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THE MELTING POING OF GERMANIUM AS A FUNCTION OF PRESSURE TO 180,000 ATMOSPHERES

BY

H. TRACY HALL

SCHENECTADY, NEW YORK

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THE MELTING POINT OF GERMANIUM AS A FUNCTION OF PRESSURE TO 180,000 ATMOSPHERES

H.Tracy. Hall[i]

Research Laboratory, General Electric Company, Schenectady, New York

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The melting point of germanium has been found to decrease linearly with increasing pressure from 936° at one atmosphere to 347 ± 18° at 180,000 atmospheres. The linear dependence indicates that there are no new solid phases formed in the region investigated. Resistance measurements indicate that the solid remains a semi-conductor while the liquid displays metallic conduction over the entire pressure range.

Experimental Procedure

The "belt" ultra-high pressure, high temperature apparatus[1] was used to measure the melting point of germanium as a function of pressure. A graphite cylinder 0.150 inch o.d., 0.090 inch i.d. and 0.450 inch long served as container and as electrical resistance element for heating the germanium. The germanium (high purity, single crystal used in semi-conductor work) was a cylinder 0.090 inch diameter and 0.300 inch long. Graphite plugs 0.090 inch in diameter and 0.075 inch long were placed in the ends of the tube. A thermocouple (Pt-Pt 10% Rh, wire diameter 0.010 inch) imbedded in the graphite cylinder measured the temperature.

After the high pressure assembly was in place, the press load was increased to the desired pressure. The pressure calibration was made by observing transitions in bismuth, thallium cesium and barium[2] (see Fig. 1). Then the voltage across the heating tube was raised until the germanium melted. The e.m.f. of the thermocouple (with 0° reference junction) was recorded automatically. The voltage across the heating tube and the current through it were also recorded. Each of the recorders detected the melting point of the germanium as shown in Fig. 2. When germanium melts, its electrical conductivity increases by a factor of about ten. This was ascertained from the voltage and current measurements before and after melting, the geometry of the system, and the known conductances of solid germanium and graphite near the germanium melting point. On melting, then, the electrical resistance of the germanium-graphite assembly decreases appreciably. This causes a large increase in the current through the assembly and a corresponding drop in the voltage across the sample. The final balance of current and voltage is determined by the internal impedance of the power supply. When the germanium melts, its thermal conductivity also increases considerably. This causes a larger flow of heat to pass out through the ends of the sample and supercools the molten germanium. This and possibly latent heat effects cause a sharp dip to occur in the e.m.f. curve. More power is required to raise the temperature of the assembly a given amount after the germanium has melted than when it is solid.. This is again due to the greater heat loss out the ends when the germanium is molten.

On lowering the power input to the sample, the germanium would eventually freeze. The freezing point could not be detected nearly as well as the melting point. The germanium usually supercooled in a non-reproducible manner. There seemed to be no relationship between the amount of supercooling and the pressure.

Experimental Results

Six runs were made. Five of them covered the range from 1 to 100,000 atmospheres. They all showed a linear decrease in melting point with increasing pressure. The slopes obtained were –3.20, -3.18, -3.36, -3.32 and –3.33 X $10^{-3°}$/atm. The sixth run covered the range from 1 to 180,000 atmospheres, showing also a linear decrease in melting point with a slope of –3.21 X $10^{-3°}$/atm. Considering all slopes, the average and the standard deviation from the mean were –(3.27 ± 0.07) X $10^{-3°}$/atm. Data from one of the runs are displayed in Fig. 3. The lower line is

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[1] H.T. Hall to be published.

[2] P. W. Bridgman, *Proc. Am. Acad. Arts & Sci.*, **81**, [4] 165 (1952).

drawn through the points as they were measured. Not that the line intersects the melting point axis at 895°. This is 28° below the one atmosphere melting point of 936°.[3] The thermocouple, because of its location, was probably conducting away enough heat to lower the junction temperature this amount. Consequently, a corrected line (the upper line) was drawn. Its upper end was located at 936°. The position of its lower end at 180,000 atmospheres was determined by assuming this relationship

$$\frac{936-895^\circ}{936-40^\circ}=\frac{y}{345^\circ+(x-40^\circ)}$$

where 40° was the average temperature of the sink to which the heat was flowing, 345° is the lower line melting point at 180,000 atmospheres, and x is the correction to be added to this value. The other runs were corrected in like manner.

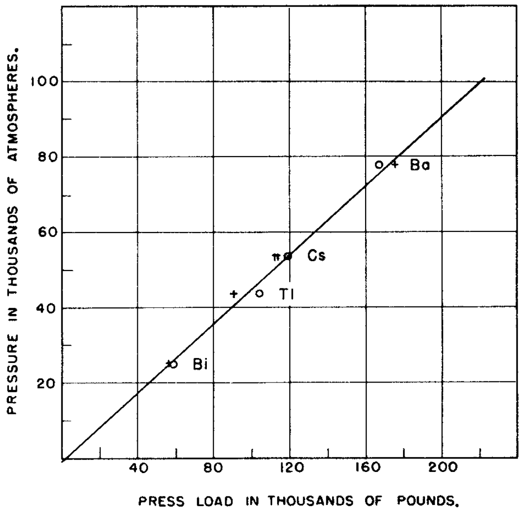

Fig. 1.—Pressure calibration of “belt” apparatus.

