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The Structure of Mercury at Low Temperatures

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The rhombohedral structure of mercury is retained on cooling to 5° K., and the transformation detected by Bridgman at pressures of 10,000 atmospheres and above does not extend to atmospheric pressure. A polycrystalline sample cold worked at 5° K. and run at 5, 78, and 206° K. showed similar diffraction patterns at each temperature, with no evidence of transformation. The structure deduced from small droplets of mercury dispersed in albumin was simple rhombohedral with $a = 2{\cdot}9863$ Å, $\alpha = 70° 44{\cdot}6'$ at 5° K., calculated density = 14·492 g.cm.$^{-3}$, and $a = 2{\cdot}9925$, $\alpha = 70° 44{\cdot}6'$ at 78° K., calculated density = 14·402 g.cm.$^{-3}$. These values are more precise than those of earlier determinations. Recrystallization occurred at 196±4° K. when a cold-worked polycrystalline sample was warmed at about ½° C. per min.

Introduction

The X-ray diffraction work of McKeehan & Cioffi indicates that mercury has a simple rhombohedral structure at −115° C., and subsequent work has confirmed this structure by determinations at −80° C., and −150° C., indicating no detectable transformations in this range at atmospheric pressure (McKeehan & Cioffi, 1922; Wolf, 1928; Terry & Wright, 1928; Lark-Horowitz, 1929). Nevertheless, the possibility of a transformation at low temperatures is strongly suggested by Bridgman's experiments at high pressures, as he has pointed out (Bridgman, 1935). A transition in the solid state was found at 23° C. under 35,000 kg.cm.$^{-2}$ pressure; it was followed at lower pressures down to 10,000 kg.cm.$^{-2}$, where it was found to occur at −109° C., and if the curve through Bridgman's measured transition points is extrapolated to one atmosphere pressure the transition would be expected near −200° C.

Experimental evidence bearing on the question may be summarized as follows. Simon's early measurements of specific heats (Simon, 1922) were regarded by Bridgman (1935) as suggesting the possibility of a transformation; Pickard & Simon (1948), however, did not think so, and on repeating the determinations they again concluded that there was no evidence for transformation. Recent specific-heat data obtained by Busey & Giauque (1953) follow a smooth curve with no evidence of a transformation. The curve of electrical resistivity versus temperature (Onnes & Holst, 1914) was cited by Bridgman as containing a deviation from linearity in the range 90–117° K. which might be credited to a transformation. However, Bülow & Buckel (1956) find that electron-diffraction patterns of mercury deposited at 4·2° K. and subsequently held at 4·2, 20, 90 and 155° K. show no evidence of a transformation, although they show that the diffraction lines of the low-temperature deposit progressively sharpen in the interval 20–90° K.

Because of the general interest in pressure–temperature phase diagrams and the importance of a knowledge of structure in interpreting physical experiments, including those on superconductivity and magnetic resonance (Reif, 1956), it was decided to apply some effective metallographic and X-ray techniques developed in this laboratory in a search for a low-temperature transformation at ordinary pressure; and because the last determination of lattice constants was done in 1928, an effort was made to achieve greater precision than was obtained in the early work.

Experimental

1. *Metallographic investigation*

A series of single crystals of dimensions 1 × 1 × 2 cm. were grown in partially filled paraffin molds at solid carbon dioxide temperature, using freshly distilled mercury. From this series, five crystals were chosen with smooth surfaces suitable for metallographic work. These were then cooled to liquid-nitrogen temperature and returned to a bath of absolute alcohol cooled by solid carbon dioxide. During inspection in this bath, which dissolved the ice that had formed on the surface, areas were marked out on the crystals which were completely free of slip lines and other markings.

The crystals were then cooled slowly in liquid helium to 1·2° K.; they were then warmed slowly to liquid-nitrogen temperature and then transferred to an alcohol bath cooled by solid carbon dioxide for further inspection. This had previously been shown to be a sensitive method to detect martensitic transformations (Barrett, 1955–6).

