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PHYSICS

MEASURING THE MELTING POINTS OF METALS AT ULTRA-HIGH PRESSURES

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Bridgman /1/ measured the melting points of some low-melting metals at ultrahigh pressures. In his experiments the metal under test was placed in a high-pressure apparatus, which was externally heated. The phase transitions were determined by the displacement of the piston that pressed against the specimen. One shortcoming of the method, as the author points out himself, is the fact that the experiment cannot be performed at temperatures exceeding 200°C because of the decrease in the mechanical strength of the steel. It should be noted that the molten metal may react with the steel walls of the pressure vessel at high temperatures and pressures, which likewise results in lowering the mechanical strength and destruction of the apparatus.

The present paper describes a method of measuring the melting points of metals at ultrahigh pressures that is free from these shortcomings and allows investigations to be made at higher temperatures, owing to the utilization of electric heating within the high-pressure vessel. The method is founded on measurement of the freezing point of the molten metals by the arrest point of the cooling melt.

The circuit diagram for these measurements is shown in Fig. 1. Within the conical high-pressure vessel, fitted with a double support (cf /2-4/ for the principle of this mechanical support) there are placed

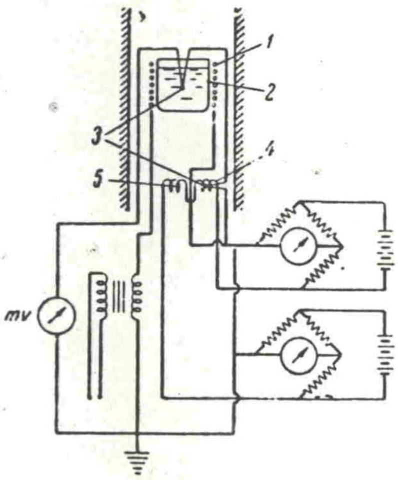

Fig. 1. Circuit diagram for measuring the melting points of metals at ultra-high pressures.

the electric heating element 1, the crucible containing the metal under test 2, a differential thermocouple 3, a resistance thermometer 4, and a manganin monometer 5. A four-wire lead-in was installed in the bottom of the vessel. Measurements were made in a medium (a mixture of isopentane and n-pentane) that does not solidify at room temperature up to a pressure of the order of 35,000 kg/cm^2. This afforded all-round hydrostatis compression of the test specimen.

Pressure was measured with a manganin manometer, with a resistance of some 200 ohms, situated in the lower part of the high-pressure vessel. The pressure coefficient of resistance at 20°C for the manganin we employed was $2.32 \cdot 10^{-6}$ cm^2/kg. As we know the magnitude of this coefficient remains invariant for pressures up to 30,000 kg/cm^2. Raising the temperature 1°C in the 0-95°C range increases the pressure coefficient of resistance for manganin by

$2.2 \cdot 10^{-4}$ of its initial magnitude /3/. This yielded a pressure correction of 60 kg/cm^2 at a maximum temperature of 31°C within the manganin coil and at a pressure of 22,000 kg/cm^2. We estimated that our measurement of pressure was accurate within 100 kg/cm^2.

The temperature of the metal was measured with an iron - nichrome differential thermocouple*. One junction of the thermocouple was placed within the crucible with the metal under test, while the other junction was situated in the lower part of the pressure vessel (in the "cold" zone, insulated from the heating element by layers of mica) within the resistance thermometer and at the same level as the manometer. That is how the temperature of the "cold" junction was measured. The tips of the thermocouple (made of iron) were joined to the electric lead-in. The e.m.f. of the differential thermocouple was measured by an indicating millivoltmeter. The temperature difference between the junctions was measured with an accuracy of 0.5°C. We disregarded the correction due to the effect of pressure upon the thermocouple's e.m.f. According to Birch's data /5/, this correction does not exceed 0.25°C for the chromel - alumel thermocouple at 600 and 4000 kg/cm^2.

The resistance thermometer was made of a thin copper wire having a total resistance of 14-15 ohms. The temperature of the "cold" junction was measured with an accuracy of 0.1°C. We know that raising the temperature from 30 to 75°C has no effect on the electrical resistivity of copper as the pressure is raised to 30,000 kg/cm^2 /6/, making such corrections unnecessary.

