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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

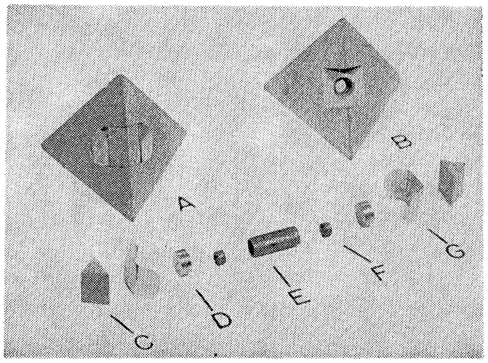

Fig. 1. Pyrophyllite sample-holder and assembly.

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[1] F. A. Lindemann, Physik. Z. **11**, 609 (1910).

[2] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A169**, 317 (1939), and **A170**, 464 (1939).

[3] C. Domb, Phil. Mag. **42**, 1316 (1951).

[4] J. de Boer, Proc. Roy. Soc. (London) **A215**, 4 (1952).

[5] L. Salter, Phil. Mag. **45**, 369 (1954).

[6] J. J. Gilvarry, Phys. Rev. **102**, 308, 317, 325 (1956).

[7] F. Simon and G. Glatzel, Z. anorg. u. allgem. Chem. **178**, 309 (1929). See also F. Simon, Trans. Faraday Soc. **33**, 65 (1937).

[8] F. Simon, Nature **172**, 746 (1953).

[9] H. M. Strong, J. Geophys. Research **64**, 653 (1959).

[10] H. M. Strong and F. P. Bundy, Phys. Rev. **115**, 278 (1959).

[11] H. T. Hall, Rev. Sci. Instr. **29**, 267 (1958).

[12] H. T. Hall, Sci. American **101**, 61 (November, 1959).

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

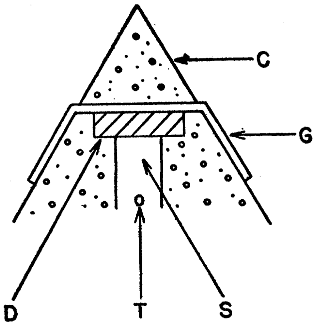

FIG. 2. Detail of sample assembly, without graphite heating tube.

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.

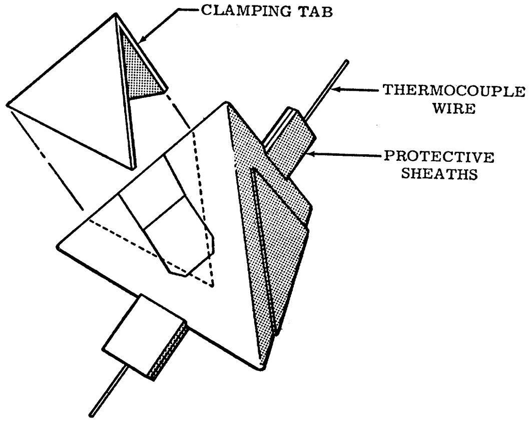

FIG. 3. Assembled sample, showing protective sheaths for thermocouple.

In order to prevent the thermocouple leads from being pinched off during the formation of the gasket, it was found necessary to use protecting sheaths of pyrophyllite. (See Fig. 3.) When these sheaths, each of thickness 0.040 in., are placed on each side of a thermocouple lead where it enters the pyrophyllite tetrahedron, the incoming carbide anvils clamp down on the sheaths before the gaskets are formed, and the securely held sheaths prevent undue flowing of the pyrophyllite adjacent to the thermocouple wire. It was found possible to keep a thermocouple intact in this manner over the entire pressure range, as long as the pressure was increasing. However, the thermocouple would invariably break as the pressure was being released, indicating that considerable flowing of the pyrophyllite was taking place as the pressure was decreased.

The measurement of the sample temperature depends upon the reliability of the P-PR thermocouple over the entire pressure range. Strong[9] reports that in the General Electric Research Laboratories, several different thermocouples were compared on the "Belt" apparatus over a wide pressure and temperature range. It was concluded there that the handbook tables for P-PR probably agree with the true high-pressure calibration to within ±10%. Further details on these tests are given in a later paper.[10] In a previous experiment at General Electric, Hall[14] had compared a P-PR thermocouple with a chromel-alumel thermocouple up to 100 000 atmospheres and 1000°C, and found agreement within 0.3% over the entire range. The question still seems to be largely unsettled.

