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Phase Transition in Solid Mercury*

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A polymorphic transition in solid mercury which was initially discovered by Bridgman has been studied at lower temperatures and pressures than those previously used. The transition would occur at zero pressure and 79°K if these data are extrapolated. However, the transition begins to show time effects and large pressure hysteresis at much higher temperatures, and below 93°K it can only be made to run irreversibly and in the α-β direction, and then only upon the application of several thousand atmos pressure. The changes in the molar volume with both temperature and pressure from 4.2°K to 200°K and from zero to 12 000 atmos have been determined in addition to the changes in the thermodynamic parameters at the transition. In particular, these results can be used to explain an anomaly which was found in work on the effects of pressure on the superconducting transition in mercury.

INTRODUCTION

The existence of a polymorphic transition in solid mercury was first discovered by Bridgman[1] at relatively low temperatures and high pressures. His experimental data for transition pressures are represented by the open circles in Fig. 1, and formed the basis for his prediction that the phase transition should be found for zero pressure at, roughly, 80°K. Specific heat,[2,3] metallographic,[4] and x-ray diffraction[4] studies have given no indication of a discontinuous change in the properties of solid mercury between its triple point (234.29°K) and liquid helium temperatures.

We became interested in this problem when measurements on the variation of the superconducting transition in mercury with pressure gave anomalous results.[5] Very briefly, two transition temperatures seemed to exist (4.149°K and 4.03°K) at liquid helium temperatures, with different values for $(\partial T_c/\partial P)_{H=0}$, depending on the previous history of the sample. Data obtained for a given sample of mercury were perfectly reproducible if the pressure were kept below 4000 atmos, but a permanent, irreversible shift in the T_c *vs* P curve resulted when the pressure was cycled several times to 11 000 atmos. In order to find a possible explanation for these effects, it was decided to look in some detail at the phase diagram for mercury at temperatures lower than those available to Bridgman. It was also hoped to obtain the equation of state $[V(P,T)]$ for mercury in the temperature region below its triple point.

The experiments which will be described in detail here consisted of a series of isotherms in which changes in volume were noted as the pressure was increased to about 13 000 atmos. The transition was observed as a discontinuity in the volume in opposite directions at increasing or decreasing pressures. As the temperature was decreased, the transition pressure also decreased, but the transition became increasingly more sluggish, with time effects appearing, until below about 95°K it would go only from the old, α, phase to the new, β, phase upon the increase of pressure, but would not transform in the opposite direction.

The curve of Fig. 1 extrapolates to about 79°K at zero pressure, and below this temperature the new phase is thermodynamically more stable. However, because of the "stickiness" of the transition, pressures of 4000 atmos at 78°K, and 10 000 atmos at 4.2°K are needed to transform the α phase into the more stable β phase. The need for this "driving force," in addition to the thermal "driving force" available, explains why the β phase has not been observed previously at zero pressure. It also offers a means for understanding the superconducting experiments.

EXPERIMENTAL DETAILS

The method used was essentially the same as that which was originally described by Bridgman,[6] and which was later modified for low-temperature work.[7,8] The mercury was placed in a Carboloy cylinder ($\frac{7}{8}$ in. o.d. and 0.250 in. i.d.), the ends of which were fitted with Carboloy pistons. Carboloy is ideal for such a sample holder because of its very high (about 90×10^6 psi) Young's modulus. A force of up to four tons was applied at room temperature to the pistons by means of tie rods and a compression member which were attached to a hydraulic press. The ratio of the force generated by the press (calculated from its piston area and the oil pressure) and the area of the sample gave the sample pressure. Oil pressures were determined precisely by the direct use of a deadweight gauge, and changes in pressure of equal increments were obtained by changing

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[1] P. W. Bridgman, Phys. Rev. **48**, 896 (1935).

[2] R. H. Busey and W. F. Giauque, J. Am. Chem. Soc. **75**, 806 (1953).

[3] P. L. Smith and N. M. Wolcott, Phil. Mag., Ser. 8, **1**, 854 (1956).

[4] C. S. Barrett, Acta Cryst. **10**, 58 (1957).

[5] C. A. Swenson and L. D. Jennings, Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957 (unpublished).

[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 9 (1945).

[7] C. A. Swenson, Phys. Rev. **99**, 423 (1955).

[8] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).

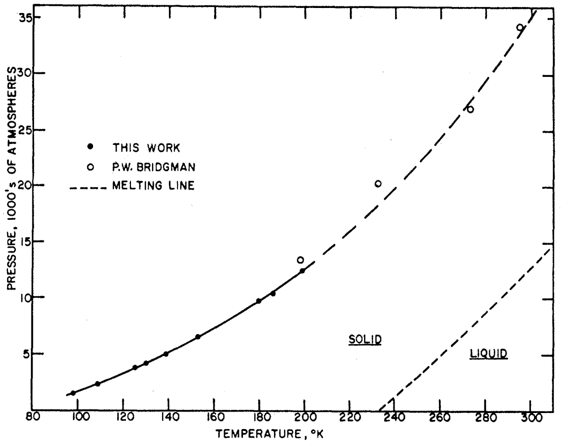

FIG. 1. The phase diagram for solid mercury.

the weights on the deadweight gauge pan by equal amounts.

The changes in the volume of the sample upon the application of pressure were observed at room temperature by means of a commercial dial gauge. The frame of this gauge was connected to the top sample holder piston by means of two quartz feeler rods, while the pin of the gauge was connected to the bottom piston by two other identical quartz rods. Thus, the extension or compression of the press members was not observed, and the main correction necessary to convert dial gauge readings to changes in length of the sample was due to the compression of the sample holder pistons. The dial gauge was graduated in 0.01-mm divisions, and the position of the needle could be estimated to 0.001 mm. The gauge was calibrated against an accurate micrometer screw over its entire range (2.5 mm), and was found to be linear. The dial gauge was completely enclosed and was read through a window, so that the space around it could be evacuated if necessary, eliminating the need for gaskets or stuffing boxes around the feeler rods.

