PHYSICAL REVIEW VOLUME 161, NUMBER 3 15 SEPTEMBER 1967

Melting Curves of Copper, Silver, Gold, and Platinum to 70 kbar*†

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(Received 16 March 1967)

The melting curves of Cu, Ag, Au, and Pt have been measured versus pressure to 60 or 70 kbar using the discontinuity in electrical resistance of a wire enclosed in parallel heating strips. The results, which compare favorably with other measurements at lower pressures, were fit to a Simon's equation. Only in the case of gold do the measured parameters in this equation closely agree with that predicted theoretically. Pressure corrections to the thermocouple measurement and temperature corrections on the pressure calibration are considered. The melting curves for Au and Ag and probably Pt are normal in the sense that they curve toward the pressure axis, but the melting curve for Cu is linear over the pressure range measured to within the accuracy of the experiment.

1. INTRODUCTION

It has long been known that the melting temperature of a substance depends upon pressure; in fact, the Clausius-Clapeyron equation was derived in 1850. And yet, because of our lack of knowledge about the liquid state, there is no theory which satisfactorily explains the various melting curves. On the other hand, Simon's semiempirical equation[1] has proved quite successful for a large variety of substances over a wide range of pressures. The major difficulty in most theories of melting appears to be that of determining the appropriate physical parameters which can be used to specify the melting point. Such criteria as critical amplitude of harmonic vibration,[2] vanishing of Young's modulus of elasticity,[3] critical vibrational energy,[4] vanishing of the shear modulus,[5] disappearance of long-range order,[6] and free energy of glide dislocation cores becoming negative[7] have all served as bases for theories of melting. It has been demonstrated that most of these theories are consistent with Simon's equation[8–10]; in fact, they have served as a means of semitheoretically determining the constants A and c in Simon's equation which may be written in the form

$$P_m/A=(T_m/T_{m,0})^c-1\,, \tag{1}$$

where P_m and T_m are the pressure and temperature at melting and $T_{m,0}$ is the melting temperature at atmospheric pressure. Several theoretical estimates for the parameter c have been proposed,[11,12] but with only limited success.

Experimentally the situation is just as confusing. The major experimental difficulties are the effects of pressure on the thermocouple calibration and the effects of heating upon the pressure calibration. Most experiments have essentially ignored these problems. While many experimentally measured fusion curves can be represented by Eq. (1), yet several show maxima and cannot be fit with a Simon's function with any choice of A and c. Even those melting curves which have the form of Eq. (1) generally give values of the parameter c which differ greatly from the theoretical predictions.[11]

This paper reports measurements of the fusion curves of copper, silver, and platinum to 70 kbar and is an extension of earlier measurements on gold.[13] Experimental fusion curves for all of these materials have been reported in the literature[14–17]; however, this measurement extends those to higher pressures.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

The details of the experimental apparatus were fully discussed in a previous article[13] (hereafter referred to as I). Only certain specific items will be presented here. The tetrahedral anvil press[18] was calibrated for each sample geometry by noting the beginning of the electrical resistance transitions on increasing pressure in Bi (26 kbar), Yb (40 kbar), and Ba (57 kbar) at room tem-

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* Work partially supported by the U. S. Air Force Office of Scientific Research.

† Paper based on a dissertation submitted by N. R. Mitra to the Brigham Young University in partial fulfillment of the requirements for the Ph.D. degree.

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perature.[19] The raw data are presented as well as those calculated after a correction to the pressure calibration was made above 15 kbar and finally, except for the measurement on Pt, a thermocouple correction was considered.[20]

The silver and copper samples were in the form of 0.075-mm-diam wires of 99.999% purity obtained from Sigmund Cohn Corporation. The pure platinum wire was 0.125-mm diam and was obtained from Baker Platinum Division of the Engelhard Industries, Inc. The wires were placed in pyrophyllite tetrahedrons using the same assembly as discussed in I except no potential leads were used to measure the resistance in the hot region alone. For melting Ag and Cu the heater strips were formed from 0.05-×6.25-mm steel shimstock, and for melting Pt the heaters were 0.05-×6.25-mm tantalum strips. The temperature was monitored by 0.25-mm-diam butt-welded thermocouples. For the experiments on Ag and Cu, the thermocouples were chromel-alumel, and for the Pt the thermocouples were W–3% Re versus W–25% Re obtained from Baker Platinum Division of Engelhard Industries. The measurements on Au were reported in I. Some of those results have been reanalyzed here for completeness.