As in the "Belt" apparatus, the pressure cannot be measured directly, but must be determined in terms of the applied load from a previous calibration of the apparatus. The pressure chamber can be calibrated by means of certain elements which undergo sharp resistance changes at certain fairly well-known pressures. These elements, for which the transitions and pressures at which they occur were measured by Bridgman,[15] are Bi (24 800 atm), Tl (43 000 atm), Cs (53 500 atm), and Ba (77 400 atm). Because of the difficulty encountered in working with cesium (extremely reactive, spontaneously igniting when exposed to air, and a liquid above 28.5°C), and because of some uncertainty in the transition pressure of thallium, only the bismuth and barium transitions were used for calibration purposes. The calibration curve is plotted in Fig. 4. The pressure calibration is thought to be accurate to ±5%.

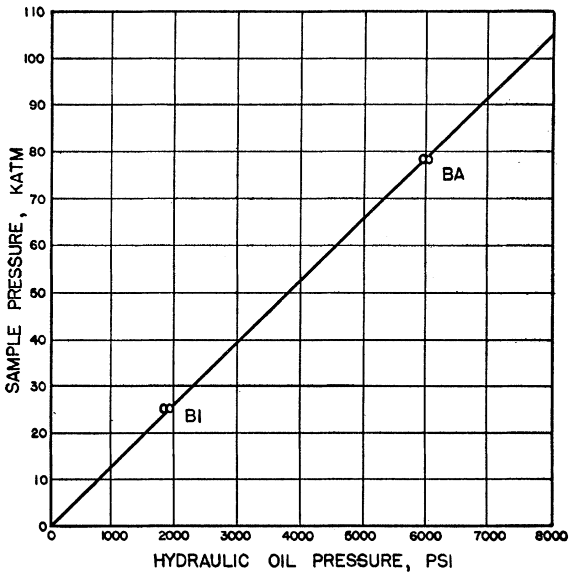

FIG. 4. Calibration curve for tetrahedral-anvil apparatus.

EXPERIMENTAL PROCEDURE

At a given pressure, the melting temperature is detected essentially by means of an electrical resistance change in the sample. The resistivity of molten indium, for example, is about three times that of the solid, and liquid tin has a resistivity of about four times that of the solid. (See *International Critical Tables*, Vol. 1, pp. 103–104.) In an experimental run, the heating power is increased very slowly as the melting point is approached, in order to approximate a condition of equilibrium as far as heat flow and temperature distribution are concerned. Under this condition, the maximum temperature of the sample should occur at its center, near the thermocouple junction. As the melting temperature is attained at this hottest point, the sample begins to melt at its center, and increases in resistance. Now the resistance of the entire sample is a fairly small fraction of the total resistance in the leads, connections, etc., in the heating circuit, so that even though the sample resistance may increase by several times its initial value, the effect on the total circuit resistance is small. This means that the current remains nearly constant as the sample melts, while the voltage drop through the sample increases significantly. Hence, as the sample begins to melt, the heating power is sharply increased in the molten portion, and the temperature accordingly undergoes a sharp increase. This effect causes the entire sample to quickly melt from the center outwards, in a sort of "avalanche effect," and the strip-chart recorder indicates a sharp increase in the thermal emf, corresponding to a jump of about 55°C in indium, or about 85°C in tin. (See Fig. 5.) The melting temperature is taken to be the thermocouple-recorded temperature at which the "avalanche" begins; that is, the value of the temperature at the initial point of its sudden increase.

The lowest pressure at which melting point measurements were made was about 6500 atmospheres. Readings at pressures below this point were found to be inconsistent and inaccurate. Gasket formation takes place from about 3000 to 5000 atmospheres, and evidently pressure is not effectively transmitted from the anvils in to the sample until the gaskets are fully formed. The melting temperature was usually measured at about

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[14] H. T. Hall (unpublished).

[15] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 165 (1952).

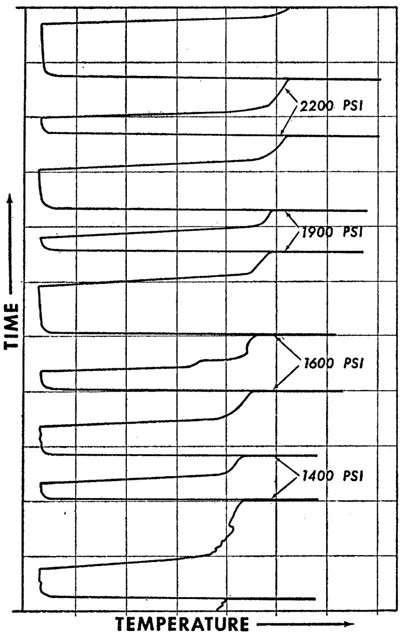

FIG. 5. Typical strip-chart record of melting.

every 6500 atmospheres, although on some runs measurements were made at about every 1300 atmospheres. (The 6500-atmosphere increment corresponds to an increment of 500 psi in the oil pressure of the hydraulic rams. This means that measurements were made at every 500 psi up to a maximum of 8000 psi, which corresponds to 105 000 atmospheres.)

