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MELTING CURVES OF GRAPHITE, TUNGSTEN, AND PLATINUM UP TO 60 KBAR

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Melting curves are plotted for graphite up to 60 kbar, tungsten to 50 kbar, and platinum to 40 kbar, using an optical method based on thermal radiation. The results agree well with those obtained for platinum by thermal analysis, but less well with those obtained for graphite by means of electrical measurements. The melting curve of tungsten was obtained for the first time. The pressure dependence of the melting point is found to be quadratic for graphite, but linear for tungsten and platinum.

MUCH of high pressure physics is concerned with investigations of phase transitions, particularly melting and solidification. An enormous amount of data has been accumulated in the course of many years, but only during the past decade has it become possible to study melting at pressures above 100 kbar and at temperatures above 1000°K.[1-4]

It is well known that when the pressure dependence of a melting point is investigated both the pressure and temperature must be measured at the moment of melting. At the present time no fundamental difficulties prevent the production of pressures of the order of 100 kbar. However, some uncertainty is still attached to the pressure measurements, because more than one method exists for fixing reference points and different procedures do not always yield identical results.[5-8]

Thermal analysis is usually used to measure melting points up to 2000°K at high pressures and to determine the moment when a sample melts. However, these measurements often become difficult and sometimes impossible because the materials of thermocouples may melt; consequently, corrections are required to allow for pressure dependence of the thermoelectromotive force. Measurements at higher temperatures are based on parameters of the electric current used for heating. The thermal energy insertion Q is then calculated either, as in the case of graphite, from the equation

$$Q = \int_{T_0}^{T} C_p(T)\,dT, \tag{1}$$

or by comparing the heat input with thermocouple measurements or with known temperature standards and then extrapolating to higher temperatures. In such work it is difficult to guarantee high accuracy, first, because we have no reliable experimental data on the temperature dependence of C_p, and secondly, because it is difficult to calculate the loss of thermal energy in electrical conduction, since we know that at high temperatures and pressures all insulating materials become electrical conductors to some degree.

It therefore becomes of decided interest to measure melting points optically, on the basis of the laws of thermal radiation, and to compare the results with those obtained through thermal analysis and electrical measurements. For this purpose we chose materials having melting points above 2000°K under normal conditions.

We have previously published[9] descriptions of our apparatus and technique for investigating melting points up to 3 kbar and to 40 kbar. We determine the color temperature from the Planck distribution. From the analytic form

$$E_{\lambda T} = kI_{\lambda T} = \frac{2\pi hc^2}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}, \tag{2}$$

of this distribution we determine T for a black or gray body by measuring the relative intensities

$$I_{\lambda_1 T} = \frac{1}{k}E_{\lambda_1 T}, \quad I_{\lambda_2 T} = \frac{1}{k}E_{\lambda_2 T}$$

of two arbitrarily selected wavelengths λ_1 and λ_2 and then obtaining their ratio $I_{\lambda_1 T}/I_{\lambda_2 T}$. For brevity we shall use the notation $I_{\lambda_1 T} = I_1$, $I_{\lambda_2 T} = I_2$, and $I_{\lambda_3 T} = I_3$,

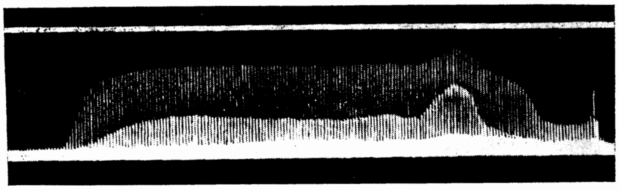

FIG. 1. Oscillograph traces of intensities I_2 and I_3 vs. time (for heating and melting of graphite).

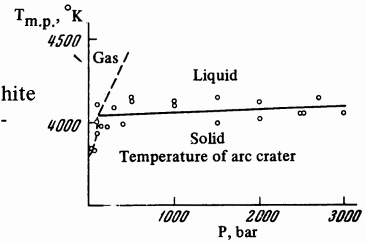

FIG. 2. Melting curve of graphite to 3 kbar. The dashed curve represents data from [11].

where $\lambda_1 = 420$ mμ, $\lambda_2 = 622$ mμ, and $\lambda_3 = 825$ mμ.

