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POLYMORPHISM IN SOLID MERCURY—A CORRECTION

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Abstract—Solid mercury is now known to undergo a phase transformation from the familiar rhombohedral structure to a tetragonal body-centred form. This transition occurs at 79°K, and is of the same martensitic type observed for lithium and sodium discovered by BARRETT. The existence of this polymorphic form was predicted by BRIDGMAN, from high pressure measurements, in about 1935, but was verified only in the work of SWENSON in 1958.

IN A RECENT paper[1] by the senior author it was stated that solid Hg "... does not show polymorphism and over the whole solid range from the melting point down to 5°K, it has the same lattice."

This statement, apparently, is no longer valid, and evidence of polymorphism in solid mercury has been accumulating since 1958. The question of phase transformations in solid Hg is intriguing, and has a long and interesting history. BRIDGMAN,[2] in his compressibility studies on mercury in 1935, observed a phase transformation in solid Hg at elevated pressures and stated "Extrapolation of the transition curve to atmospheric pressure suggests that the transition should run in the neighbourhood of liquid–air temperature. Such a transition has not been reported, but should now be searched for..." This suggestion was apparently ignored for some years.

In the late 1940s, the National Bureau of Standards measured the high temperature heat capacity of Hg, using carefully purified material prepared at the Knolls Atomic Power Laboratory of the General Electric Company. These data were published[3] in 1951 and led to a most puzzling anomaly. Combining the NBS measurements with the low temperature C_p data of PICKARD and SIMON[4] a third law calculation of the absolute entropy of Hg(*l*) at the triple point gave a value of 16·72 e.u. A statistical mechanics calculation of the same quantity (Sackur–Tetrode equation, corrected for gas imperfections, entropy of fusion, etc.) yielded a value of 16·50 e.u. DOUGLAS *et al.* remarked that this 0·2 e.u. difference was "...more likely due to errors in the low temperature heat-capacity data than to any other source." One of us (L. F. E.) suggested to him, and to several others, than this discrepancy could arise from BRIDGMAN's postulated phase transition. GIAUQUE and BUSEY[5] repeated the

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low temperature heat capacity work and found that PICKARD and SIMON's data were, indeed, in error; and using their new data, the entropy discrepancy was reduced from 0·2 e.u. to the trivial difference of only 0·07 e.u. There was no evidence reported in this study of a phase transition. It was suggested[6] that if there were a phase transformation "...the kinetics of transition ... (*at low temperatures*) would be extremely unfavourable, and it might be necessary to cold-work the metal in order to induce the phase change, as BARRETT found necessary for Li", but there was no immediate follow-up on this suggestion.

So the matter stood, and BRIDGMAN's zero pressure transition remained an elusive will-o'-the-wisp until 1958, when it was finally found and reported by SWENSON.[7] As predicted, the transformation was sluggish and required cold work, and it occurred at 79°K. In a later paper,[8] the structure of this so-called β-Hg was studied in great detail. It was found that the normal rhombohedral α-Hg was transformed into a tetragonal body-centred structure, with

$$a = 3{\cdot}995\ \text{Å}, \qquad c = 2{\cdot}825\ \text{Å}.$$

A few years later,[9] SCHIRBER and SWENSON studied the transformation kinetics further, and reported that it was martensitic, like the corresponding phase changes in Li and Na.[10] Finally, the thermodynamics of the $\alpha \rightarrow \beta$ transition was studied by KLEMENT, JAYARAMAN, and KENNEDY.[11]

The references cited are by no means complete, but include the most important ones. There is, at the present time, no room for doubt that the transformation is real. It is interesting to note that it took 23 years to verify BRIDGMAN's speculations on this subject.

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