The liquid mercury was placed in the Carboloy cylinder, the bottom of which was roughly sealed by the lower piston and a piece of scotch tape. Pressure was not applied to the complete assembly until the mercury was solidified, and loss of the solidified mercury by extrusion was prevented by using triangular steel closure rings on the end of each piston.[7] These rings fitted tightly in the cylinder, and prevented the pistons from compressing the liquid mercury with their own weight when the assembled sample holder was placed in the press. A calibrated copper-constantan thermocouple was clamped to the outside of the sample holder, and it was assumed to read the temperature of the sample.

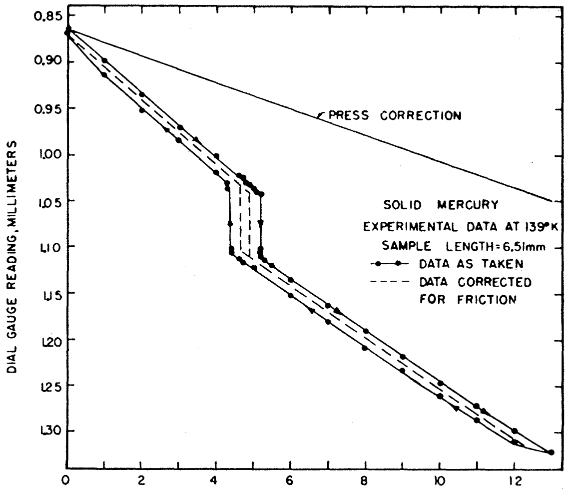

FIG. 2. A typical experimental curve, showing the α-β transition in solid mercury. The pressures are in units of approximately 1000 atmospheres.

The hydraulic press, with the sample holder in position, was placed in a cryostat of the type which has been described previously.[9] After the cryostat temperature had become stabilized at a desired temperature (the drifts during any run were never more than 0.5° as indicated by a potentiometer-recorder combination), the pressure on the sample was increased slowly to 13 000 atmos and then released gradually to a value slightly greater than zero (150 atmos), which was given by the weight of the deadweight gauge pan when empty. The approximate pressure of the transition was noted by observing the dial gauge (and the temperature) for both increasing and decreasing pressure. The sample pressure was then slowly increased in steps of about 1000 atmos by adding weights to the deadweight gauge until the transition pressure was approached, at which time the steps were changed to 100 atmos. Once the transition was completed, the steps were again increased to 1000 atmos, and the procedure repeated for decreasing pressure. A typical experimental curve is shown in Fig. 2. The difference between the increasing and decreasing pressure curves is due to friction, and the true curve is the mean of these, also shown.

In order to obtain the actual change in the volume of the sample with pressure, it was necessary to correct for the changes in piston length and cylinder area with pressure. Since the latter correction, in particular, is a strong function of the sample length, these were determined by means of a comparison experiment using samples of indium of the same length, and by assuming that the compressions of indium were known at both room temperature and 78°K.[6,8] Thus, these measurements are not absolute, but relative to indium. The resulting calibration curve (that is, the effect of the pistons and cylinder only) is also given in Fig. 2 to show its order of magnitude. The "calibration" curve was found to be linear from 2000 atmos to 13 000 atmos, although curvature was found below 2000 atmos. The change in calibration with temperature was slight (ten

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[9] C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608 (1954).

percent), so indium runs were made only at room temperature and 78°K, and an interpolation was made assuming that the calibration would not change between 78°K and 4.2°K.[8] The curvature in the experimental P-V curves below 2000 atmos was generally ignored, and blamed on the nonlinear calibration; in effect, zero pressure values of ΔL were obtained by extrapolation of higher pressure data.

The linear thermal expansion coefficient of the 55B Carboloy used is rather small ($6.5\times10^{-6}/°\mathrm{C}$)[10] so that its effect on the area of the sample holder in pressure determinations was not corrected for. This thermal expansion had an effect on the changes in (extrapolated) sample length with temperature at "zero" pressure, however, and this effect was determined from the indium runs, since the thermal expansion of indium is well known.[8] The resulting correction (obtained from three runs) was small, and the total effect of the pistons and dial gauge support system was to give changes in length which were too large by 0.023 (±0.005) mm when the sample was cooled from room temperature to 78°K. This was almost compensated for by the apparent increase in length of the samples as the area of the cylinder decreased due to thermal expansion, so the net effect (which depended on sample length) was quite small.

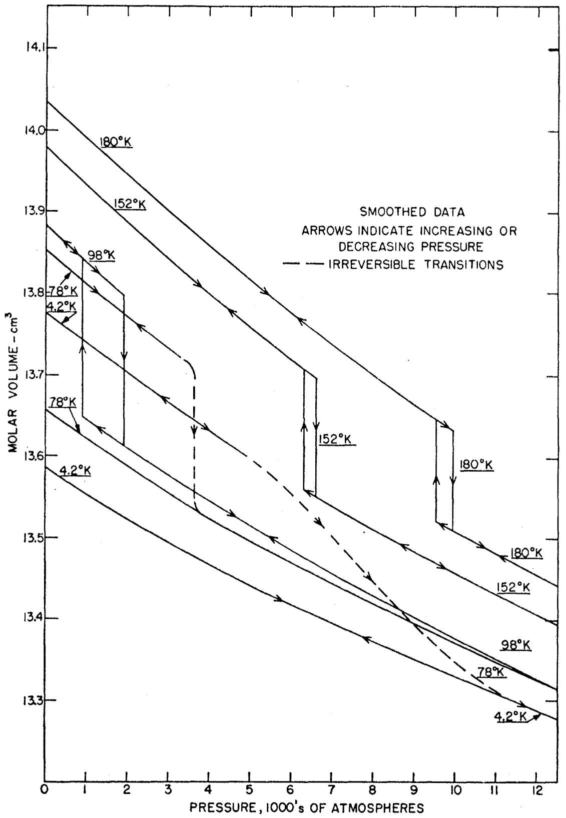

FIG. 3. Pressure-volume isotherms for various selected temperatures. The data have been corrected for the thermal expansion and distortion of the sample holder, and normalized to an assumed thermal expansion at zero pressure (see Fig. 7).