The intensities of particular spectral regions were determined by sending the radiation from each test sample through a system of interference filters. In this way we isolated narrow bands from the continuous emission spectrum. After traversing the system of periodically alternating filters the light impinged on an FÉU-22 photomultiplier for conversion into an electric signal that was amplified (using the dc amplifier of Moroz[10]) and registered with an MPO-2 loop oscillograph. The oscillograms in Fig. 1, obtained during the heating and melting process, are semisinusoidal. The amplitudes represent intensities, while their envelopes represent the time variation of the line intensities I_1 and I_2 passing through the corresponding light filters. The intensity ratio characterizes the temperature of the radiation; melting is indicated by the temperature plateau. In the present paper we confine ourselves to results obtained by investigating graphite, tungsten, and platinum.

1. GRAPHITE

Our sample of spectroscopically pure graphite was investigated in an argon atmosphere up to 3 kbar. Temperatures resulting from heating by an electric current flowing through the sample were determined from the I_2/I_3 ratio. The results obtained by least squares are shown in Fig. 2, where we observe that the melting point of graphite rises from 4040°K at 100 bar to 4090° at 3000 bar. Temperature measurements below 100 bar revealed a break in the fusion curve, corresponding to the carbon triple point (of gaseous, liquid, and solid states) at $P = 100$ bar and $T = 4040$°K; the same result had previously been obtained independently in [11] and [12]. Our measurements can be represented by the linear equation

$$T_{\text{m.p.}} = 4035 + 1{,}96 \cdot 10^{-2} P, \qquad (3)$$

where $T_{\text{m.p.}}$ is the melting point in °K and P is the pressure in bars. The deviations of the experimental points from the smooth curve indicated ± 1.0% probable error in the temperature measurements, with a maximum deviation of not more than ± 3%. The error of pressure measurements was ± 1%.

At pressures to 40 kbar the sample, encased in rock salt, was heated by an alternating current. Pressures were measured with a manometer located on the press, and were converted according to a calibration curve. The pressure calibration of the apparatus was based on polymorphic transformations of bismuth and thallium (the Kennedy–La Mori scale). Temperatures were measured by means of the I_2/I_3 intensity ratio. The initial temperature was 4070°K at 2 kbar and was determined from measurements extending to 3 kbar. However, the ratio I_2/I_3 obtained experimentally for this temperature is only one-half of the ratio representing this temperature on the calibration curve. We attribute this discrepancy to selective absorption of the radiation by graphite vapor that appears around the sample at the moment of melting and diffuses into the salt to form a kind of filter. Following the experimental work the salt tablet revealed a distinct dark gray layer surrounding the residue of the sample. Assuming that higher temperatures and pressures enhance the density of this vapor without greatly changing its selectivity, which depends essentially on the type of absorbing material, we introduced the same correction for absorption in all later I_2/I_3 ratios corresponding to melting points at higher pressures.

To improve the accuracy of these corrections we subsequently measured each temperature using the ratios I_1/I_2 and I_2/I_3 simultaneously; for this purpose three filters were attached to a single rotating disk. The measurements were extended up to 60 kbar; the ratios I_1/I_2 and I_2/I_3 were corrected for absorption as in the case of the measurements up to 40 kbar. The temperatures based on the two different ratios disagreed slightly (by at most 5%); those obtained from I_1/I_2 were lower. However, the discrepancy does not exceed the experimental deviation from the smooth curve. The relationship was reversed in the case of tungsten, for which I_1/I_2 yielded higher temperatures than those obtained from I_2/I_3 (using arithmetical averages in the calculations).

Figure 3 shows the experimental results obtained in runs up to 40 kbar and to 60 kbar, in a least squares treatment. We note that the melting point of graphite rises from 4070°K at 2 kbar to 5100°K at 60 kbar.

The experimental data can be represented by the quadratic equation

$$T_{\text{m.p.}} = 4006 + 25{,}78 \cdot 10^{-3} P - 0{,}12 \cdot 10^{-6} P^2. \qquad (4)$$

The deviations from the smooth curve were used to compute errors. In the series going to 40 kbar the probable error of the temperatures was ± 2.5%, and the maximum deviation did not exceed ± 7.8%. In the series going to 60 kbar the probable error was ± 4.0% and the maximum deviation was ± 13%.