Melting was detected by a sharp increase in the specimen resistance as discussed in I and could be determined to a precision of ±2°C. A typical x-y record of relative resistance of Cu versus thermocouple emf is shown in Fig. 1, and the point of melting is quite evident.

Each run consisted of a set of melting temperatures at various pressures. In some cases the several runs for each element did not lie exactly on the same curve. This was believed to be caused by the uncertainty in the thermocouple calibration which was ±5°C, or by temperature differences due to thermal gradients along with the difficulty of placing the thermocouple junction at the hottest point along the wire. For Ag and Cu the scatter for a given run was usually less than ±3°C, and the variation from run to run less than 7°C.[21] In the case of Pt, only one melting point could be obtained per run since the wire always separated upon melting and the scatter is much larger, of the order of ±20°C.

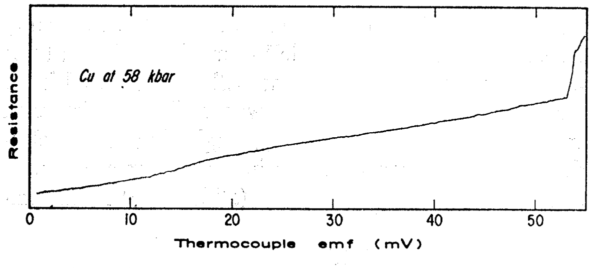

FIG. 1. Resistance of a copper wire in arbitrary units versus temperature as indicated by the emf of a chromel-alumel thermocouple. The sudden break in the curve appears at the instance of melting.

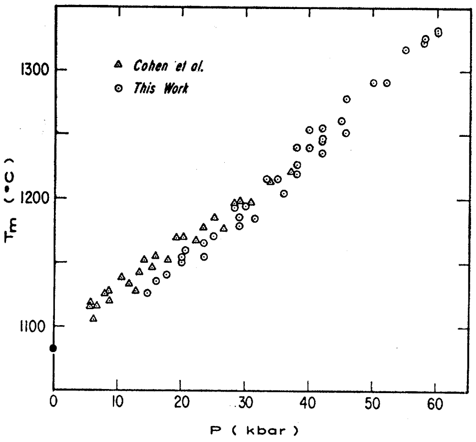

FIG. 2. Melting temperature versus pressure for copper. Uncorrected raw data.

The raw melting curves were analyzed by a least-squares fit with Eq. (1) using an IBM 7040 computer. The program was capable of minimizing the deviations of a set of data from a general function with a large number of parameters using the variable metric technique.[22] For the measurements on Au and Ag we used (1) two arbitrary parameters A and c and (2) three arbitrary parameters A, c, and B, where B is a term to account for a change in the pressure calibration due to thermal expansion and possible rearrangement of pressure gradients at high temperature. As demonstrated by the results, a much better fit to a smooth curve follows if we correct the pressure calibration by the expression

$$\begin{aligned}\Delta P &= 0, && P<15\\ &=\tfrac{1}{2}B(T_m-T_r)\\ &\qquad\times[1-\cos\pi(P-15)/25], && 15<P<40 \quad (2)\\ &= B(T_m-T_r), && P>40\end{aligned}$$

with P in kbar and T_r the room temperature. For Cu and Pt, the parameter B was not free, but fixed at 3.0×10^{-3}, the average value from the Au and Ag measurements, because there were not a sufficient number of low-pressure points to accurately determine B.

3. RESULTS AND DISCUSSION

A. Copper

A graph of the raw melting data to 60 kbar along with the 40-kbar measurements of Cohen, Klement, and Kennedy[16] is given in Fig. 2. As is seen in the graph, our

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TABLE I. Simon's parameters and initial slope of melting curve.

Parameter		Copper	Silver	Gold	Platinum
A (kbar)	raw data	374±50	73±12	107±6	393±60
	with pressure correction	354±60	80±12	111±6	443±70
	thermocouple correction	301±35	78±13	108±8	
c	raw data	0.83±0.09	2.45±0.3	2.02±0.07	1.1±0.2
	with pressure correction	0.93±0.13	2.40±0.3	2.07±0.07	1.1±0.2
	thermocouple correction	1.07±0.09	2.39±0.3	2.08±0.07	
B (10^{-3} kbar/°C)	pressure correction	3.0	2.7 ±0.7	3.2 ±0.3	3.0
	thermocouple correction		2.7 ±0.7	3.2 ±0.4	
$\frac{dT}{dP}$ (°/kbar)	raw data	4.4 ±0.5	6.9 ±0.9	6.18±0.26	4.7±0.7
	with pressure correction	4.1 ±0.6	6.4 ±0.8	5.78±0.26	4.2±0.7
	with pressure and thermocouple correction	4.2 ±0.4	6.7 ±0.9	5.97±0.3	
	Predicted[a]	3.65±0.27	5.9 ±0.3	6.0 −6.6	
	Previous work[b]	$4.{}_3$ $-4.{}_9$	$6.{}_0$ $-6.{}_9$	$6.{}_5$ $-7.{}_2$	