The mercury used in these experiments was the same as that used in the superconducting work, and was described on the container as "chemically pure, triply distilled, impurities less than 0.004%." The as-cooled value of the superconducting transition temperature and the sharpness of both the superconducting and the pressure transitions indicated that the purity was adequate for both experiments. Systematic errors were checked for, in part, by using samples of two different masses, 2.934 g (0.01564 mole) and 1.586 g (0.007906 mole), respectively, designated as mercury 1 and mercury 2. Their lengths at 78°K were approximately 6.50 mm and 3.48 mm. The corrected ΔL data were, in general, converted to changes in molar volume by using conversion factors which related a change in sample length of 0.01 mm to volume changes of 0.02160 cm^3/mole and 0.03997 cm^3/mole, respectively, for the two samples.

The reproducibility in the dial gauge readings at any given temperature was about 0.002 mm, whereas the reliability of changes in corrected sample length is probably ±0.004 mm, due in part to the press correction which must be subtracted from the actual data. The consistency in any given run, however, or in any series of runs, may be higher, since the corrections were assumed to vary smoothly with temperature.

RESULTS

The experimental data which were obtained fall naturally into two separate parts, those which refer to the thermodynamic parameters of the α-β transition alone, and those which refer to the general thermodynamic properties of the individual phases. The corrections which must be applied to the transition parameters are quite small, and have little effect on the data analysis. This can be seen from Fig. 2, where the transition pressure and the volume change for a given temperature can be read directly off the experimental curve once the friction correction has been made. In order to obtain the molar volumes of the individual phases as functions of temperature and pressure, however (and, hence, their thermal expansions and compressibilities), it is necessary to apply corrections for both the thermal expansion and the mechanical distortion of the sample holder. These latter data are, then, more subject to errors in detail.

The transition pressure measurements were marked by two peculiarities, which were also noted by Bridgman at higher pressures.[1] First, once the transition started to take place at a given pressure, it continued to completion except for the lowest temperatures. Even here, except for the 4.2°K run, the transition pressure extended over only a few hundred atmospheres. Once

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[10] "Properties of Carboloy Cemented Carbides," Engineering Bulletin HM-100A, Carboloy Department, General Electric Company, Detroit 32, Michigan (1951).

TABLE I. Actual experimental data for the solid mercury runs. Column 2 gives the assumed molar volume of the phase at each temperature, while all other data are as calculated from smoothed isotherms, of the type shown in Fig. 3. Columns 9 and 10 refer to the compressibility $[k=-(1/V)(\partial V/\partial T)_P]$ at the transition pressure for the two phases.

1 T °K	2 $V_{0\alpha}$ cm³/mole	3 $10^6 \times k_{0\alpha}$ atmos⁻¹	4 $10^3 \times P_{\mathrm{up}}$ atmos	5 $10^3 \times P_{\mathrm{down}}$ atmos	6 V_α cm³/mole	7 V_β cm³/mole	8 ΔV cm³/mole	9 $10^6 k_\alpha$ atmos⁻¹	10 $10^6 k_\beta$ atmos⁻¹
				Mercury 1					
199	14.070	3.62	12 550	12 200	13.568	13.463	0.105	2.42	···
180	14.035	3.30	9970	9550	13.636	13.515	0.121	2.60	1.95
153	13.987	3.24	6630	6330	13.707	13.562	0.145	2.77	2.13
139	13.961	3.08	5130	4900	13.740	13.590	0.150	3.08	2.18
125	13.936	3.02	3960	3460	13.778	13.612	0.166	3.02	2.24
109	13.908	3.12	2730	1920	13.807	13.627	0.180	3.12	2.26
98	13.888	3.15	1920	918	13.823	13.636	0.187	3.15	2.39
78[a]	13.855	2.84	0	···	13.855	13.647	0.208	2.84	2.36
	13.855	2.84	3700	···	13.698	13.530	0.167	2.84	2.02
				Mercury 2					
186	14.047	3.36	10 700	10 200	13.609	13.499	0.110	2.63	1.93
130	13.946	3.13	4480	3880	13.764	13.584	0.180	2.97	1.95
78[a]	13.855	2.80	0	···	13.855	13.647	0.208	2.80	2.19
	13.855	2.80	4100	···	13.687	13.515	0.172	2.80	1.92
4.2[a]	13.788	2.62	0	0	13.788	13.592	0.196	2.62	2.19
93[a]	13.878	···	0	0	13.878	13.680	0.198	···	···

[a] Irreversible transitions.

started, the transition rate was very temperature dependent, with the transition taking place in only a few seconds at 199°K, while it required about 30 minutes to go to completion at 98°K. This rate could be speeded up by applying excess pressure, so, at any temperature, there is some ambiguity in the assigned transition pressure due to this cause.

The second peculiarity is most likely connected with the first, and can be noted in Figs. 2 and 3. Even after the friction correction has been made, there exists an excess pressure needed to make the transition take place. This results in a hysteresis between the pressure increasing and pressure decreasing transitions (see Fig. 3, and columns 4 and 5 of Table I), and, following Bridgman, we will call this a "region of indifference." This effect became more marked as the temperature decreased until at 98° K this region was about one-third the average transition pressure. At lower temperatures the region of indifference seems to become greater than the transition pressure itself, since the transitions become irreversible, going from α to β upon the application of sufficient pressure, but not returning.

This was demonstrated by a typical experiment in which solid mercury was cooled to 78°K at zero pressure, with no sign of the transition occurring, although the high temperature transition curve extrapolates to zero pressure at 79°K. When a pressure of, roughly, 4000 atmos was applied to the sample, however, the β phase was produced and the transition occurred quite sharply but irreversibly (see Fig. 3). This phase remained stable upon repeated cyclings of the pressure at this temperature. If the temperature of this resulting β phase was increased slowly at zero pressure, the phase remained stable until about 93°K (Fig. 4), when it began to transform back into the α phase. If the sample were then cooled, it remained stable in the α phase until a high pressure was again applied.