The extension of the pressure range necessitated changes in the design of the pressure vessel and pistons. In order to reduce the deformation of its effective volume the vessel (Fig. 4) was made of two coaxial parts (a and b) pressed together (with a conical fit). Each piston c was made of a single piece of metal having a conical lateral surface. Both (movable) pistons were insulated (by Teflon) from the walls of the vessel; they served simultaneously to create pressure and as

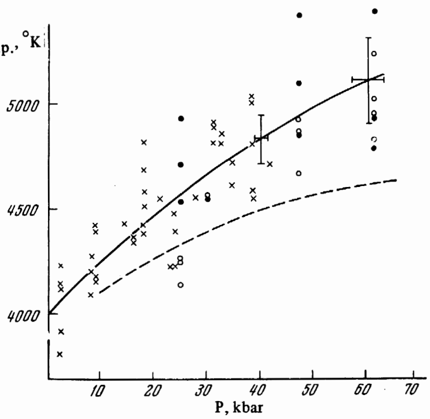

FIG. 3. Melting curve of graphite to 60 kbar. The dashed curve represents the results given by Bundy in [2]. Temperature measurements are represented as follows: X from I_2/I_3 up to 40 kbar; O from I_1/I_2, and ● from I_2/I_3, to 60 kbar.

electrical conductors. The new vessel was pressure calibrated by means of polymorphic transformations in bismuth, thallium, and barium (the Kennedy–La Mori scale). We obtained ± 6% accuracy with the apparatus used to 60 kbar, and ±4% accuracy with the apparatus used to 40 kbar.

It should be noted that the melting points of graphite obtained in the present work differ somewhat from those given in our earlier papers,[9] where the apparatus and experimental technique were described. Our earlier temperatures are unfortunately somewhat too high because of calibration errors that arose because in our calibration we used interchangeable type NS filters mounted before the slit of the photomultiplier. Light transmission by these filters in the wave bands $\Delta\lambda_1$, $\Delta\lambda_2$, and $\Delta\lambda_3$ was measured by means of an SF-4 spectrophotometer with errors that introduced corresponding errors in the temperature measurements.

The optical parameters of the filters were subsequently measured with SF-4 and DFS-4 instruments independently. The results were in agreement, and our earlier temperatures (in runs up to 3 kbar and to 40 kbar) were properly corrected. To eliminate errors originating in the instrument that measured the filter parameters, we began for the 60-kbar apparatus to combine the absorption and interference filters, using the same combinations for calibrating and measuring.

In spite of the correction, the melting curve of graphite still lies a little above the curve that Bundy obtained[1, 2] by measuring the electrical parameters (the dashed curve in Fig. 3). This discrepancy increases, and reaches 400–500°K at 60 kbar; this is 8–10% of the measured magnitude. We find the cause of the disagreement in the measurement procedure. Bundy[2] determined melting points from Eq. (1) and assumed a linear increase of C_p with temperature on the basis of work done by Spencer, and also by Currie, Hamister, and MacPherson, who showed that the specific heat increases monotonically from 300° to 1500°K, as well as on the measurements of Hove, who showed that C_p increases linearly from 1400° to 3400°K, followed by a very rapid increase (Fig. 5). Considering this

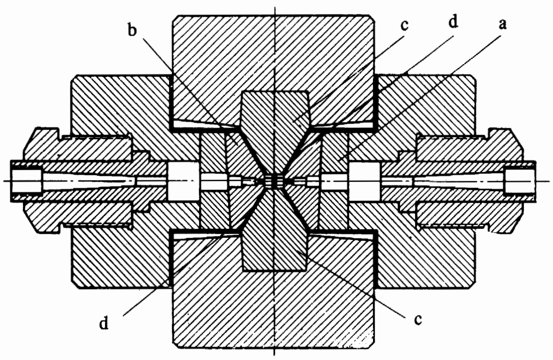

FIG. 4. Diagram of pressure vessel used for optical investigations of melting curves up to 60 kbar.

rapid increase of C_p to be unlikely and attributing it to experimental errors above 3400°K, Bundy extrapolates the linear portion of the C_p vs T curve up to 5000°K and bases his temperature calculations on this extrapolated value of C_p. Also, in calculating the thermal energy insertion Q he introduced corrections for the conductivity of the insulating materials. These corrections combined with those for superheating could amount to half of the total energy expended in heating. Corrections of 30–70% for the fraction of the graphite that participated in the melting process were determined from photomicrographs. Under these conditions corrections for the specific heat could be omitted. It seems to us that even if a satisfactory correction were introduced for the loss incurred in measuring the thermal energy Q expended for heating, it remains doubtful whether Bundy's form for the relative temperature and pressure dependences of C_p is justified; experimental confirmation is needed. If we assume the possibility of a somewhat more rapid increase of C_p with temperature at atmospheric pressure, higher melting points of graphite are obtained from Bundy's measurements.