Considerable variance existed in the measured fusion curves for a given substance, due to the difference in heat loss of the various samples. For example, out of the fusion curves that were measured for indium (three with graphite sleeves, two with Nichrome sleeves, and two without any sleeves, the sample being placed directly in the pyrophyllite with the thermocouple junction in the center of the sample), the measured melting temperatures at about 80 000 atmospheres were as follows: for the three with graphite sleeves, 335°C, 329°C, and 301°C; for the two with Nichrome sleeves, 308°C and 303°C; and for the two without sleeves, 336°C and 259°C. This represented a spread of about 25%, compared to the average.

In order to correct for this heat loss (due in this case to thermal conduction radially outwards from the midpoint of the sample), the following first-approximation correction formula was used:

$$t = t_m + k(t_m - t_a), \tag{1}$$

where t is the corrected temperature at the center of the sample where melting begins, t_m is the measured temperature recorded by the thermocouple, and t_a is the ambient temperature of the anvils, taken to be the temperature to which the thermocouple immediately drops just when the power is shut off after detection of a melting point. The proportionality constant k for a given sample was determined by extrapolating the fusion curve for that sample into the temperature axis, comparing the extrapolated value of the normal melting temperature with its known value, and using Eq. (1). The gratifying and rather astonishing result of applying this temperature correction to the measured fusion curves of both indium and tin was a very close correspondence of the corrected curves in each case over the entire pressure range. For example, the total spread in the corrected values of the melting temperature for a given pressure was less than 4% of the average. (Compare this to 25% for the uncorrected values.)

The largest source of error in the corrected values of melting temperature was considered to be the extrapolation involved in the temperature correction. This involved a rather arbitrary extension of the measured fusion curve from a pressure of about 6500 atm down to zero, where the variation of reasonably extrapolated values (in the case of indium) was as great as ±6% from the value finally used. This variation led to uncertainties of up to ±4% in the corrected temperatures, and it is estimated that the total uncertainty in corrected temperatures, taking into account the extrapolation, heat loss through the thermocouple wires, uncertainty in temperature readings at the beginning of the melting "avalanche," etc., is about ±5%.

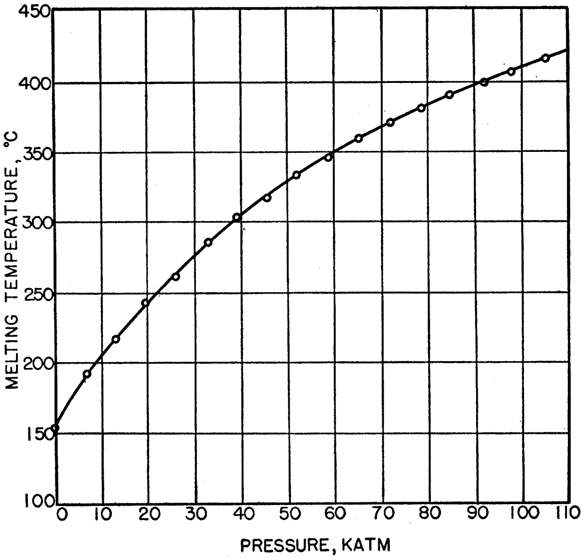

FIG. 6. Fusion curve of indium.

RESULTS AND CONCLUSIONS

The experimental fusion curve for indium is shown in Fig. 6. It is found to rise smoothly with increasing pressure from the normal melting temperature of 156°C at atmospheric pressure to about 416°C at 105 000 atmospheres. The curve is normal in the sense of Bridgman over the entire pressure range; it is concave towards the pressure axis, with no observable tendency to approach either a maximum or a horizontal asymptote. No indication of polymorphism is observed. The data can be fitted very well by the Simon fusion equation:

$$P/15\,000\text{ atm}=(T/429°\text{K})^{4.34}-1, \qquad (2)$$

the corrected melting temperatures never varying more than 1% from this curve. The values of the constants in Eq. (2) were determined by the method of least squares. In order to estimate the uncertainty in these values, the Simon equation was also fitted by the method of least squares to the maximum and minimum curves, which were drawn through the extremities of the range of uncertainty for the measured melting temperatures. The results indicated that a could vary as much as ±20%, while c changed only by ±2%.