The same experimental results were obtained when the α phase was cooled to 4°K, with no sign of the β phase appearing. Here, however, the transition appeared to take place over a range of pressures (Fig. 3), and is only complete for pressures over 10 000 atmos. The fact that it is almost complete is borne out by the difference in molar volume between the two phases at 4°K which is, within the experimental error, the same as at 78°K.

The actual experimental data for the various runs are given in Table I, with the transition pressure (columns 4 and 5, averaged) and volume change (column 8) data plotted in Figs. 1 and 5. One interesting fact that emerges is that the volume change (ΔV) is roughly independent of the temperature, but is quite

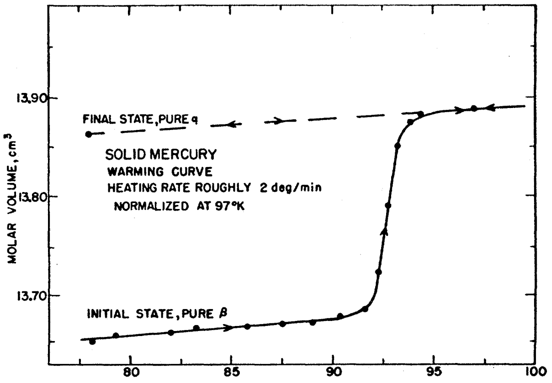

FIG. 4. The warming curve for a sample which was initially in the β phase.

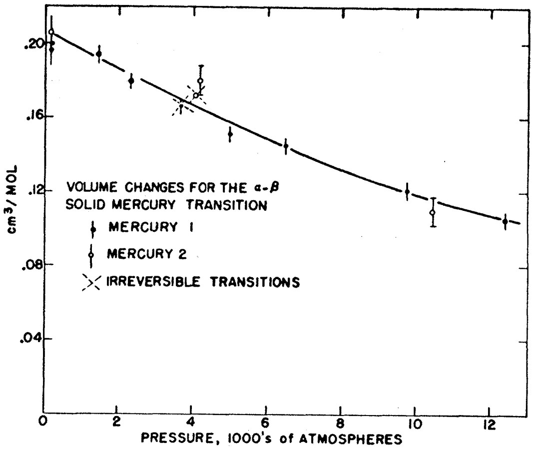

FIG. 5. The molar volume changes ($\Delta V = V_\alpha - V_\beta$) at the transition.

dependent on the pressure. This is undoubtedly due to the fact that the compressibilities of the two phases are very different, while their thermal expansions are almost the same. This will be discussed in detail later. In particular, the ΔV at 3700 atmos as determined in the irreversible transition at 78°K agrees well with the ΔV obtained for a reversible transition at 125°K and the same pressure.

The smoothed values for the transition parameters ($P,T,\Delta V$) are given in Table II, along with the entropy change and the latent heat as calculated from the Clausius-Clapeyron equation. Smoothed curves have been drawn through the above data and those of Bridgman for higher pressures. The relatively small importance of thermal effects is again emphasized by the effect of 30 000 atmos on the entropy (about a 25% increase) as compared with the change in ΔV of about a factor of three.

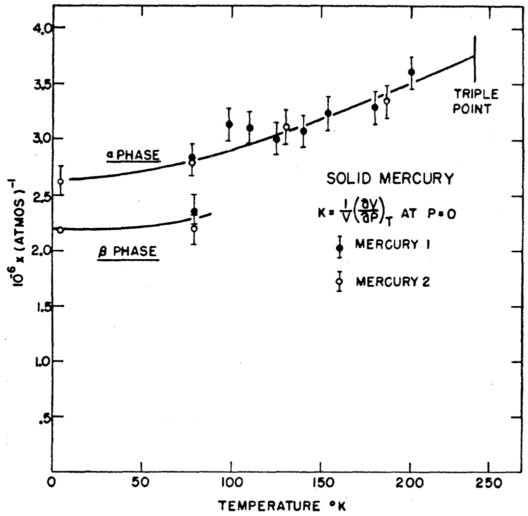

FIG. 6. The zero-pressure compressibilities of the two phases of solid mercury.

The compressibilities of the two phases at various temperatures and pressures are determined by the slopes of the corrected P-V curves of Fig. 3, and these are dependent on the press corrections. The resulting accuracy in the compressibilities is estimated to be about 5%. The compressibilities at zero pressure are tabulated in column 3 of Table I, and are plotted in Fig. 6. Smoothed values are given in Table III for various temperatures. Our value of the compressibility at 82°K ($2.8_5 \times 10^{-6}$ atmos^{-1}) is in satisfactory agreement with the value of 3.1×10^{-6} atmos^{-1} (±10%) given by Grüneisen and Sckell,[11] which was obtained by calculation from measured values of the elastic constants at this temperature.

Figure 2 shows qualitatively that the β phase is much less compressible than the α phase when the slopes of the experimental curve above and below the transition are compared. This is easily seen in Fig. 3, and the tabulated compressibilities of the two phases at the transition pressure are given in columns 9 and 10 of Table I. In general, the ratio (k_α/k_β) is of the order of 1.4 (±0.1) for high pressures, although it is only about 1.2 at zero pressure. This large difference in the compressibility is undoubtedly the cause of the large change in ΔV with pressure, and was also commented upon by Bridgman.[1]

The final information which would be useful, and which can be obtained from these data, concerns the thermal expansion of both phases at various pressures. The apparent zero pressure lengths of the two samples were corrected by comparison with the indium runs so as to give approximate values for the changes in the volumes of the two samples as functions of the temperature. However, because of the uncertainties in the setting up of the press for each run, it was not possible to assign an exact length to the sample at any given temperature, and, hence, it was not practical to try to compute an exact value for the molar volume or density at each point. The changes in length with temperature could be determined much more accurately.

It was therefore decided to assume the molar volume (density) of solid mercury in the α phase at 78°K, and to calculate the changes in molar volume from this value. For reasons which will be outlined below, the

TABLE II. Smoothed values for the changes in the thermodynamic parameters along the transition line.

