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THE MELTING POINT OF GERMANIUM AS A FUNCTION OF PRESSURE TO 100,000 ATMOSPHERES

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Abstract: The melting point of germanium has been found to decrease linearly with increasing pressure from 936°C at one atmosphere to 611° ± 6°C at 100,000 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 condition over the entire pressure range.

The ultra-high-pressure, high-temperature apparatus used to make the measurements is described elsewhere (H.T. Hall, "The Belt": Ultra-High-Pressure, High-Temperature Apparatus," GE Research Lab. Rept. No. RL-1064). A new, simple technique for inserting several electrical leads into the high-pressure, high-temperature chamber is described.

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EXPERIMENTAL PROCEDURE

The "belt" ultra-high-pressure, high-temperature apparatus[i] was used to measure the melting point of germanium as a function of pressure. A graphite cylinder 0.150-inch OD, 0.090-inch ID and 0.450 inch long was substituted for the metal heating tube of Reference 1. This graphite tube served as container and an 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. Tantalum end disks 0.350 inch in diameter and 0.010 inch thick were used. A thermocouple (Pt-Pt 10 percent Rh, wire diameter 0.10 inch) was placed as shown in Fig. 1.

The location of the thermocouple junction posed a difficult problem. The most desirable location would be in the body of the germanium itself. Germanium, however, dissolves any of the ordinary thermocouple materials. An attempt was made to coat the thermocouple with various inert materials such as sintered MgO, fired kaolin, fused SiO_2, glass, and "Sauereisen." None of these was satisfactory. The germanium at high pressure and temperature would always break through the coating and destroy the thermocouple. In another scheme, a 0.100-inch plug was left in the middle of the graphite tube by drilling holes in from each end to a depth of 0.175 inch. Then a 0.100-inch long cylinder of germanium was placed on each side of the plug. A 0.020-inch hole was drilled through the center plug perpendicular to the centerline of the assembly, and the thermocouple was placed inside. Several of these assemblies were tried, always with the same result: the germanium broke through the graphite and destroyed the thermocouple. The only arrangement tried that gave results was the scheme in Fig. 1. The germanium dos not break through to the thermocouple even though only 0.005 inch of graphite separates them.

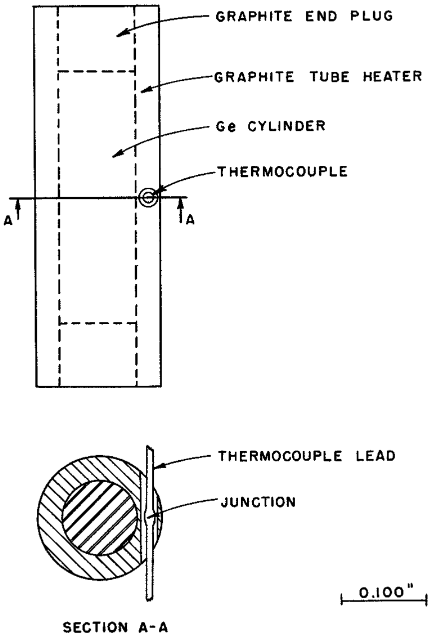

Fig. 1 Arrangement of germanium, heating element, and thermocouple.

Prior to the instigation of this work it was found that Formex covered thermocouple wires could be placed in shallow grooves on the surface of the lava gasket and then taken through a hole to the sample chamber. This arrangement worked most of the time without shorting at pressures to 10,000 atmospheres. For use above 10,000 atmospheres tiny holes could be drilled through the thin shell of the gasket (a difficult and tedious task) to the final junction location. The wires were threaded through the holes. This scheme worked only a fraction of the time, the usual difficulty being that the wire broke through the lave and shorted to cone (9) or chamber (2) of Fig. 1 of Reference 1 [note that when assembled, cone (9) is in contact with conducting ring (5)].

