	41.06	1.7846	55.80			3.0945	94.54
0.7538	57.02	0.7967	53.25	1.2941	41.61	1.8663	59.35			3.2352	99.61
0.7885	53.10	0.8729	48.18	1.3852	42.94	1.9518	63.54			3.3801	104.78
0.8371	50.38	0.9562	44.59	1.4810	45.08	2.0416	68.76			3.5308	110.73
0.8888	47.44	1.0451	42.21	1.5858	48.14	2.1353	74.12			3.6899	117.09
0.9435	45.09	1.1375	41.09	1.6954	52.02	2.2322	78.28			3.8566	123.78
1.0008	43.20	1.2310	41.16	1.8174	57.16	2.3331	80.38			4.0341	130.33
1.0600	41.93	1.3325	42.16	1.9624	64.49	2.4404	79.87				
1.1205	41.26	1.4395	44.12	2.1308	74.14	2.5533	80.30				
1.1927	41.01	1.5492	46.95	2.3317	79.23	2.6701	82.17				
1.2754	41.60	1.2893	41.69	2.5670	79.46	2.7876	84.98				
1.3568	42.57	1.3982	43.28	2.8206	85.11	2.9065	88.55				
1.4491	44.26	1.5101	16.01			3.0242	93.26				
1.5505	46.87	1.6395	50.06	0.4266	127.12	3.2673	102.12				
1.6574	50.46	1.7941	56.16	0.4582	115.49	3.3897	106.47				
1.7832	55.38	1.9513	63.98	0.4931	104.25	3.5123	110.53				
1.9465	63.46	2.1149	73.33	0.5320	93.41	3.6410	115.49				
2.1882	75.52	2.3164	79.77	0.5754	83.33						
2.4924	79.02	2.5669	79.75	0.6242	73.91						
		2.8429	85.75	0.6792	65.54						

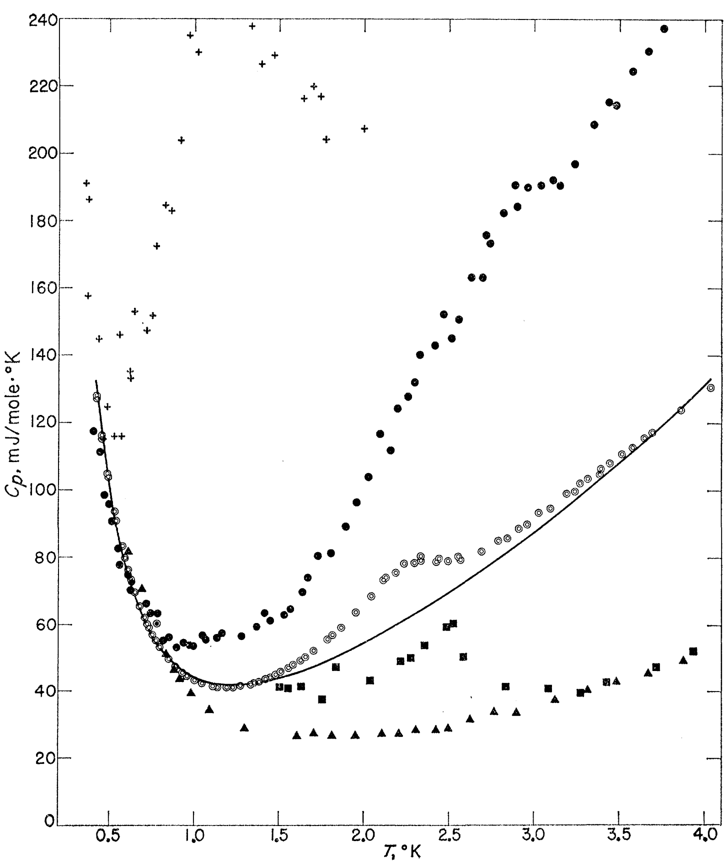

FIG. 3. The specific heat of dysprosium metal. ◎, present results; +, Dash *et al.*[1]; ●, Parks[2]; ▲, Dreyfus *et al.*[3] sample A; ■, Dreyfus *et al.*[3] sample B.

separated very accurately. On the other hand, the nuclear specific heat is predominant below 1°K and it can be determined with higher precision. It is therefore estimated that the above values of B and C are correct within 10% and the value of D within 2%.

The absence of any magnetic specific heat in the data of Dreyfus *et al.*[3] led us to try to find whether this could be due to differences in the speed with which the sample was cooled down from room temperature, since experiments[7,21] on other rare earths have shown that the magnetic specific heat depends on the time the sample spends in the region near the Curie point. During run II the metal was cooled from room temperature to 4.2°K in 30 hr by using the heat switch only; during run III this temperature range was covered in 1 hr with the help of exchange gas. However, no differences were observed in the specific heat.