P atmos	T °K	dP/dT atmos/deg	ΔV cm³/mole	ΔS cal/mole-deg	ΔH cal/mole
0	79	74	0.206	0.368	29.2
2000	105	84	0.186	0.378	39.7
4000	128	95	0.167	0.384	48.2
6000	148	111	0.149	0.400	59.1
8000	166	127	0.133	0.409	67.8
10 000	182	140	0.119	0.400	72.8
12 000	196	153	0.108	0.40	78.4
20 000	240	206	0.088	0.44	105
30 000	281	270	0.072	0.47	132

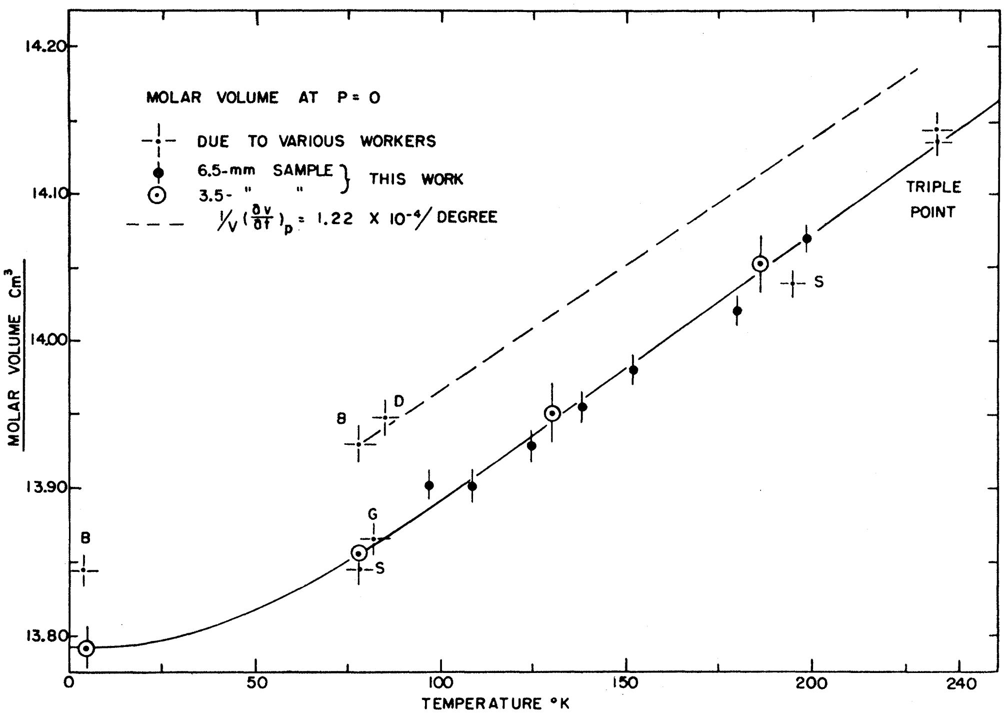

FIG. 7. A summary of the various data for the density of solid α mercury. The letters refer to various workers: *G*, Grüneisen and Sckell[11]; *S*, Sapper and Biltz[11]; *B*, Barrett[4]; *D*, Dewar.[12] The triple-point densities are as given in the text.

value of the density which was given by Grüneisen and Sckell[11] at 82°K (14.469 g/cm³ or 13.865 cm³/mole) was chosen as correct, and the resulting molar volume-temperature curve as given by our data is shown in Fig. 7, along with the data used in its determination. In particular, the curve extrapolates to the molar volume which seems correct for the triple point density of solid mercury (14.19° g/cm³ or 14.135 cm³/mole) as given in Landolt-Börnstein[12] and as calculated from the liquid density[13] and the volume change on melting for mercury at zero pressure as given by Bridgman.[14]

A straight line can be drawn through the data to give a mean volume thermal expansion coefficient of $\beta = 1.28 \times 10^{-4}$/°C, which is, again, in good agreement with the work of Grüneisen and Sckell. Their thermal expansion determination was independent of their density determination. This expansion coefficient is also in good agreement with other density measurements by Sapper and Biltz,[11] indicated by *S* on Fig. 7.

There is an apparent disagreement with densities which were calculated by Barrett from his accurate x-ray diffraction studies at 78°K and 4.2°K.[4] Barrett concludes that his data at 78°K can be explained by a simple rhombohedral structure with a lattice constant of 2.9925 A and an angle of 70° 44.6′. This gives a density of 14.402 g/cm³, or a molar volume of 13.929 cm³, in definite disagreement with the other data. There seems to be an old value of the density at 82°K of 14.383 g/cm³ proposed by Dewar[12] which is quoted in several references and which also seems to be inconsistent with other data. The discrepancy between the x-ray and bulk deteminations of the density is in the wrong direction to be explained by vacancies in the bulk specimen.

The smoothed curve of Fig. 7 has been chosen as correct in the following calculations, and the smoothed molar volumes corresponding to mercury at zero pressure are given in column 2 of Table I for each of the experimental runs. This curve is also given for the α phase in Table III, along with values of the molar volume of the β phase as deduced from the ΔV data.

Once the molar volume of the sample at zero pressure has been determined, it is then possible to determine the molar volumes corresponding to each point on each of the experimental isotherms. This has been done for

TABLE III. Smoothed values for the molar volumes of the α phase (as assumed), β phase, and their compressibilities, all at zero pressure.

T (°K)	$V_{\alpha 0}$ cm³/mole	$V_{\beta 0}$ cm³/mole	$K_{0\alpha} \times 10^6$ atmos⁻¹	$K_{0\beta} \times 10^6$ atmos⁻¹
0	13.792	13.586	2.63	2.2°
50	13.817	13.611	2.71	2.2°
100	13.891	...	2.93	...
150	13.981	...	3.20	...
200	14.072	...	3.52	...
234	14.132	...	(3.75)	...

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[12] Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (Verlag Julius Springer, Berlin, 1923), fifth edition, Vol. 1, p. 289.

[13] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1927), Vol. 2, p. 458.

[14] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949), p. 197.

[11] E. Grüneisen and O. Sckell, Ann. Physik **19**, 387 (1934).