[a] As calculated in Ref. 16 from thermodynamic measurements at atmospheric pressure using Claperon's equation.
[b] Reference 16. The two values correspond to two different thermocouple corrections.

data drop below those of Cohen *et al.* at the lower pressures and extrapolate to a melting temperature at atmospheric pressure about 13°C below the correct value. Even though this difference may be due to high-temperature effects on the pressure calibration, the measured T_m was raised 13°C for the numerical analysis of the 11 runs with Cu. The least-squares fit to a Simon's equation gave the parameters in Table I. A and c in the table are the Simon's parameters, and B is the parameter in Eq. (2) that corrects the pressure calibration. A and c were calculated for the three conditions: first using the raw data; second correcting the pressure calibration using Eq. (2); and third adding a thermocouple correction using the results of Hanneman and Strong[20] and extrapolating where necessary. The table also gives the calculated initial slope of the melting curve for these three cases as well as the value predicted by the Clapeyron equation at atmospheric pressure and the most recently published measurements. Our results give a linear melting curve with pressure to 60 kbar to within the experimental accuracy of the data. This does not agree with the measurements of Cohen *et al.*, which show some curvature at the maximum pressures in their experiment. This difference would probably be removed after correcting their results for effects of pressure on the thermocouple calibration. At high pressure, Pt versus Pt–10% Rh thermocouples tend to read lower than chromel-alumel thermocouples used in this experiment, and this difference increases with pressure. Our initial slope is in agreement with the lower value given by Cohen *et al.* and would indicate that the appropriate thermocouple correction for Pt versus Pt–10% Rh thermocouples is that proposed by Kennedy.[23]

B. Silver

The raw data comprising seven separate runs are graphed in Fig. 3 for the melting curve to 65 kbar. All runs extrapolated to within ±2°C of the correct melting point at atmospheric pressure. The results of fitting the data to a Simon's equation are given in Table I. These results agree reasonably well with the more recent measurements of Cohen *et al.*[16]; however, our measured points are on the average 8°C higher than theirs. This difference is probably due to the use of different thermocouples in the measurements. In fact, Hanneman and Strong[20] would suggest that even a larger difference should appear between these measurements. In the earlier measurement of the melting curve of Ag by Kennedy and Newton[15] to 40 kbar, they used chromel-alumel thermocouples but their measurements gave temperatures well below either of the more recent results. The fact that our measurements using chromel-alumel thermocouples give a melting curve above that of Pt versus Pt–10% Rh indicates that chromel-alumel

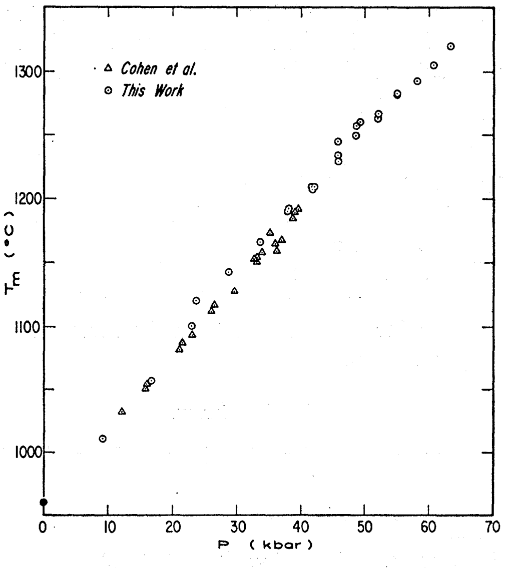

FIG. 3. Melting temperature versus pressure for silver. Uncorrected raw data.

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[23] See footnote 9 in Ref. 16.

