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 $H_{\text{eff}} = 3.5 \times 10^6$ gauss and when this result is recalculated according to Pauthenet's[27] magnetization measure-

ments, for 0°K one obtains $H_{\text{eff}} = 7.3 \times 10^6$ gauss, in good agreement with our calorimetric value.

The value 9.5 millijoules/mole °K^2 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.

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Fusion Curve and Polymorphic Transitions of Cesium at High Pressures

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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

[1] P. W. Bridgman, *Physics of High Pressures* (G. Bell and Sons, London, England, 1952).
[2] F. P. Bundy, Phys. Rev. 115, 274 (1959).
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to 100 kbar by Bridgman[4,5] did not reveal the existence of other transitions. The relative resistance versus pressure graph showed a sharp discontinuity corresponding to the 23-kbar transition. The resistance increased an order of magnitude on further compression and thereafter began to fall, showing a cusp at about 54 kbar. In reference 5, p. 191, Bridgman says, "The mean pressure of the cusp with increasing and decreasing pressure varied in three runs from 43 000 to 44 000 kg/cm², nearly the same as the pressure of the electronic transition, 45 000, previously found." The pressure coordinates of the two transitions have recently been accurately redetermined in this laboratory by a free-piston gage technique[6] and have approximate values of 22.6 and 41.7 kbar, respectively. Bardeen[7] had earlier noted that the transition at 22.6 kbar was probably one in which the cesium atoms were rearranged in a cubic close-packed configuration. Fermi[8] first suggested that the second transition at 42 kbar may represent an electron shell collapse. This was given some theoretical justification by Sternheimer[8] who has computed that the energy change in the 42-kbar transition is approximately that which would result from collapse under pressure of the $6s$ electron to the vacant $5d$ shell.

The questions that are of much interest in connection with the fusion curve of cesium are thus:

(1) Does the fusion curve show a maximum analogous to that of Rb?

(2) If so, how is the downward trend of the melting points eventually terminated?

(3) What effect does the supposed electronic collapse have on the fusion curve where its $P-T$ trajectory intersects the latter?

(4) Can the supposed electronic collapse take place in the liquid state?

The present investigation was undertaken in order to find answers to these questions.

EXPERIMENTAL METHOD

A piston and cylinder device was used to generate pressures up to 50 000 bars. In this device, a 2-in.-long cylindrical tungsten carbide piston of $\frac{1}{2}$-in. diameter advances into a hole of the same dimensions in a tungsten carbide cylinder, which is tightly pressed into hardened steel plates. A 1000-ton ram is employed to push the piston into the pressure chamber. The pressure medium is talc. The sample in an appropriate container was placed within a carbon sleeve which served as an electrical resistance heater. See Fig. 1. An iron cup with a stopper of boron nitride satisfactorily contained

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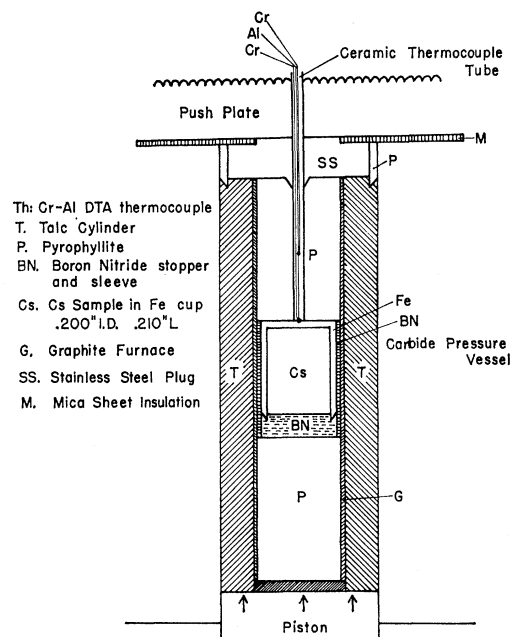[8] R. Sternheimer, Phys. Rev. **78**, 235 (1950).

FIG. 1. Furnace assembly and sample arrangement for determining melting points of cesium.

the sample of cesium liquid and solid, through any amount of pressure and temperature cycling, without leakage or contamination. Iron was chosen because it is known to be completely inert to the presence of alkali metals even at their boiling temperatures. Figure 1 shows the arrangement.