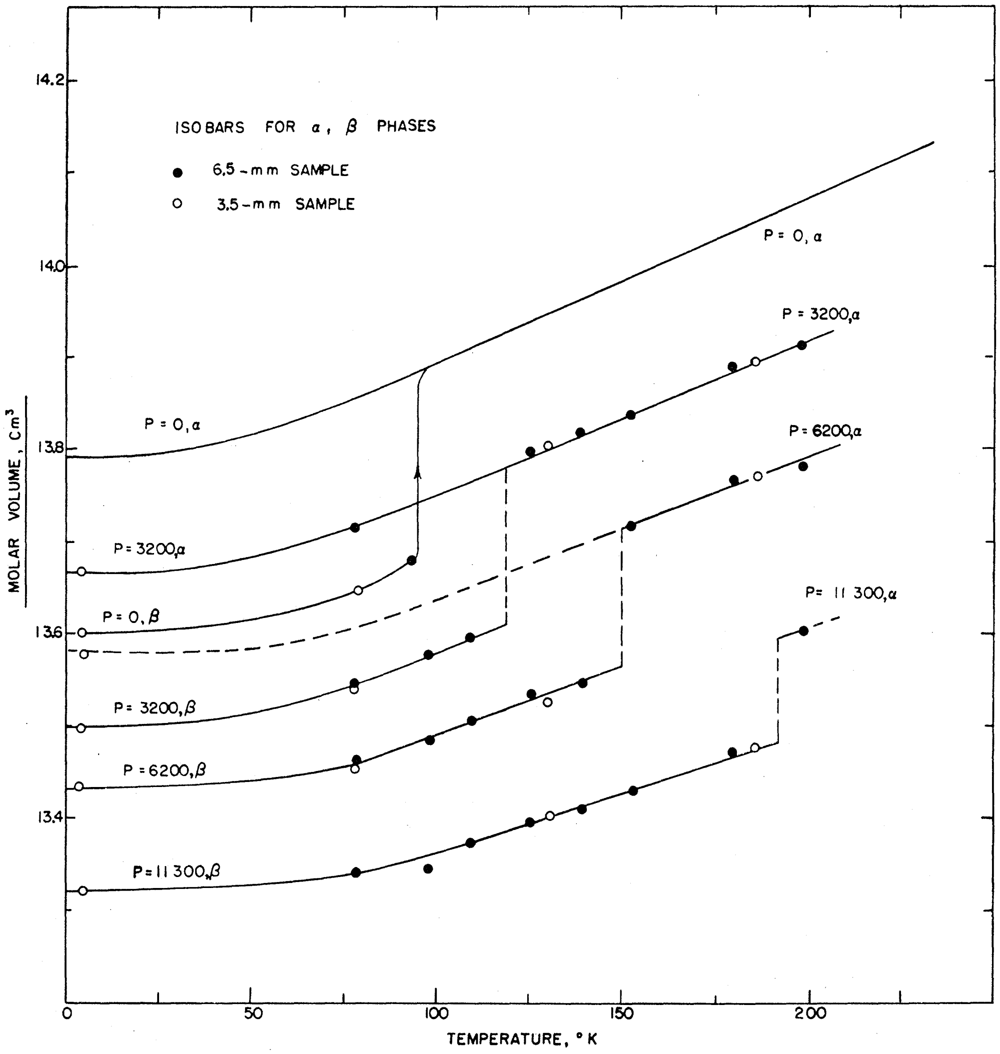

FIG. 8. Isobars for the two phases of solid mercury as determined from the corrected isotherms, which are indicated by the experimental points.

the plots in Fig. 3, and the molar volumes of the two phases at the transition have also been given in columns 6 and 7 of Table I. This information can be transformed into a form which is sometimes more useful by plotting it as isobars on a molar volume-temperature plot, and this has been done for all the data in Fig. 8. The points indicate readings from smoothed isotherms for each of the experimental runs, at the pressures indicated.

The quantity of greatest interest is the change in entropy of the mercury upon the application of pressure, and this can be calculated from $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, a Maxwell relation, where the second term can be read directly from Fig. 8. Very little can be said about the behavior of the curves below 100°K, but above this temperature they can all be represented within experimental accuracy by straight lines. If curvature had been assumed in the zero pressure curve, this would also have been reflected in the other isobars. If better thermal expansion data become available at some later date for the zero pressure curve, these curves (Fig. 8) could be transformed by merely keeping their spacing in the vertical direction constant while the V-T curve at zero pressure was altered.

If the straight line approximation is assumed, then the thermal expansion in cm³/mole-deg between 100°K and 200°K can be written as follows, where the pressure, P, is, in atmos,

$$(\partial V/\partial T)_{P,\alpha} = 1.80\times 10^{-3} - 0.38\times 10^{-7}P.$$

$$(\partial V/\partial T)_{P,\beta} = 1.72\times 10^{-3} - 0.40\times 10^{-7}P.$$

The corresponding entropy changes in this region can be given in cal/mole-deg, with the pressures again in atmos, as

$$(S_\alpha - S_{0,\alpha}) = 2.39\times 10^{-5}(1.80 - 0.19\times 10^{-4}P)P.$$

$$(S_\beta - S_{0,\beta}) = 2.39\times 10^{-5}(1.72 - 0.20\times 10^{-4}P)P.$$

Both sets of equations have been extrapolated to zero pressure, and the actual pressure regions in which each of them applies can be determined from Fig. 1. For an order of magnitude, the total entropy change in 10 000 atmos as given by these equations is about 0.385 cal/mole-deg for the α phase and 0.364 cal/mole-deg for the β phase. This is of the same order of magnitude as the entropy change at the transition, but corresponds to a volume change twice as large.

The Grüneisen constant, $\Gamma = V\beta/C_v k$, can be evaluated for the α phase from the data obtained in these experiments and the specific heat data of Busey and Giauque.[2] Γ ranges from 2.5 at 100°K to 1.9 at 200°K, and is not as constant as one would hope. However, this is probably due to the assumption that the thermal expansion is constant over this temperature range. The fact that this assumption is incorrect is also emphasized by the calculation that the changes in the entropy of the solid as induced by pressure are independent of the temperature in this same temperature region. If this were true, then the entropy curves for various pressures would have to be parallel to each other, and therefore, the specific heat would have to be independent of pressure. This cannot be true and simultaneously have the entropy decrease with pressure. This inconsistency could be removed by assigning a proper curvature to the molar volume-temperature curves, but the accuracy of the available thermal expansion data does not suggest how this should be done.