Effect of Pressure on Thermocouple E.M.F.—This is a peculiarly difficult problem and will be discussed in detail in a future paper. For the present, let it be known that the temperature (from standard, one atmosphere e.m.f. *vs.* temperature charts) recorded by the couples, platinum-platinum 10% rhodium and chromel-alumel, have been compared at pressures to 100,000 atmospheres and simultaneous temperatures to 900°. Both couples give the same temperature within the limits of experimental reproducibility of the measurements. This reproducibility has an average deviation from the mean temperature of ±3° at 900° (the deviation is smaller at lower temperatures). This means that the effect of pressure on the e.m.f. of these couples is negligible within the limits of experimental error or that the pressure affects both couples in an identical manner. The latter seems improbable; so the assumption has been made that the e.m.f.'s of these couples are not affected by more than the equivalent of 3° by the pressures and temperatures used in the germanium melting point experiments.

Discussion

Sulman and VanWinkle[4] by application of the Clapeyron-Clausius equation have calculated $dT/dp = -2.4 \times 10^{-3}$ degree/kg./cm.^{2} for the melting point of germanium. They used 935° as the melting point, 5% for the volume change on melting, and 110 cal./g. as the latent heat of fusion. The source of their data is not given. The 5% volume change is probably an estimate and is changed to 6.7% would bring their calculation into line with the results of this work.

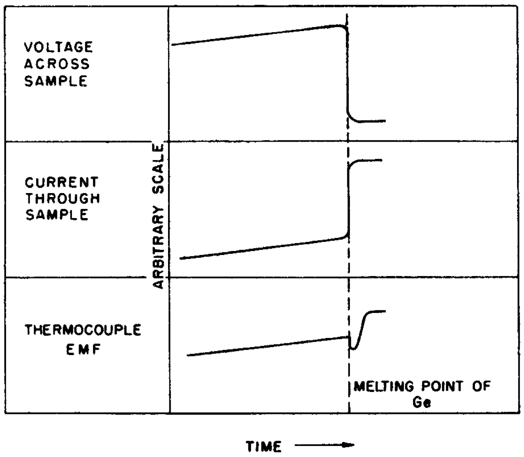

Fig. 2.

The linear dependence of melting point on pressure up to 180,000 atmospheres indicates that the liquid remains the denser phase at this extreme pressure. The electrical resistance (from the current and voltage measurements on the sample) indicated that over the entire pressure range the conductance of the molten germanium is greater than that of the solid germanium. This means that the solid remains a semi-conductor while the liquid displays metallic conduction even at these extreme pressures.

The germanium melting curve does not give the usual “concave downward” curvature

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[3] Esther Conwell, I.R.E., 1336, November, 1952.

[4] R.G. Sulman and D.M. VanWinkle, *J. Appl. Phys.*, **24**, 224 (1953).

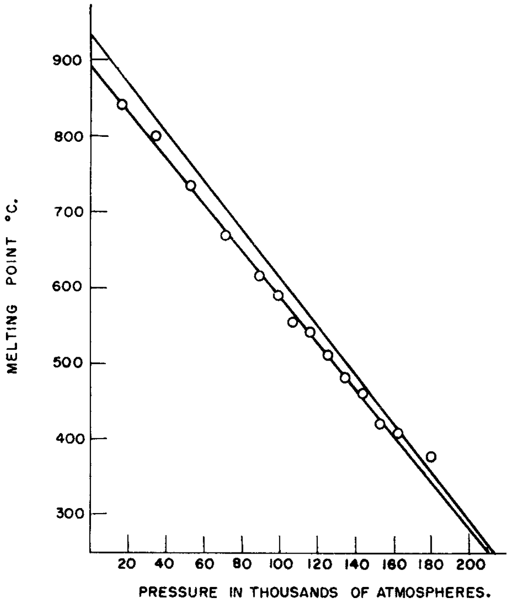

Fig. 3.—Sample of melting point data lower line, as obtained upper line, corrected.

found by Bridgman for many substances.[5]

The determination of the melting point of germanium in a high pressure, high temperature apparatus can be used as a secondary pressure standard. In designing new equipment, the problem of determining its ultimate capabilities is always encountered. The measurement of the germanium melting point as a function of applied load will give this information. When the pressure limit of an experimental design is approached, the melting point will cease to fall with increasing press load. At lower pressures, the change in electrical resistance of a manganin wire has been used for this purpose.[6] However, mechanical deformation of the wire in the necessarily solid pressure transmitting media at the very high pressures used here causes the gage to give uncertain results. The germanium melting point, being a discontinuous phenomenon, is independent of change in shape brought about by application of pressure.

Conclusion

The melting point of germanium has been measured as a function of pressure up to 180,000 atmospheres. The melting point decreases linearly from 936° at one atmosphere with a slope of $-(3.27 \pm 0.07)$ X 10^{-3°/atm. As far as is known, this represents the most extreme condition of simultaneous high-pressure, high temperature under which a measurement of this nature has been made. An extension of the techniques employed here to measure the melting points of other materials should eventually shed light on the old question as to the eventual character of the melting curve as pressure is indefinitely increased. Does it end in a critical point, rise to a maximum, or behave otherwise?

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[5] P.W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London 1949, see Chapter VII.

[6] Ibid. Chapter III.

[i] Brigham Young University, Provo, Utah.