Melting points at various pressures were detected by the method of differential thermal analysis. Details of the differential thermal analysis method, as well as the high-pressure apparatus are described elsewhere.[9] Cesium is extremely reactive, and hence the sample container was filled and the furnace parts assembled in an argon dry box.
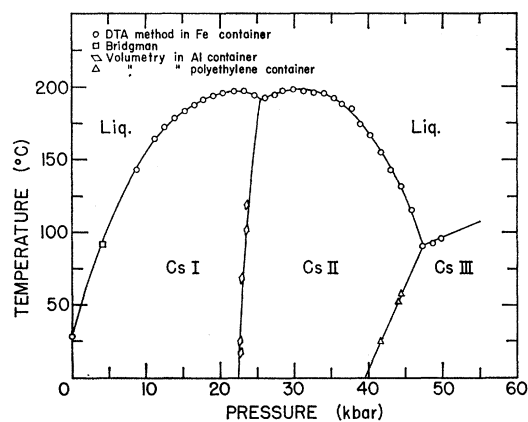

FIG. 2. Fusion-curve and solid-solid transitions in cesium.

[9] G. C. Kennedy and R. C. Newton in *Solids under Pressure* (to be published).

The problem of estimating the correction for friction in a setup of this type is a difficult one. In order to reduce friction, the wall of the carbide pressure cylinder was first coated with molybdenum disulfide and the entire sample furnace and talc assembly was wrapped in lead foil. A series of melting points were obtained with increasing pressure, as the piston continuously advanced into the pressure chamber. Then, the ram pressure was reduced and a sequence of values was determined with decreasing pressure. Our past experience has shown that friction in such a setup is reasonably symmetrical. Therefore, the in-stroke and out-stroke values of the ram pressure for a given temperature on the melting curve were averaged. The double value of friction, i.e., the difference between in-stroke apparent pressure of melting and out-stroke apparent pressure of melting amounted to approximately 10% of the total ram thrust and in view of the previous experience that friction is essentially symmetrical, the pressures reported are believed to be accurate within approximately 1%.

The method of differential thermal analysis could not be used in the determination of the solid-solid transitions in cesium because of the extremely small latent heat of the transition. Therefore, the points delineating the solid-solid phase boundaries were determined by the method of volume discontinuity. In these runs involving a large sample, the cesium was encased in either aluminum or polyethylene containers. Unfortunately, with our technique of encapsulation, cesium frequently ruptured the container and escaped at pressures above 40 kbar. In every case where the metallic cesium came in contact with the carbide pressure cylinder, the carbide pressure cylinder ruptured almost explosively. Neither polyethylene nor aluminum proved to be ideal encapsulating material, as time-dependent flow made the exact location of the transition pressure somewhat uncertain in both cases.

EXPERIMENTAL RESULTS

Figure 2 shows the phase diagram of cesium as determined by differential thermal analysis and by volume measurements. The melting points plotted are those determined on the last and most carefully carried out of five separate experiments in iron containers. In each run the melting curve was determined on both in-stroke and out-stroke of the pressure cycle. A sixth run was made using a platinum container with identical results. The reproducibility of the results plus the similarity of the results with a platinum container and with an iron container, render the possibility that the melting phenomena have been influenced by alloying extremely remote. Unfortunately, since the seal of the sample container could only be maintained under pressure, it was impossible to recover the cesium after the run. The interior of the iron sample cup, however, showed no sign of corrosion or alloying.

TABLE I. Some properties of cesium.

Initial melting slope (in degrees per kbar)		
Cs I	Cs II	Cs III
~20	2.0	2.3

Triple points					
Cs I	Cs II	Liquid	Cs II	Cs III	Liquid
P		T	P		T
25.4 kbar		191°C	47.2 kbar		90°C

Melting pressure and temperature at maxima			
Cs I		Cs II	
P	T	P	T
22.5 kbar	197°C	30.5 kbar	198°C

Slope of solid-solid boundary (in degrees per kbar)	
Cs I–II	Cs II–III
~50	11.8

Two different maxima in the fusion curve were discovered. Cs I has a maximum in its fusion curve at approximately 22.5 kbar and Cs II shows a maximum at approximately 30.5 kbar. Three points corresponding to very strong melting signals were obtained on the melting curve of Cs III. There remains a remote possibility that the triple point shown in Fig. 2, between Cs II, Cs III, and liquid is actually between three different solids and that the true melting points at these pressures lie at substantially higher temperatures. However, the region marked as liquid was thoroughly explored by the method of DTA up to 300°C without finding the slightest trace of any thermal event. The pronounced and characteristic melting signals were traced continuously from the known melting point at 1 atm., without finding any discontinuity other than those associated with the two recorded triple points. The pertinent data for the melting curve of cesium are given in Tables I and II.