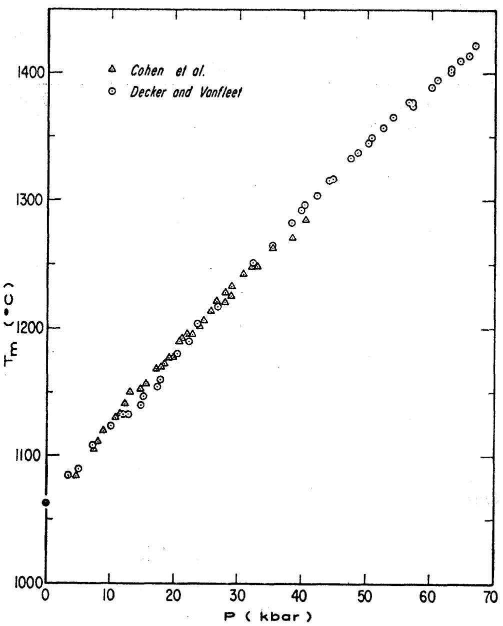

FIG. 4. Melting temperature versus pressure for gold. Uncorrected raw data.

thermocouples can be used at these elevated temperatures and pressures. The initial slope seems a little high, but, to within the uncertainty in this result, it agrees with former measurements. The large uncertainty in the calculated slope is due to the larger scatter in the measurements on silver.

C. Gold

The results on gold have been previously published,[13] but there has been some question as to our method of correcting the data for thermal effects on the high-pressure calibration.[24] We therefore show the raw data in Fig. 4 along with the measurements of Cohen *et al.*[16] for comparison. There is rather good agreement of these results at lower pressures, but again the measurements of Cohen *et al.* tend to drop below ours at the upper limit of their pressures. In the case of gold, our corrected initial slope is definitely lower than that of Cohen *et al.* after their thermocouple correction. It should be pointed out that both the correction to the pressure calibration as well as the thermocouple correction are so small that they do not alter the value of A, c, or dT/dP by an amount significantly greater than the mean deviations of the parameters.

D. Platinum

The raw melting data for Pt are shown in Fig. 5. Strong and Bundy's[17] data were corrected to the new pressure scale[25] and are also displayed in this figure. If one considers some curvature in the melting curve, it appears that these measurements would extrapolate to a value below the normal melting temperature at atmospheric pressure, but in fitting to a Simon's equation the raw measurements were used. The parameters for this curve are shown in Table I. No correction for pressure effects on the thermocouple emf was attempted, for we know of no measurements of the effects of pressure on the emf of W-3% Re versus W-25% Re thermocouples. There is considerable scatter in the data but problems of thermocouple degradation at these high temperatures as well as thermal gradients in the sample make this a rather difficult measurement. We believe that our measured melting temperatures are low even though our results are between 50 to 100°C higher than those of Strong and Bundy.

4. HIGH-TEMPERATURE CORRECTION TO THE PRESSURE CALIBRATION

It is obvious that if one increases the temperature of a constant-volume system its pressure must rise. In fact,

$$(\partial P/\partial T)_V=\alpha/K_T, \qquad (3)$$

where K_T is the isothermal compressibility and α is the coefficient of thermal expansion. The ratio α/K_T is approximately constant, giving

$$\Delta P\simeq B\Delta T \qquad (4)$$

for the pressure increase upon heating at constant volume, where $B=\alpha/K_T$.

Once the gaskets between the anvils in a tetrahedral anvil press cease to flow, the pressure chamber is essentially a constant-volume system if the temperature of

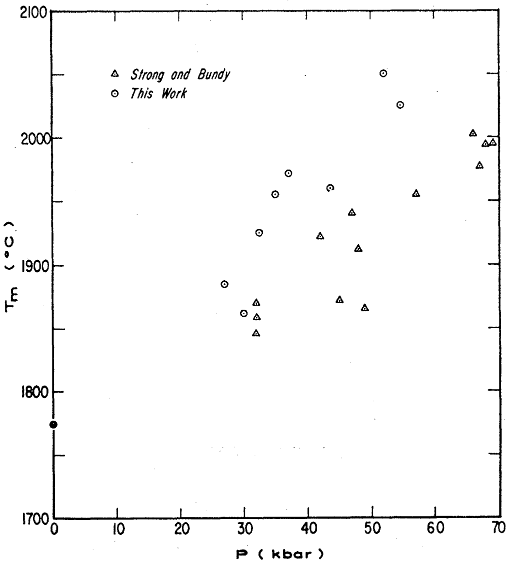

FIG. 5. Melting temperature versus pressure for platinum. Uncorrected raw data. The pressure calibration for Strong and Bundy's measurements was corrected (see text).