Measurement was made with a multiplier. The given pressure was

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* Use of a thermocouple of the ordinary type results in substantial error.

produced in the apparatus by moving a piston through the channel of the tapered pressure vessel. Then the electric heating was switched on, the temperature rise being indicated by the millivoltmeter readings. At first we reached a temperature that was about 50°C above the melting point, which was manifested by the arrest of the millivoltmeter's pointer. Then we allowed the melt to cool slowly, noting the freezing point, which was indicated by the millivoltmeter's pointer coming to rest for a substantial interval of time. At the same time we measured the temperature of the "cold" junction and the pressure at the freezing point. Eight to ten separate readings were made at constant pressure; this yeilded discrepancies that did not exceed 0.5°C from the mean value of the freezing point. This method enables the curve of melting point versus pressure to be plotted in the course of a single experiment.

The fusion of bismuth was used for comparing the results obtained by the method described with Bridgman's measurements. As we know, bismuth is one of the few substances whose volume diminishes when it is melted at atmospheric pressure, so that their melting points fall as the pressure is raised. Bridgman measured the melting point of bismuth up to a pressure of 17,500 kg/cm^2; at that pressure its melting point was 197°C, or 74°C below the m.p. at atmospheric pressure. He was unable to extend his research to higher pressures because his apparatus was destroyed by the action of molten bismuth at ultrahigh pressures.

purity

We used pure granulated bismuth for our measurements. Its melting point at mospheric pressure was 271°C. Our findings are given in Table 1 and Fig. 2.

TABLE 1 Таблица 1

P, kg/cm² (Р, кг/см²)	Temp. of the "cold" junction (Т-ра „холодного" спая в °C)	Temp. Diff. between junctions (Разность т-р спаев в °C)	Melting point (Т. пл. в °C)
1	32,3	239	271
2800	27,2	233	260
5000	25,8	224,5	250
8800	28,1	204	232
13200	27,9	182	210
18700	26,6	160	187
22200	31,0	159	190

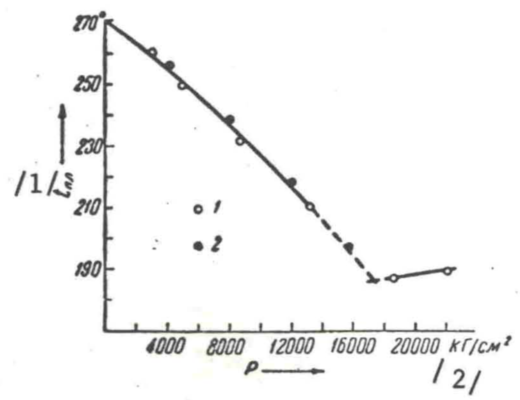

Fig. 2. Melting point of bismuth as a function of pressure.
/1/ Our findings; /2/ Bridgman's findings.

Table 1 shows that the m.p. of bismuth is no more than 187°C at 18.700 kg/cm^2, rising to 190°C at 22,000 kg/cm^2. This is due to the polymorphic transformation of bismuth I to the denser modification, bismuth II. The intersection of the descending and ascending branches of the t,P curve (shown as the intersection of the dashed lines in Fig. 2) gives the following as the parameters of the triple point bismuth I -

bismuth II - melt: P = 17,400 kg/cm^2; t= 186°C. This figure agrees closely with the extrapolated value for this triple point obtained by Bridgman at the intersection of the fusion curve of bismuth I with the curve for the polymorphic transformation bismuth I - bismuth II (P = 17,300 kg/cm^2; t = 183°C).

As we see in Fig. 2, the melting points of bismuth at various pressures determined by us experimentally are 1 to 3°C below those measured by Bridgman. It should be noted in this connection that the method of moving the piston he employed was occasioned by the need to allow for friction in the apparatus, which has a serious negative effect upon the accuracy of the results obtained. This shortcoming is completely eliminated in the method described above, which is, moreover, not restricted to comparatively low temperatures, as is Bridgman's method.

The method described here makes it possible to determine the melting points of various metals at ultrahigh pressures reliably.

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