By way of comparison, Butuzov and Ponyatovskii[16] found a nearly linear change up to a melting point of 280°C at 30 000 kg/cm², with a mean increase of 4.13×10^{-3} deg/kg/cm². The curve obtained here shows definite curvature in that range, exhibiting a melting temperature of 275°C at 30 000 kg/cm² (29 000 atm), with a mean increase of 3.96×10^{-3} deg/kg/cm². The values are in agreement to well within the experimental uncertainty.

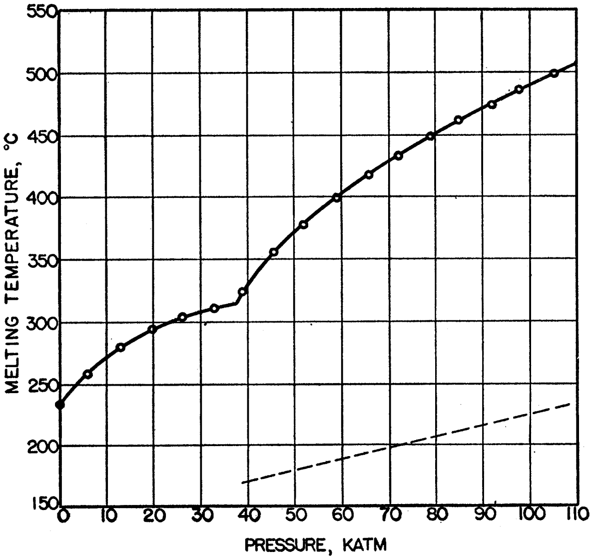

FIG. 7. Fusion curve of tin.

The experimental fusion curve for tin is shown in Fig. 7. A phase transition is indicated, with a triple point at about 38 000 atm and 318°C. The curve of the first phase rises smoothly from the normal melting temperature of 232°C at atmospheric pressure to the triple point, where a discontinuity in slope occurs. (This discontinuity was found to be reversible, and occurred consistently at the same pressure for all samples.) The fusion curve of the second phase rises smoothly from the triple point to a melting temperature of about 500°C at 105 000 atm. The curves of both phases seem to be normal in the sense of Bridgman (with the exception, of course, that the curve of the first phase does not continue indefinitely). The data for the first phase can be fitted well by the Simon equation:

$$P/7400\text{ atm}=(T/505°\text{K})^{11.3}-1, \qquad (3)$$

and the data for the second phase by the equation:

$$(P-38\,000)/21\,800=(T/591)^{5.25}-1, \qquad (4)$$

where T_0 in the transformed Simon equation for the second phase is taken to be the triple-point temperature, or 591°K. The percentage uncertainties in the Simon coefficients and exponents are about the same as those for the corresponding values in the indium equation.

These results can be compared to those of Butuzov and Gonikberg,[17] who reported a melting temperature of 309°C at 30 000 kg/cm² (29 000 atm) for tin. The value indicated at that pressure by the data of this experiment is also 309°C. Butuzov and Gonikberg only carried their experiments to 34 000 kg/cm² (32 900 atm), and hence did not detect the phase change to a higher pressure modification.

An experimental attempt was also made to determine the phase structure of tin below the fusion curve, without complete success. The electrical resistance of the sample was determined as a function of temperature (at constant pressure) up to the melting point for each of the pressures at which the melting temperature was measured, and consistent discontinuities in these curves were sought. There was some indication (by a change in slope of the resistance vs temperature curve, which seemed to appear fairly consistently over a certain pressure range) that a phase transition-equilibrium line might exist as shown by the dashed line in Fig. 7. There is considerable uncertainty in the exact position and curvature of the line, which may of course be partly due to a possible tendency of the lower temperature phase to superheat into a region of instability and therefore not consistently indicate a phase transition at the point of equilibrium. No consistent indications of phase transitions were detected at pressures below those covered by the dashed line of Fig. 7, and the phase structure in the neighborhood of the triple point on the fusion curve is uncertain. It was concluded that new and more refined experimental techniques would be necessary to determine this phase structure, and this will probably be taken up as a later project.