IV. DISCUSSION

All the specific heat data[1–3] available for dysprosium in the liquid helium range have been plotted in Fig. 3. At the lowest temperatures the agreement between various measurements is reasonably good. Results by Parks[2] agree best with our data; Dreyfus *et al.*[3] only measured six specific heat points below 1°K which limits the accuracy they achieved in evaluating the nuclear term.

At higher temperatures the disagreement is complete. Data by Dash *et al.*[1] exhibit a very large anomaly below 1°K. The present results, the work of Parks,[2] and measurements by Dreyfus *et al.*[3] on one of their samples (sample B) all show an apparent anomaly in the 2–3°K region. This anomaly decays quite rapidly on the high-temperature side and is, therefore, not of Schottky type. It is probably co-operative in nature. The entropy under the anomaly is $0.007R$ and it cannot thus be due to the dysprosium metal itself. Dreyfus *et al.*[3] suggest that the anomaly could be caused by the influence of the superconducting tantalum impurity on the spins of the dysprosium atoms. This explanation is perhaps not correct—the tantalum impurity in our sample, which exhibits the anomaly, is 0.03% and in sample A of Dreyfus *et al.*,[3] which does not show the anomaly, it is 0.05%. It is most likely that the anomalies are caused by oxide impurity in the samples. Measurements by Crane[22] show that at 2°K the specific heat of gadolinium increases by 70% when the oxide impurity is increased from 0.11% to 0.22%. Dash *et al.*[1] and Dreyfus *et al.*[3] did not determine the oxygen content of their samples; in Parks' [2] sample the oxygen impurity was 0.13% as compared with 0.08% in our sample.

Values of the constants in (7) determined by different investigators are collected in Table II. The lattice specific heat as deduced by Dreyfus *et al.*[3] corresponds to a Debye temperature $\theta=207$°K; this is considerably higher than $\theta=158$°K obtained by Skochdopole, Griffel, and Spedding[23] from measurements above 15°K, which gave $A=0.49$ millijoules/mole °K.[4] This value of A was adopted by Parks.[2] Good agreement exists between the various results on B in Table II. Coefficient D in the nuclear specific heat was calculated by Dash *et al.*,[1] Parks,[2] and Dreyfus *et al.*[3] without taking the higher terms in C_N into account. If this is done their values of D will increase by about 14%. Good agreement thus exists between our result and that of Parks.[2]

TABLE II. The specific heat of dysprosium metal. Constants in the equation C_p (millijoules/mole °K)$=AT^3+BT+CT^{\frac{3}{2}}+DT^{-2}-ET^{-3}-FT^{-4}$.

Author	A	B	C	D	E	F
Present work	0.22	9.5	9.7	26.4	1.32	0.12
Dash *et al.*[1]	0.75	10	0	20	0	0
Parks[2]	0.49	9.2	22	22	0	0
Dreyfus *et al.*[3]	0.22	9.0	0	30	0	0
Bleaney[14]	···	···	···	26.6	1.32	0.12

It is possible, within the experimental accuracy of the various measurements and by excluding the anomaly, to represent our results and the measurements of Parks[2] and of Dreyfus *et al.*,[3] above 0.8°K, by an equation of type (7), where (for specific heat in millijoules/mole °K) $A=0.22$, $B=9.5$, $D=26$, and $C=9.7$, 24, and 0 for the three sets of data, respectively. This indicates that the large discrepancies in the observed specific heat towards higher temperatures, which cannot be explained by the anomaly, are due to the magnetic specific heat. The reason for the differences is, however, not known.

By putting $K=1.91k$,[24] $c=0.028$ (hcp lattice), and $S=\frac{5}{2}$ in (1) the spin-wave theory gives $C=7.9$ millijoules/mole °K$^{\frac{5}{2}}$. Measurements by Griffel, Skochdopole, and Spedding[25] between 15 and 300°K indicated that the magnetic entropy at 20°K is 550 millijoules/mole °K, which, by assuming a $T^{\frac{3}{2}}$ temperature dependence for C_M below 20°K, would give $C=9.2$ millijoules/mole °K$^{\frac{5}{2}}$ in good agreement with our result.

Bleaney[14] has calculated the constant D for several rare earth metals from electron-spin resonance data on dilute salts. By using the values a' (Dy^{161})$=-820$ Mc/sec, a' (Dy^{163})$=1140$ Mc/sec, P (Dy^{161})$=150$ Mc/sec, and P (Dy^{163})$=180$ Mc/sec (the other stable isotopes are even-even nuclei and do not contribute to C_N) he obtains $D=26.6\pm1.2$ millijoules °K/mole. The agreement with our "calorimetric" D is thus excellent. Since the $4f$ electrons in rare earths are well shielded one would expect the same value in the metal and in the salts; the result confirms this and shows that contributions from polarized conduction electrons must be relatively unimportant in the metal.