DISCUSSION

One of the major questions raised in this work is why the transition in mercury is not observed at atmospheric pressure. The values for the transition parameters and the overpressures needed to induce the transitions, along with qualitative observations as to the actual transition rates, offer an opportunity for interpretation of the results in terms of current ideas as to the kinetics of phase transitions in solids.[15]

On a purely thermodynamic basis, the relative stability of two phases can be determined by comparing their Gibbs free energies, G, with the stable phase having the lower value of G. The equilibrium line of Fig. 1 represents the temperatures and pressures at which the Gibbs free energies of the two phases are equal. In what follows, ΔG_v will be used to denote the difference between the free energies of the new and the old phases, and must be a negative quantity for the transition to take place.

The thermodynamic treatment is exact, but does not suggest when, if ever, the transition will take place. Much work has been done on the kinetics of phase transitions in general, but exact calculations are very difficult in the case of solid-solid transitions. Nevertheless, the general ideas are felt to be quite correct, and the behavior of the solid mercury transition can be explained qualitatively in terms of these ideas. Two processes are involved; the first concerns the formation of nuclei of the new phase, and the second concerns the growth of these nuclei at the expense of the old phase.

The nucleation process depends on ΔG_v and also on the temperature, while the presence of impurities and crystal imperfections assists in the formation of the nuclei. A certain amount of undercooling (the pressure and temperature of the system must be within the region of stability of the new phase) is needed to generate the nuclei in sufficient number, and the amount of undercooling necessary is expected to decrease with increasing temperature. The amount of deformation which is experienced by the samples in these one-sided compression experiments probably induces sufficient sources for the formation of nuclei so that nucleation is not a serious problem in determining the transition rate. However, at the highest temperatures, the transition rate seems to be very rapid (of the order of a few seconds for complete formation of the new phase), and yet a finite overpressure is necessary to initiate the transition. This may be because of the difficulty in nucleating the new phase.

In general, it is difficult to separate the nucleation and the growth processes, since both depend on the undercooling of the old phase, or ΔG_v. The growth process also involves a second factor, ΔG_a, which represents the potential barrier which an atom must overcome in crossing the phase boundary into the new phase. ΔG_a should be of the order of, or less than, the activation energy for self-diffusion in the substance.

On a purely phenomenological basis, Turnbull gives the following relationship which would be proportional to the rate of growth of the new phase, if the effects of strains are ignored[16]:

$$\nu_0 \exp(-\Delta G_a/kT)[1-\exp(v\Delta G_v/kT)], \qquad (1)$$

where ν_0 is the fundamental jump frequency (and presumably increases with the temperature), ΔG_a and ΔG_v are as defined previously, and v is a function which depends on the shape of the nuclei.

The value of ΔG_v can be estimated by using the thermodynamic relationship,

$$dG = -SdT + VdP, \quad \text{or} \quad d\Delta G = -\Delta S dT + \Delta V dP. \qquad (2)$$

The transition data indicate that both ΔV and ΔS are roughly independent of the temperature and pressure, so as an approximation, it is possible to assume that $\Delta V = -0.2$ cm^3/mole, and $\Delta S = -0.4$ cal/mole-deg. In an isothermal experiment, then, $\Delta G_v = \Delta V(P - P_{\text{eq}})$, and for an isobaric experiment, $\Delta G_v = -\Delta S(T - T_{\text{eq}})$. When the numbers are inserted into these expressions, it is found that for the most extreme case (78°K and $(P - P_{\text{eq}}) = 4000$ atmos), ΔG_v is of the order of $kT/8$.

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[15] For a survey of the current state of the theory of phase transitions, see the article by D. Turnbull, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, pp. 225–306.

[16] Reference 15, p. 280.

The expression, (1), then can be replaced approximately by

$$-v\nu_0(\Delta G_v/kT)\exp(-\Delta G_a/kT), \qquad (1')$$

where v has been assumed to be of the order of unity.

Thus, the transition rate in an isothermal experiment should depend directly on the excess pressure, and this was observed qualitatively. As the temperature decreases, the term in ΔG_a has a large effect, and this can be compensated for by an increase in ΔG_v, or by an increase in ΔG_v, or by an increased value of $(P-P_{\text{eq}})$. The experimental method used consisted of increasing the pressure in small increments (100 atmos) until "creep" (motion) was observed, and then waiting for the completion of the transition at this pressure, as denoted by the cessation of the "creep." At high temperatures, the transition took place almost instantaneously (a few seconds) once an appropriate overpressure had been applied. This overpressure was roughly constant at 250 atmos for all the reversible runs except at 98°K. Similar effects in mercury have been mentioned by Bridgman as existing even at room temperature and 30 000 atmos. As the experimental temperatures were decreased, the transition rate became successively slower until at 98°K, after the first signs of "creep" were noted, an additional 100 atmos had to be added in order to decrease the transition time to 30 minutes.

The relatively constant value of the overpressure needed to initiate the transition is hard to explain. The decreasing transition rate after initiation, however, can be explained qualitatively in terms of the ideas implied by Eqs. (1) and (1′). Firstly, the transition rate must depend on the amount of undercooling, whether obtained by pressure or by temperature. Secondly, a potential barrier must exist which opposes the motion of the boundary of the new phase, and the new phase must possess a certain amount of thermal energy, which can be enhanced by undercooling, in order for the boundary to move.

In general, cooling the old phase at constant temperature through the equilibrium line causes these two factors to change in opposite directions, with the decrease in rate due to the influence of the potential barrier probably having the greater dependence on temperature. The ν_0 term also presumably decreases with temperature. Thus, as the transition rate is small at 98°K, the disappearance of the transition at lower temperatures and pressures is not unexpected.

