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Experimental Fusion Curves of Indium and Tin to 105 000 Atmospheres*†

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The experimental fusion curves of indium and tin have been determined to a pressure of 105 000 atmospheres. The melting point was detected at various pressures by means of a sharp increase in the electrical resistance of the sample, which gave rise to a sudden increase in the sample temperature. The melting temperature of indium was found to rise smoothly from a normal value of 156°C to a value of 417°C at 105 000 atm. The experimental data are fitted very well by the Simon equation $P/a=(T/T_0)^c-1$, with $a=15\,000$ atm, $c=4.34$, and $T_0=429$°K. No evidence of polymorphism is observed. A phase transition is found for tin, with a triple point on the fusion curve at 38 000 atm, 318°C. The melting temperature for the first phase rises smoothly from its normal value of 232°C to the triple point, and the data are fitted very well by the Simon equation with $a=7400$ atm, $c=11.3$, $T_0=505$°K. The melting temperature for the second phase rises smoothly from the triple point to a value of 500°C at 105 000 atm, and the data are fitted very well by the Simon-type equation $(P-38\,000)/21\,800=(T/591)^{5.25}-1$. The uncertainty is estimated to be approximately ±5% in the measured melting temperature, ±5% in the pressure calibration, ±20% in the Simon coefficient a, and ±2% in the Simon exponent c.

INTRODUCTION

SEVERAL attempts have been made in the past to theoretically predict the nature of fusion curves at high temperatures and pressures. The most notable have been those of Lindemann,[1] Lennard-Jones and Devonshire,[2] Domb,[3] de Boer,[4] Salter,[5] and Gilvarry.[6] Of particular interest in the foregoing treatments are their theoretical justifications of a semiempirical fusion curve first proposed by Simon,[7] which has had remarkable success in fitting the experimental data of a wide variety of substances. This curve takes the form $P/a=(T/T_0)^c-1$, where T is the melting temperature at pressure P, T_0 is the intersection of the fusion curve with the temperature axis, or essentially the normal melting point, and a and c are empirical constants, taken to be closely related to the "internal pressure" and interatomic forces, respectively. The Simon equation was originally thought to be valid only for the frozen inert gases, but recent experimental work with metals[8–10] has clearly demonstrated its validity in this area as well.

With the development of a new super-pressure apparatus[11] capable of generating pressures in excess of 100 000 atmospheres simultaneously with temperatures up to about 3000°C, it was felt that significant contributions could be made to the problem of fusion curves of metals. Indium and tin were chosen for the first experiments because of their relatively low normal melting points, malleability, low reactivity, and (in the case of tin) promise of interesting behavior with respect to polymorphism. This paper presents the detailed data of these experiments.

APPARATUS

The tetrahedral-anvil apparatus, which was used in these experiments, has been adequately described with photographs and diagrams in other papers.[11,12] In essence, four cemented-tungsten-carbide anvils, with equilateral triangular faces, are driven simultaneously against the four faces of a pyrophyllite[13] sample-holder shaped in the form of a regular tetrahedron (see Fig. 1). The edge length of the pyrophyllite tetrahedron is 25% greater than the edge length of the triangular face of each anvil (being $\frac{15}{16}$ in. and $\frac{3}{4}$ in, respectively, in the experiments described below). Because of this, some of

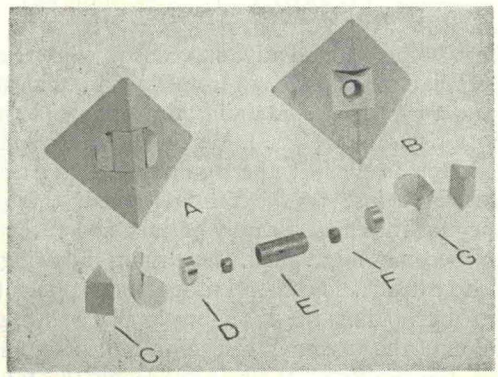

FIG. 1. Pyrophyllite sample-holder and assembly.

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[13] This is a hydrous aluminum silicate, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, sometimes known as Tennessee Grade-A Lava.

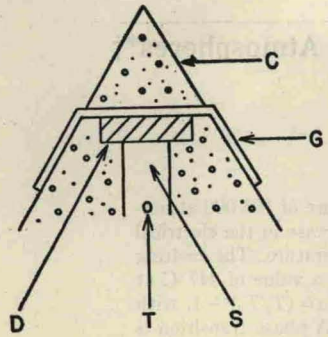

FIG. 2. Detail of sample assembly, without graphite heating tube.

the pyrophyllite is forced to flow into the space between adjacent anvils when they are driven together, thus forming a compressible gasket. The pyrophyllite has sufficient internal and surface friction to do this, and yet not so much as to be unsuitable in its pressure-transmission properties. The surface friction of the pyrophyllite, which is particularly important for the formation of a gasket that will hold in place between adjacent carbide faces without blowing out, is enhanced by painting the outside surface of the tetrahedron with red iron oxide powder. The gasket thus formed, in a run up to 105 000 atmospheres, is about $\frac{1}{4}$ in. in width and 0.020 in. in thickness.