Bridgman has published data on the density of solid cesium as a function of pressure at room temperature. The density change of cesium on melting at one atmosphere is known. Further, the value of dT/dP at the two maxima in the melting point curve is zero indicating that the liquids and solids have identical densities at these points, thus providing two points for the density of liquid cesium at these two pressures. From these data we have prepared a plot (see Fig. 3) of specific volume, which is the reciprocal of density, as a function of pressure for solid and liquid cesium along

TABLE II. Cesium melting points.

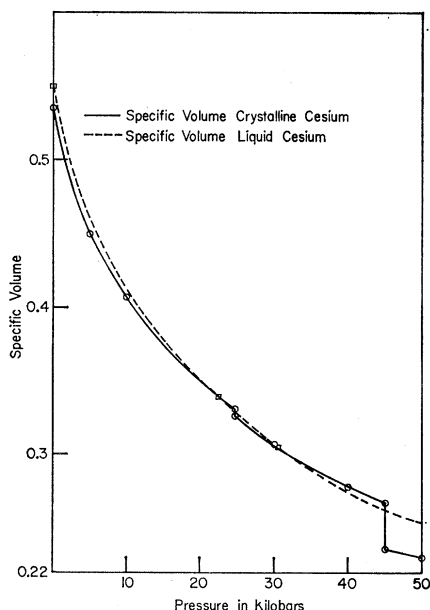| Pressure	Temperature	Pressure	Temperature
1 atm	29°C	30 kbar	198°C
5 kbar	104°C	35 kbar	193°C
10 kbar	155°C	40 kbar	168°C
15 kbar	182°C	47.2 kbar	90°C
20 kbar	195°C	50 kbar	96°C
25.4 kbar	191°C		

FIG. 3. Specific volume of coexisting solid and liquid cesium.

the melting curve. We have, however, ignored the effect of thermal expansion. To obtain the compressibility curve of liquid cesium we have drawn a smooth curve connecting the three points mentioned. It appears from this that the rather odd shape of the melting curve of cesium is due to the high compressibility of liquid cesium contrasted with the compressibility of the crystalline phases. It is possible that at high pressures a high coordination exists in the liquid state than in cesium II resulting in a denser liquid.

DISCUSSION OF RESULTS

Certain results from this investigation are noteworthy. The melting of a metallic element can apparently show much more complexity than is generally supposed and particularly the often quoted[3,10–14] Simon fusion equation,

$$(T/T_0)^c = (P+a)/a$$

(where T_0 is the normal melting point, T the melting point at pressure P, and c and a are constants for a given metal), cannot describe the complexities encountered in the melting of cesium to 50 kbar and perhaps many other metals at high pressure. The Simon equation as originally formulated by Simon[13] forbids a

fusion curve with a maximum. Knopoff[15] has modified the Simon equation in that he regards a and c not as constants but as functions of pressure. With his equation a fusion curve maximum is allowable.

It is clear that the estimates of the temperature of the earth's liquid core boundary based on the initial slope of the iron melting curve and extrapolated by the Simon fusion equation to 1.5 million bars should not be favored with a large amount of confidence.

The DTA signals associated with the fusion of Cs III were large and sharp, which suggests the fusion of Cs III was accompanied by a strong absorption of heat. This supports the conclusion of Sternheimer[8] that the Cs II $\rightleftharpoons$ III transition is probably not the result of the $6s$ electron being squeezed into the $4f$ shell, since the electron would in that case be entirely removed from the valence band, and Cs III would be expected to have only the weak cohesive forces of a van der Waals' solid and hence only a small heat of fusion.

The Cs II $\rightleftharpoons$ Cs III transition is doubtless associated with substantial evolution of heat, as the slope dT/dP of this transition is much steeper than that of the Cs I $\rightleftharpoons$ Cs II transition, even though the volume change of the latter is much smaller.

The well-known transition in cerium at approximately 10 kbar has been ascribed to the promotion of a $4f$ electron into the $5d$ shell. Lawson and Tang[16] have shown by-high pressure x-ray study, that fcc cerium remained face-centered cubic even after the transition, although there is a volume discontinuity of about 16%. The structures of Cs II and Cs III have not been determined and therefore it is impossible to state whether these are isostructural, which seems to be a criterion for an electronic collapse. In any case, no hint of a critical point in the Cs II $\rightleftharpoons$ Cs III transition was noted in the present experiments which would correspond to that suggested for Ce I $\rightleftharpoons$ II.[17]

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[17] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 15, 234 (1960).