An isothermal experiment in which the undercooling is accomplished by means of an overpressure leaves the ν_0 and barrier terms unchanged to a first approximation, and since the rather large difference between the volumes of the two phases gives a large value for ΔG_v, it is not surprising that the transition can be made to occur irreversibly at 78°K upon the application of sufficient pressure (or undercooling). The pressure needed at 78°K was roughly 4000 atmos, and in a third set of experiments (not recorded here in detail) the transition also was observed to occur at 65°K in exactly the same irreversible manner as at 78°K, but at a pressure of 6000 atmos. The excess overpressure at 98°K (about 300 atmos) and the overpressures at 78°K and 65°K cannot be explained by a unique barrier potential in Eq. (1′).

While the irreversible transitions at 78°K and 65°K resembled the higher temperature transitions, the transition at 4.2°K was quite different in character, and the sample length was not observed to change except as the pressure was applied. The changes in volume with pressure gave an indication that the transition started at pressures of 5000 atmos, and the P-V curve obtained on an initial compression (Fig. 3) of the α phase could be interpreted as due to increasing amounts of the sample transforming at successively higher pressures until at 12 000 atmos the sample was completely transformed into the new phase. It is possible that the shearing deformation which is inevitably involved in experiments of this type causes the transition to proceed only while the sample length is changing, and, in effect, replaces thermal fluctuations which should be very small for these very low temperatures.

The transition has also been observed at liquid helium temperatures in the superconducting experiments, where, because the sample was surrounded by a bath of solid hydrogen, the deformation was much less. The solid hydrogen does not form a perfectly hydrostatic "bath", however, and pressure gradients of a few hundred atmos are believed to exist at the highest pressures. The superconducting transition temperatures which were found for the new phase varied from run to run, and this may serve as an indication that the transition did not go to completion in these experiments.

It does not seem likely that this is a true shear-induced transition of the martensite type, since martensitic transitions always have been observed to proceed spontaneously upon change of temperature, and no indications of this type of behavior have been reported for mercury. It would perhaps be of interest to cool a sample from 78°K to 4.2°K under a pressure of 3000 atmos to see whether or not a spontaneous transition would take place. This was not done.

One would hope that these experiments would help to explain the anomalous effects discovered by Buckel and Hilsch[17] in their experiments on thin films of mercury deposited at liquid helium temperatures. Mercury shows a decrease in its superconducting transition temperature when prepared in this way, a behavior opposite to that of the other elements which were tested. However, these effects seem to begin annealing out at temperatures as low as 50°K, much lower than the 93°K which was observed for the temperature at which the β phase would transform spontaneously into the α phase under zero pressure. Thus, it is difficult to

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[17] W. Buckel and R. Hilsch, Z. Physik **138**, 109 (1954).

decide whether or not they are observing the β phase in their experiments.

CONCLUSIONS

The transition in solid mercury has not previously been observed at low pressures because of the rapid decrease in the transition rate as the transition pressures decrease. The overpressure needed to initiate the transition increases until at 93°K it is of the order of the transition pressure itself, and the transition can only be made to proceed irreversibly. The transition cannot be made to take place at constant pressure below 93°K because of the increased hindering effect of the potential barrier which more than offsets the increased thermal driving force furnished by undercooling. The transition can be observed in an isothermal experiment upon the increase of pressure because the large difference in molar volume between the two phases allows a great deal of effective undercooling to aid the thermal driving force. The mechanism for the phase change which was observed at 4°K must be quite different, and may be due to the shearing deformation experienced by the sample.

Certain discrepancies were observed in the density of solid mercury at zero pressure, and these led to inconsistencies in the calculated thermodynamic properties of the two phases. These discrepancies should be investigated in some detail. The structure of the new phase, as well as its other physical properties, would be of interest, also, although the temperature region in which it is stable (below 93°K), and the conditions needed to produce it make these experiments quite difficult.†

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† *Note added in proof.*—Dr. C. S. Barrett has informed the author (private communication) that a re-examination of the x-ray data has removed to a great extent the discrepancies in the mercury data at 78°K.

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Analysis of Low-Energy Sputtering*

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It is postulated that for low-energy sputtering the interatomic energy and distance relation can be represented by a Morse curve, and that the energy transfer in the lattice proceeds essentially by two-particle (i.e., binary) collisions.

Based on these assumptions, a two-collision sputtering mechanism near the threshold is described. Under optimum energy transfer conditions, the analysis of this process gives the ion energy for a sputtering threshold of a surface particle tied by N bonds.

It is shown further that under a prolonged ion bombardment a surface contains particles with a number of bonds N, ranging from a maximum determined by a complete surface to a minimum determined by inaccessible bonds to underlying surface layers.

Based on this information, the form of the sputtering yield-energy function is derived, consisting of a parabolic and a linear part. Predicted and experimental Pt-Hg^+ curves are compared, and the agreement is excellent.

Two thresholds are defined: the lower threshold is the actual intercept of the yield curve, whereas the upper threshold corresponds to the intercept of the linear part of the yield curve. The two thresholds are computed for 20 metals bombarded by the Hg^+ ion. The agreement with experimental values and the empirical threshold formula of Wehner is satisfactory.

1. INTRODUCTION

CURRENT experimental work in low-energy sputtering[1] provides strong evidence that a classical collision mechanism may explain satisfactorily the observed phenomena. Two such collision theories recently have been proposed: one by Henschke,[2] and the other by the author.[3,4] Both theories rely basically on the description of low-energy sputtering as a series of two-particle collisions.

There are, however, important differences: Henschke[2] assumes that the ejecting collision is always between the deflected ion and an atom; the analysis presented here postulates a final collision between two lattice atoms. The former work[2] uses a rigid collision radius

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* Based on a dissertation presented to the Department of Electrical Engineering at Princeton University in partial fulfillment of the requirement for the Ph.D. degree.

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[1] An excellent review and a list of references of the theoretical and experimental work to 1955 are given by G. K. Wehner, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 239.

[2] E. B. Henschke, Phys. Rev. **106**, 737 (1957).

[3] Edwin Langberg, Ph.D. thesis, Princeton University, April 25, 1956 (unpublished).

[4] Edwin Langberg, Bull. Am. Phys. Soc. Ser. II, **2**, 83 (1957).