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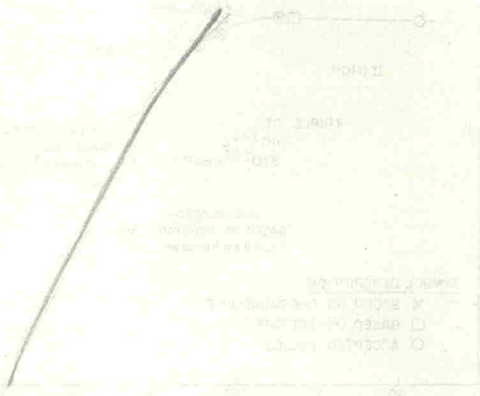

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The Pressure-Temperature Diagram of Solid Thallium

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Univariant equilibria between the I_{bcc}, II_{hcp}, and III_{fcc} phases of thallium have been determined and indicate a triple point at 110°C and 37 kbars. Calculated II → I transformation curves are compared with the experimental. Transformation volumes and/or enthalpies are calculated and enthalpies are compared with available data.

THE triple point of solid thallium has been reported by Bridgman as 153°C and 38 kbar.[1] More recently, Jayaraman *et al.*[2] have reported the triple point as near 115°C and 39 kbars. Meyerhoff and Smith,[3] assuming the elevated-pressure modification of thallium is fcc, as Kaufman suggested,[4] and that it is continuous with the room-temperature fcc phase in the Tl-In system, have used pressure data up to 5 kbars to predict the triple point at 162°C and 35.8 kbars. Piermarini and Weir[5] have indeed found the elevated-pressure phase to be fcc.

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The effect of variations of pressure and temperature in the $II_{hcp} \rightarrow I_{bcc}$ transformation in thallium have also been reported by Werner[6] and more recently by Ponyatovskii.[7]

The work reported here is part of an investigation of the effects of temperature and pressure on the Tl-In system.

I) EXPERIMENTAL PROCEDURE

The onset and progress of transformation were determined by changes in resistance. A commercially available tetrahedral-type pressure apparatus was used. Specimens of 0.060 in. diam, representing 0.63 pct of the cell volume, were encased in AgCl and mounted in pyrophyllite, as shown schematically in Fig. 1. It can be seen that the specimen is in series with the graphite furnace. Resistance changes of 0.1 pct could be detected with a Kelvin bridge. Resistance of the sample was of the order of 1 milliohm. Other pertinent details in regard to calibration and cell-assembly design are given elsewhere.[8]

Temperature calibration of the cell was carried out in two ways as a function of input wattage. Through a hole drilled in the graphite furnace, a chromel-alumel thermocouple was inserted into the AgCl to a point 0.010 in. from the sample, with the

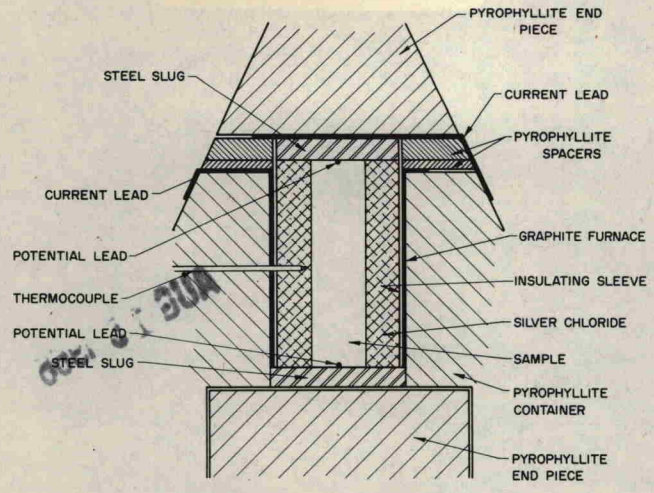

Fig. 1—Schematic of sample cell.