The rather outstanding success of the Simon equation in fitting the experimental data of not only indium and tin but also the Group VIII metals investigated by

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[16] V. P. Butuzov and E. G. Ponyatovskii, Kristallografiya **1**, 736 (1956).

[17] V. P. Butuzov and M. G. Gonikberg, Doklady Akad. Nauk S.S.S.R. **91**, 1083 (1953) (English translation NSF-tr-144, December, 1953).

Strong and Bundy would seem to indicate that the equation has real physical validity. However, it would seem equally clear that the physical nature of the Simon constants is not as yet understood. Simon sought to relate the coefficient a to the "internal pressure" by the relationship $a=\Delta E/V$ where ΔE is taken to be approximately equal to the heat of vaporization or sublimation, and V is the atomic volume. Using the values $\Delta E=57.5$ kcal/g-atom, $V=15.7$ cm^3/g-atom for indium, and $\Delta E=70.0$ kcal/g-atom, $V=16.3$ cm^3/g-atom for tin,[18] one obtains $a=151\,000$ atm for indium and $a=177\,000$ atm for tin, which are not even of the same order of magnitude as the experimental values. Also, the relationship $c=(6\gamma+1)/(6\gamma-2)$ between the Simon c and the Gruneisen γ, which was derived by both Salter[5] and Gilvarry,[6] gives values of c considerably too low for any of the metals. On the other hand, the value of c determined for tin comes very close to the smooth curve through the points representing the alkali metals and the Group VIII metals on the c-γ plot of Strong and Bundy.[10] This corroborates their suggestion that some definite functional relationship exists between c and γ. The point representing indium, however, falls in the neighborhood of the rhodium point, far from either curve. Of course, the calculated value of the Gruneisen constant[19] may well be in error because of its dependence upon the compressibility and the thermal expansion, both of which are evidently quite difficult to measure in the case of indium.

It would seem rather significant that the Simon equation can be applied equally as well to both phases of tin. In considering its application to the high-pressure phase, it becomes rather difficult to give the constant a any physical meaning, since the curve extrapolates to a temperature of absolute zero on the pressure axis at a *positive* pressure of 16 200 atm. It would be interesting to see if the Simon equation fits the fusion curves of other high-pressure phases of polymorphic substances, such as those of bismuth. All in all, it begins to appear that the Simon relationship may be some sort of an inherent fundamental property of fusion curves, in addition to having validity as an interpolation formula.

One other question which arises in connection with the ultimate behavior of any fusion curve is that of the possible existence of a liquid-solid critical point, analogous to the gas-liquid critical point. Such a point would necessarily be characterized by the vanishing of both the latent heat of fusion and the volume change of the sample in melting. No indication either in favor of or against such a phenomenon was indicated by these experiments. With this particular experimental arrangement, it was impossible to make measurements of either changes in sample volume or latent heat of fusion. The relatively small volume change of the sample upon melting was evidently absorbed by the large volume of compressible pyrophyllite in the tetrahedral sample-holder, and the heat loss through the large anvils was great enough to effectively mask any latent heat effects. (For example, when the sample was melted, and the heating power suddenly cut off, the temperature dropped very fast to the ambient level, without a break in the cooling curve.) Therefore, the only indication of approaching a critical point that would be given by this experiment would be a lessening of the "avalanche effect" on the temperature as the sample is melted. (Even this would be inconclusive, since it could conceivably be affected by volume change and latent heat in such a way as to compensate for the effect of the resistance change.) However, such an indication was not given in this case, with either the indium or the tin. With both metals, the percentage increase in temperature upon melting was approximately constant over the entire pressure range.

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[18] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes* (Reinhold Publishing Corporation, New York, 1950), 3rd edition, p. 323.

[19] See E. Gruneisen, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 1–59.

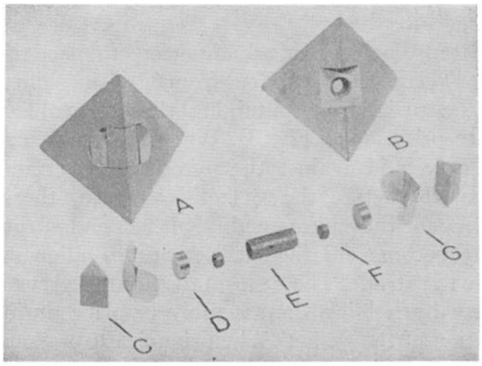

FIG. 1. Pyrophyllite sample-holder and assembly.