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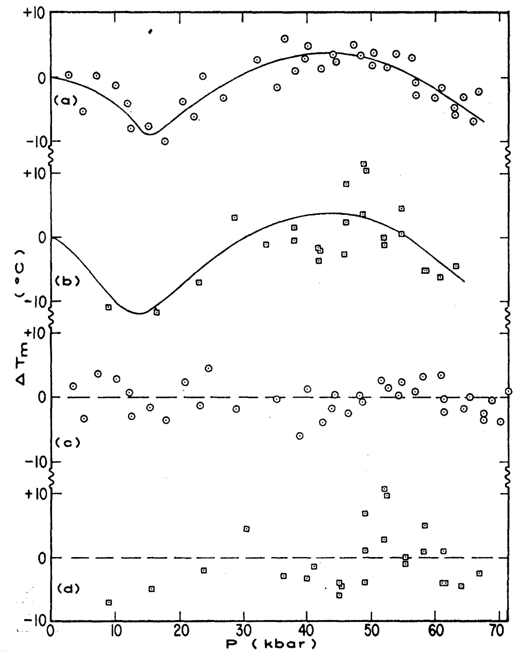

FIG. 6. Measured melting temperature minus that calculated from the least-squares fit to a Simon's equation. (a) and (b) are for gold and silver, respectively, without a correction to the pressure calibration. (c) and (d) are for gold and silver, respectively, after correcting the pressure calibration for the effects of high temperature.

the rams and anvils remains constant and the oil pressure behind the rams does not change. Internal heating as used in this experiment does not materially affect the temperature of the press and at high pressures does not alter the oil-pressure reading; thus, one might suppose that the pressure at the sample must increase. However, it is not as simple as this, since there are large pressure gradients set up in the surrounding pyrophallite in attaining the pressure, and these gradients may change with heating. Evidence was presented in I to show that, for this geometry, the gaskets flow upon heating at pressures below 15 kbar and do not flow if the pressure is above 40 kbar. Further evidence of this effect as well as the need for considering a correction to the room-temperature pressure calibration is given in Fig. 6. In curves a and b the difference between the measured points and a least-squares fit of the raw data to a Simon's equation is shown for Au and Ag. Curves c and d depict the same quantity, but the computer was allowed to find the best correction to the pressure calibration using Eq. (2). Curves a and b in Fig. 6 show a definite anomaly between 15 and 40–45 kbar, which is greater than the scatter in the data. This anomaly is removed in *c* and *d* by the proposed correction of the pressure calibration.

The least-squares analysis including the pressure correction gives approximately the same value for the correction parameter B for both Au and Ag. It is also interesting to compare this experimental value with the value calculated for α/K_T for BN which is the principal material in the hot region. The values for α[26] and K_T[27] for BN at room temperature and atmospheric pressure are $13\times10^{-6}\ ^\circ\mathrm{C}^{-1}$ and 3.8×10^{-3} kbar^{-1}, giving $B=3.4\times10^{-3}$ kbar/°C which, interestingly, agrees with the best-fit value calculated for B. As has been clearly demonstrated,[28] the Simon's equation does give a very good representation of melting temperature versus pressure for many materials, at least over the range of pressures encompassed by the measurements. Thus it is very unlikely that this anomalous kink should appear in both the melting curves of Au and Ag,[29] and we conclude that a correction to the pressure calibration for high-temperature use is not only valid but necessary. For Pt and Cu this pressure correction does not shift the melting curve beyond the scatter in the raw data and is thus not too significant. From the results in Table I one observes that this correction does not alter the character of the melting curves enough to change the parameters of Simon's equation beyond their uncertainties determined by the scatter in the measurements. For Au, which constitutes the most accurate measurement, this pressure correction does make a significant change in the calculation of the initial slope of the melting curve.

Since the computer-determined correction parameter agrees so well with the estimated correction for a constant-volume system, it is tempting to think of the source of this correction arising from the pressure increase due to heating an almost-constant-volume system. But as mentioned above, the pressure gradients may play an important role here and, in fact, there is some evidence to show that at lower pressures where the gaskets might still flow, the sample pressure may actually drop with heating.[30]

ACKNOWLEDGMENTS

We wish to thank H. Tracy Hall for providing the tetrahedral anvil press with which this experiment was performed.

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