These difficulties have been resolved by using the simple scheme pictured in Fig. 2. The numerical nomenclature is the same as used in Reference 1. A hole (a) is drilled in (4) and into (3) where the junction is to be located. A straight saw cut (b) is made in (10). Components (8) and (9) are glued together with waterglass. (Waterglass can be used to glue all the components together. Organic glues will not due on surfaces where friction is important. They are too slippery. Waterglass must be used with care, however, where minute emfs are involved, for it is electrically conducting at high temperature and can become become the electrolyte for a battery in the cooling system.) A tab of asbestos paper (c) is tacked to the rim of (8) with a drop of organic glue. This paper will prevent the electrical lead to be placed in the slot (b) from coming in contact with (9). The components are assembled with the wire in the slot as shown at (e). Some organic glue at (g) holds the wire in place, and plastic tubing (f) sheathes the wires if they are bare. Finally, kaolin powder is worked into the slot with a dental spatula as at (d). Several leads may be inserted in this manner. These leads will not pinch off, blow out, or short to other components at pressures to 100,000 atmospheres.

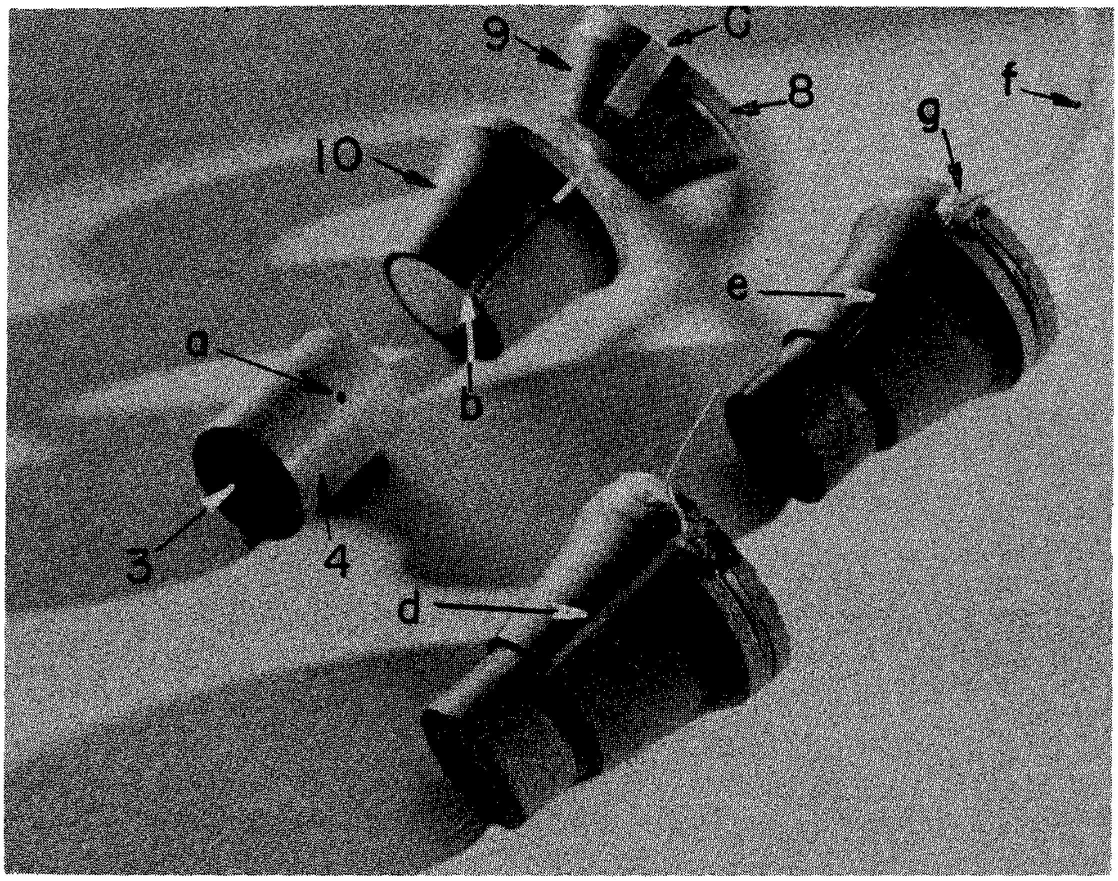

Fig. 2 Method of introducing electrical leads into the high-pressure, high-temperature zone (see text).