The sample itself is in the form of a small cylinder, $\frac{1}{4}$ in. long and $\frac{1}{8}$ in. in diameter, aligned through the center of the pyrophyllite sample-holder, coaxial with a line joining the mid-points of two opposite edges. As shown in Fig. 2, the sample S is simply placed into a cylindrical hole drilled in the pyrophyllite, and bounded on the ends by mild steel plugs D, which are $\frac{1}{16}$ in. thick and $\frac{5}{32}$ in. in diameter. (These were found to effectively prevent extrusion of the sample through the ends of the container.) Electrical connections are made to the sample through 0.005-in. metal "contact tabs" G, and thermal insulation is provided at the ends of the sample container by the pyrophyllite prisms C. The metal tabs G from the ends of the sample each make contact with the faces of a pair of anvils which bring in the ac heating current.

It has also been found advantageous to place triangular steel "clamping tabs" (cut from 0.005-in. shim stock) over the two edges containing the removable pyrophyllite prisms (see Fig. 3). When the anvils are just being driven in against the pyrophyllite tetrahedron, particularly before the gasket is formed, there is a tendency for the edge assembly on each end of the sample to become misaligned, sometimes allowing the sample to extrude. These steel tabs seem to prevent this problem by holding the assembly in place during the formation of the gasket. When significant pressures are applied, the pyrophyllite breaks through the tab and forms a normal gasket, so that the clamping tab does not interfere with a symmetrical load being applied to the sample.

The temperature of the sample is measured by means of a platinum-platinum+10% rhodium (P-PR) thermocouple, the hot junction of which is embedded directly in the center of the sample at T. The wires, each 0.010 in. in diameter, are fused together at the hot junction. The cold junction is maintained at 0°C in an ice-water bath outside the apparatus, and the thermal emf is recorded automatically on a strip-chart recorder. The leads from the hot junction are brought out through opposite edges of the pyrophyllite tetrahedron, through the gaskets formed between adjacent anvil faces. It was found that with this arrangement, the sample had a tendency to flow out along the thermocouple leads upon melting, thus short-circuiting the thermocouple. (This effect was particularly pronounced with the indium, which is the more fluid of the two substances investigated. In some cases, the flow was of such magnitude that indium could be found out at the edges of the tetrahedron following a run.) This would cause the thermocouple to read some kind of an average temperature over the short-circuited region, which would introduce error by yielding a temperature reading considerably lower than the sample temperature. In attempts to eliminate this source of error, two other types of sample assemblies were used. In one case, the sample was contained in a Nichrome sleeve, of $\frac{1}{8}$ in. outside diameter and 0.005-in. wall thickness, containing end caps, with the thermocouple junction spot-welded to the outside of the sleeve. The other assembly contained the sample in a graphite sleeve of $\frac{1}{8}$-in. o.d. and about 0.014-in. wall thickness, bounded by $\frac{1}{32}$-in. graphite end plugs (as shown in Fig. 1), with the thermocouple junction embedded in the pyrophyllite just outside and adjacent to the sleeve. (In both of these arrangements, assembly was effected by using two pyrophyllite half-tetrahedrons, such that the axis of the sample lay in the dividing plane.) All three types of sample assembly were used with each of the materials investigated.

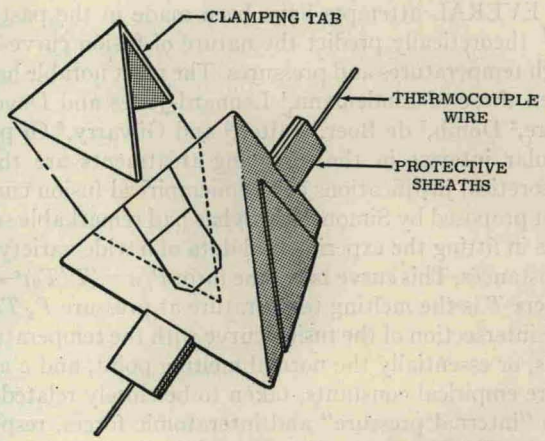

FIG. 3. Assembled sample, showing protective sheaths for thermocouple.

In order to prevent the thermocouple leads from being