The result of the experiments was that no transformation was detected in the metallographic test following this cooling cycle.

2. *Diffraction study of mercury droplets*

A sample of finely divided mercury was furnished by F. Reif, who had produced it by reducing mercurous

Table 1. *Powder diffraction patterns for mercury*

Rhombohedral indices *HKL*	At 78° K. d_o (Å)*	d_c (Å)†	I_o§	I_c	At 5° K. d_o (Å)*	d_c (Å)†
100	2·7372	2·7368	*vs*	88	2·7312	2·7312
101 } 111 }	2·2279	2·2315 2·2257	*s*	74	2·2236	2·2270 2·2212
$1\bar{1}0$	1·7324	1·7323	*m–w*	30	1·7289	1·7287
$1\bar{1}1$ } 211 }	1·4611	1·4636 1·4586	*m*	38	1·4575	1·4607 1·4557
200 } 201 }	1·3667	1·3684 1·3670	*m*	49	1·3647	1·3656 1·3642
212	1·2195	1·2200	*vw*	13	1·2175	1·2175
$2\bar{1}0$ } 202 } 222 }	1·1172	1·1180 1·1157 1·1128	*m–w*	36	1·1149	1·1157 1·1135 1·1105
$2\bar{1}1$	1·0736	1·0738	*w*	22	1·0722	1·0716
$1\bar{2}1$ } 311 }	0·9978	1·0000 0·9974	*w*	21	0·9960	0·9981 0·9954
301 } 312 }	0·9369	0·9380 0·9363	*m*	47	0·9350	0·9361 0·9344
$2\bar{1}2$ } 300 } 322 }	0·9115	0·9122 0·9091	*w*	36	0·9097	0·9104 0·9072
$2\bar{2}0$ } 302 }	0·8646	0·8661 0·8644	*m*	43	0·8641	0·8643 0·8626
$2\bar{2}1$	0·8253	0·8258	*m*	40	0·8248	0·8241
$3\bar{1}0$ } $3\bar{1}1$ }	0·8076	0·8075 0·8072	*m–s*‡	100	0·8060	0·8058 0·8055
331 } 323 }	0·8056	0·8049 0·8041	*m–s*‡	52	0·8040	0·8033 0·8025

* The observed spacings have been corrected for absorption and specimen-position error, using an internal standardization based on a Nelson–Riley plot the linear extrapolation line of which could be drawn with high accuracy.

† Calculated for $\alpha = 70° 44{\cdot}6'$ and $a = 2{\cdot}9925$ Å for 78° K., $\alpha = 70° 44{\cdot}6'$ and $a = 2{\cdot}9863$ Å for 5° K.

‡ Not completely resolved.

§ The observed intensities of the first 8 lines decrease in the same order as the calculated intensities. The observed intensities for the high-angle lines become systematically lower with increasing θ owing to their increasing width, much of the intensity being lost in the background. The intensities have been calculated for the spacings at 5° K., but the term $(1+\cos^2 2\theta)/\sin^2\theta\cos\theta$ for the structure at 78° K. is only 1 % higher at most.

nitrate with hydrazine, the droplets being dispersed in albumin. When originally prepared the particles were 100–1000 Å in diameter, but they had aged to somewhat larger sizes, most of them being less than 3000 Å in size.

The sample was inserted in a holder of the cryostat attachment of the low-temperature X-ray spectrometer described elsewhere (Barrett, 1956).

The sample, surrounded by radiation shields at liquid-helium temperature and liquid-nitrogen temperature, was cooled to 5° K., and the powder diffraction pattern was recorded in both directions of scanning. It was then warmed overnight to liquid-nitrogen temperature, 78° K., and scanned again. The two records were identical and were in reasonable agreement with the crystal structure as reported by McKeehan & Cioffi (1922). The reflections are listed in Table 1. There was no evidence for a transformation.