We recall that our measured melting points of graphite are actually color temperatures, which are somewhat higher than the true temperatures.

2. TUNGSTEN

The tungsten used in our experiments contained 0.01% niobium. The same measuring procedure was used as for graphite up to 60 kbar. Temperatures were determined by means of three filters simultaneously, from the ratios I_1/I_2 and I_2/I_3. The initial point of the curve was the melting point, 3655 ± 60°K,[13] of tung-

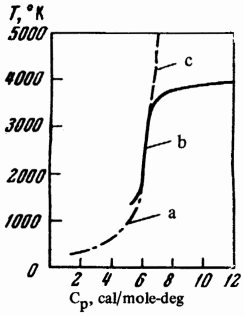

FIG. 5. C_p vs. T as given by Bundy [2]: a–data of Spencer, and of Currie, Hamister, and MacPherson to 1500°K; b–data of Hove to 3400-3900°K; c–Bundy's extrapolation to 5000°K.

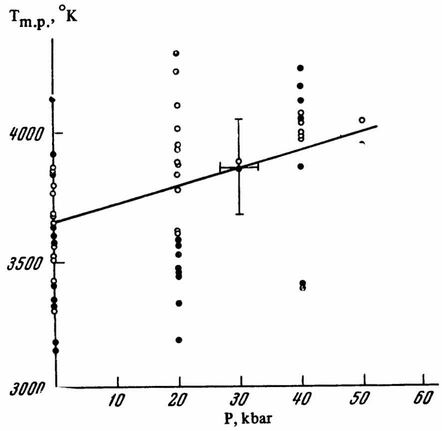

FIG. 6. Melting curve of tungsten up to 50 kbar. ○ – I_1/I_2, ● – I_2/I_3.

sten at atmospheric pressure. Comparing the experimental intensity ratios at the initial temperature with the corresponding ratios on the calibration curves, we introduced corrections for absorption as in the case of graphite. The results, treated by least squares, are shown in Fig. 6, where we observe that the melting point of tungsten rises gradually with pressure, and reaches 4000°K at 50 kbar. The experimental results can be represented by the linear equation

$$T_{\text{m.p.}} = 3642 + 7.46\cdot 10^{-3}P. \qquad (5)$$

The differences between the experimental points and the smooth curve were used to calculate errors. The probable error of the temperature measurements is ±47%; the maximum deviation from the curve is ±13%. The accuracy of the pressure measurements is ±6%.

3. PLATINUM

We used type Pl-O platinum for our experiments. Platinum was of interest because of its relatively low melting point, whose pressure dependence was investigated, using the thermal analysis method, by Strong and Bundy[3] and by Mitra et al.[14] (the dashed curve and the dot-dash curve, respectively, in Fig. 7). We determined melting points only from the ratio I_2/I_3; I_1/I_2 was omitted because the intensities I_1 had very low values.

A comparison between the I_2/I_3 ratio for the initial temperature, 2040°K, on the melting curve and the ratio of intensities on the calibration curve showed that no appreciable selective absorption was present in our measurements. This was also evident from the appearance of the salt tablet containing fragments of the samples following the experimental work. The platinum fragments were bright and shiny, and were not surrounded by darkened salt as in the cases of graphite and tungsten. The solid curve in Fig. 7 represents our measurements, treated by least squares. Our results agree, within the error limits, with those obtained using the method of thermal analysis.

Our experimental results can be represented by the linear equation

$$T_{\text{m.p.}} = 2027 + 6.04\cdot 10^{-3}P. \qquad (6)$$

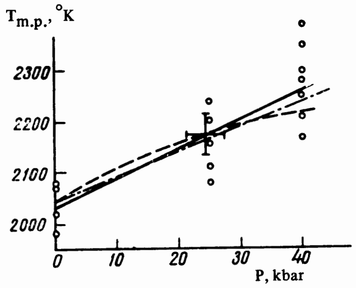

FIG. 7. Melting curve of platinum up to 40 kbar. The dashed curve represents the data of Strong and Bundy [3]; dot-dash curve-Mitra et al. [14]; continuous curve-our data. ● designates I_2/I_3.

The errors were computed using the deviations of the experimental points from the smooth curve. The probable error of our temperature measurements is ±2%; the maximum deviation from the curve is ±5.4%. The accuracy of the pressure measurements is ±6%.

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