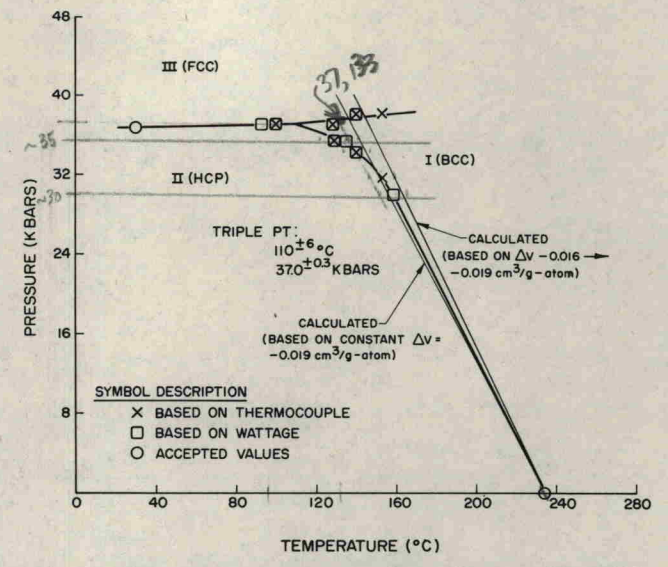

Fig. 2—Pressure-temperature phase diagram for solid thallium.

thermocouple exiting through the edge of the tetrahedron and the flash. This thermocouple was identified as the external thermocouple. The second technique was to insert the thermocouple wires in place of the specimen, with the tetrahedral faces of the apparatus serving as the cold junction. In this procedure, the thermocouple was identified as the internal thermocouple.

In both cases, it was found that temperature differences between various runs occurred at fixed wattages and increased with increasing temperature. The average temperature spread between runs for the external thermocouple was ±3.5 pct of the mean temperature, whereas the spread for the internal thermocouple was ±6 pct up to 200°C. The mean temperature for a given wattage coincided in both cases to within less than 1°C and no effect of pressure was observed on temperature differences between the two thermocouples. This permitted the external thermocouple to be used as the measure of mean sample temperature.

The spread for the internal thermocouple was regarded as being caused by thermal gradients arising from the contact of the thermocouple wires with the anvil faces. Since the possible heat transfer between specimen and anvil was reduced when the actual specimen was used, it was felt that the temperature spread was less than the ±6 pct of the internal thermocouple. However, because of the uncertainty as to the actual spread in sample temperature, the ±6 pct uncertainty figure has been retained. Since the pressure effect[9] on electromotive force of chromel-alumel thermocouples is less than the spread of temperature observed, no correction was made. Both wattage and thermocouple readings were utilized to determine temperature.

Runs were made isothermally and transformations were determined as a function of increasing pressure. Because of anticipated requirements for determination of equilibrium in the Tl-In system, the effect of loading rate on the initiation of the thallium transformation was made at room temperature. Two rates of loading in the vicinity of the transformation, 0.25 kbar per min and 0.25 kbar per 30 min,* were employed. Four runs were made for the faster loading rate and two for the slower. The slower loading rate showed a 0.6 kbar lower transformation. However, this difference is within the range of reproducibility of the faster loading rate. Thus for the loading rates used there appears to be no significant effect of loading rate on the transformation pressure of thallium.

*Pressure was held for 30 min after an increase of 0.25 kbar.

No attempt was made to make corrections for increase in actual pressure due to specimen expansion on heating.

II) RESULTS AND DISCUSSION

Results obtained are shown in Fig. 2. Bridgman's designations[1] for the phases have been used. The data of Bridgman,[1] Jayaraman *et al.*,[2] Ponyatovskii,[7] and the present work are shown in Fig. 3.

A) Transformation $II_{hcp} \rightarrow I_{bcc}$. The values obtained for dP/dT at atmospheric pressure for the various investigations are shown in Table I. There is relatively little spread in the initial slopes. However, divergencies appear at higher pressures. There is a curvature in the plots of Jayaraman *et al.*,[2] Ponyatovskii,[7] and this investigation, where the major curvature is close to the triple point.

It is possible to calculate the II → I curve as a function of temperature and pressure from the relationship

$$\Delta G(T,P) = \Delta G(T) + \int \Delta V \, dP \qquad [1]$$

as Kaufman[10] has done for the α-γ transformation in iron. $\Delta G(T,P)$ is the free energy as a function of temperature and pressure, $\Delta G(T)$ is the free-energy change as a function of temperature, and ΔV is the difference in volume between the II and I phases over the pressure and temperature range of interest.