The observed spacings agree considerably better with calculated spacings if the parameters are chosen as

$$a = 2{\cdot}9925 \text{ Å}, \ \alpha = 70° 44{\cdot}6' \text{ for } 78° \text{ K.}$$
$$\text{and } 2{\cdot}9863 \text{ Å}, \ \alpha = 70° 44{\cdot}6' \text{ for } 5° \text{ K.},$$

rather than the values given by McKeehan & Cioffi, $a = 3{\cdot}025$ kX., $\alpha = 70° 31{\cdot}7'$ at 158° K., or those given by Terry & Wright, $a = 2{\cdot}996$ kX., $\alpha = 70° 31{\cdot}7'$ at −150° C. (123° K.), the angle being that for which the cosine is $\frac{1}{3}$. Since it is unlikely that appreciable distortion of the unit cell occurs between 123° K. or 158° K. and 78° K. when no measurable change is found between 78° K. and 5° K., it appears probable that the present value of α would be the preferred one at all these temperatures. The average discrepancy between calculated and observed spacings in the present work is clearly smaller than in the earlier investigations, and reflections at higher angles are available. Furthermore, better agreement is noted between the present calculated and observed densities than was the case before. The present values at 78° K. give a calculated density of 14·402 g.cm.$^{-3}$ (the observed density in liquid air may be taken as 14·382 g.cm.$^{-3}$); the X-ray density at 5° K. is 14·492 g.cm.$^{-3}$.

3. *Diffraction from cold-worked mercury*

A sample of polycrystalline mercury was prepared by casting in the copper holder of the X-ray spectro-

meter at dry-ice temperature, the copper having previously been lacquered to prevent amalgamation. Diffraction patterns were run at 5° K., after cold working the mercury severely while mounted in the X-ray spectrometer, using a stainless steel chisel cooled to approximately the same temperature (Barrett, 1955–6), then at 78° K. after warming overnight, and finally at 206° K. (solid carbon dioxide temperature). The similarity of all patterns indicated that severe cold work at 5° K. produced no detectable transformation.

Discussion

In view of the present results, there is no evidence that the line on Bridgman's pressure–temperature diagram representing the transition from one solid phase to the other extends to pressures as low as atmospheric. This may or may not represent equilibrium between the phases at these low temperatures. Three possibilities may be listed, the first two dealing with equilibria and the third with non-equilibrium:

(1) If the slight curvature seen in Bridgman's line were to increase considerably in the range below 10,000 atmospheres it might drop below 5° K. at a pressure above one atmosphere.

(2) As has been suggested (Bridgman, 1935), the line might end at a triple point; the phase stable over the range of temperatures investigated here would then be different from both phases investigated at high pressures by Bridgman.

(3) The known transformation may fail to occur at low temperatures if thermally induced atomic motion is required for it, as might be expected if the transformation found at high pressures is of the reconstructive type (Buerger, 1951) and is not replaced at low temperatures by a martensitic type. In this connection it is noted that the change of volume accompanying the high-pressure transformation is rather high (about 1% at 10,000 kg.cm.$^{-2}$) (Bridgman, 1935); it is higher than might be expected for a martensitic-type transformation and it increases as the pressure is decreased. If the movement of a high-energy boundary between phases is required for the mercury transformation to occur, the transformation should become very sluggish in the temperature range around 200° K. In the present experiments recrystallization was observed to take place, as shown by the X-ray diffraction patterns, when a specimen that had been cold worked at lower temperatures reached 196±4° K. during warming up at the rate of about ½° C. per min.

It might be expected that the pressure arising from the surface tension of the small droplets of mercury used here should operate (as do Bridgman's pressures) to raise the transformation temperature or to produce a transformation when one is not found at atmospheric pressure. However, a rough calculation, neglecting the effect of albumin, assuming the surface tension of mercury as 400 dyne cm.$^{-1}$ and the drop radius at 10^{-5} cm., indicates a pressure of $2\times400\times10^5 = 80\times10^6$ dyne cm.$^{-2}$; and this pressure (80 atmospheres) is too small a fraction of the 10,000 atmospheres of Bridgman's lowest pressure experiment to be significant.

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