[21] D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Phys. Soc. (London) **A207**, 137 (1961).
[22] L. T. Crane, J. Chem. Phys. **36**, 10 (1962).
[23] R. E. Skochdopole, M. Griffel, and F. H. Spedding, J. Chem. Phys. **23**, 2258 (1955).
[24] L. D. Jennings, E. D. Hill, and F. H. Spedding, J. Chem. Phys. **34**, 2082 (1961).
[25] M. Griffel, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **25**, 75 (1956).

At the lowest experimental temperature of 0.4°K the terms ET^{-3} and FT^{-4} contribute 12% and 3%, respectively, to the nuclear specific heat. If these terms are ignored in the analysis the fit of the calculated curve to the experimental points will become worse and a value for D is obtained which is about 14% lower; the agreement with Bleaney's[14] value would thus become considerably poorer. This indicates that the quadrupole contribution to the nuclear specific heat is quite important in dysprosium.

The effective magnetic field produced by the $4f$ electrons at the dysprosium nucleus can be calculated approximately from (4) by putting $a'=\mu H_{\text{eff}}/kI$. The calculation was made by assuming a nuclear spin $I=\frac{5}{2}$ for both isotopes and a magnetic moment of 0.38 and 0.53 nuclear Bohr magnetons for the two isotopes. The effective field thus becomes 7.1×10^6 gauss. Bauminger, Cohen, Marinov, and Ofer[26] have recently measured H_{eff} for Dy^{161} in dysprosium iron garnet at 85°K using Mössbauer techniques. At this temperature they get $H_{\text{eff}}=3.5\times10^6$ gauss and when this result is recalculated according to Pauthenet's[27] magnetization measurements, for 0°K one obtains $H_{\text{eff}}=7.3\times10^6$ gauss, in good agreement with our calorimetric value.

The value 9.5 millijoules/mole °K² for the coefficient B in the electronic specific heat of dysprosium can be compared with the experimental results $B=10.1$ for lanthanum,[28] 12.1 for samarium,[7] and 9.5 for lutetium.[29] It thus seems that C_E is similar for these rare earths. However, recent measurements by Dreyfus *et al.*[12] gave for coefficient B: Pr, 19.0; Ho, 26; Er, 13; Tm, 21.5. The measurements have been reported very briefly but since the magnetic specific heat was ignored in the analysis it is probable that these values are too high.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. D. W. Osborne and Dr. M. Durieux for many helpful discussions concerning the design of the cryostat and the measuring circuits. We are also indebted to H. J. Grzelewski for technical help, to P. R. Roach for help with the calculations, and to B. D. Holt and J. P. Faris for analyses of the dysprosium sample.

[26] R. Bauminger, S. G. Cohen, A. Marinov, and S. Ofer, Phys. Rev. Letters **6**, 467 (1961).

[27] R. Pauthenet, Ann. Phys. **3**, 424 (1958).

[28] A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).

[29] L. D. Jennings, R. E. Miller, and F. H. Spedding, J. Chem. Phys. **33**, 1849 (1960).

PHYSICAL REVIEW VOLUME 126, NUMBER 4 MAY 15, 1962

Fusion Curve and Polymorphic Transitions of Cesium at High Pressures

G. C. Kennedy, A. Jayaraman, and R. C. Newton
*Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California**

(Received January 15, 1962)

The fusion curve of cesium metal has been studied up to 50 000 atmospheres. The curve is unique among elements studied, in that it shows two maxima, one at approximately 22.5 kbar and 197°C, and a second at approximately 30 kbar and 198°C. Two triple points have been located. At 195°C, cesium has four different melting-freezing points and possibly another one at still higher pressures.

INTRODUCTION AND PREVIOUS WORK

The melting points of the alkali metals at one-atmosphere pressure progress regularly and systematically with the atomic weight, cesium having the lowest melting point at 29°C and lithium the highest at 186°C. However, Bridgman in his studies of the fusion curves of the alkali metals to 8 kbars, found systematic progression in the initial slopes of the fusion curves. Cesium has the steepest initial slope, 20°/kbar and lithium the lowest with an initial slope of 2.0°/kbar. Bridgman[1] predicted that somewhere above 30 kbar the order of melting points among the alkali metals would be completely reversed, with cesium having the highest melting point and lithium the lowest.

Bundy[2] has recently reported a maximum in the fusion curve of Rb and has indicated that the melting of the alkali and other metallic elements at high pressures might be considerably more complicated than the simple picture envisioned by Bridgman. The possibility that the melting points of elements and compounds can do otherwise than rise *ad infinitum* with pressure introduces new orders of complexity in phase diagrams.

Bridgman[3] has reported two phase transitions in cesium at room temperature. He located a small transition with a volume discontinuity of about 2% at approximately 23 kbars, and a large discontinuity with a volume change of about 10% at 42 kbar. Further explorations by measurement of resistance and volume

* Publication No. 229, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California.

[1] P. W. Bridgman, *Physics of High Pressures* (G. Bell and Sons, London, England, 1952).

[2] F. P. Bundy, Phys. Rev. **115**, 274 (1959).

[3] P. W. Bridgman, Phys. Rev. **60**, 351 (1941).