After the high-pressure assembly was in place, the press load was increased to the required pressure (pressure calibration was made as per Reference 1). Then the voltage across the heating tube was raised until the germanium melted. The emf of the thermocouple (with 0°C 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. 3. When germanium

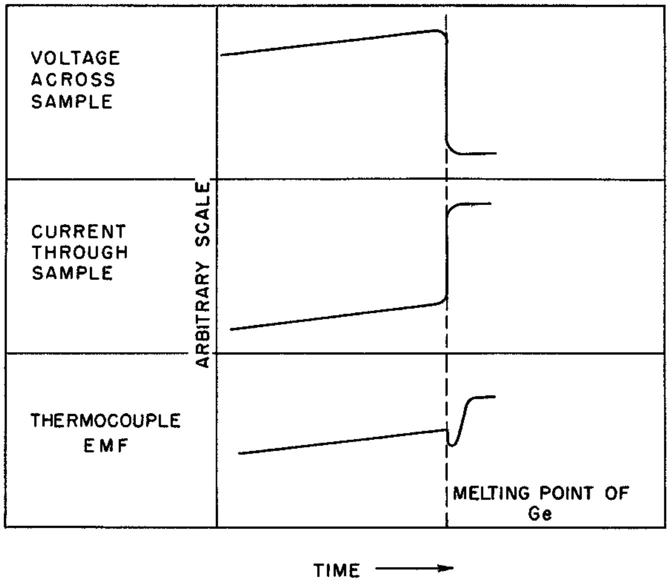

Fig. 3 Diagram showing the sudden changes occurring in voltage, current, and thermocouple emf at the melting point of germanium.

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 emf 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. The process of slowly raising the temperature until melting occurred and then lowering until freezing occurred was repeated about ten times at each pressure setting. About twenty minutes was taken to run through the melting point ten times. The melting point dropped exponentially something of the order of 8°C from the first time through until the last time through. Usually the last four runs through gave the same temperature, and this was taken as the melting point. The 8°C drop was due to the lagging of the stone pressure transmitting medium in reaching its final equilibrium pressure.

EXPERIMENTAL RESULTS

Three separate runs were made over the full pressure range. They all showed a linear decrease in melting point with increasing pressure. The three slopes obtained were –3.20, -3.18, and –3.36 x 10^{-3} degree C/atmosphere. Data from one of the runs are displayed in Fig. 4. The lower line is drawn through the points as they were measured. Note that the line intersects the melting point axis at 923°C. This is 13°C below the one atmosphere melting point of 936°C.[ii] 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°C. The position of its lower end at 100,000 atmospheres was determined by assuming the relationship

$$\frac{936^\circ - 923^\circ}{936^\circ - 40^\circ} = \frac{x}{608^\circ + x - 40^\circ},$$

where 40°C was the average temperature of the chamber (2) (see Fig. 1 of Reference 1), 608°C is the lower line melting point at 100,000 atmospheres, and x is the correction to be added to this value. The other runs were corrected in like manner.

Effect of Pressure on Thermocouple emf

This is a particularly difficult problem and will be discussed in detail in a future paper. For the present, let it be known that the temperatures (from standard, one atmosphere emf vs. temperature charts) recorded by the couples, platinum-platinum 10 percent rhodium and chromel-alumel, have been compared at pressures to 100,000 atmospheres and simultaneous temperatures to 900°C. 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°C (the deviation is smaller at lower temperatures). This means that the effect of pressure on the emf of these couples is negligible within the limits of the 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 emf's of these couples are not affected by

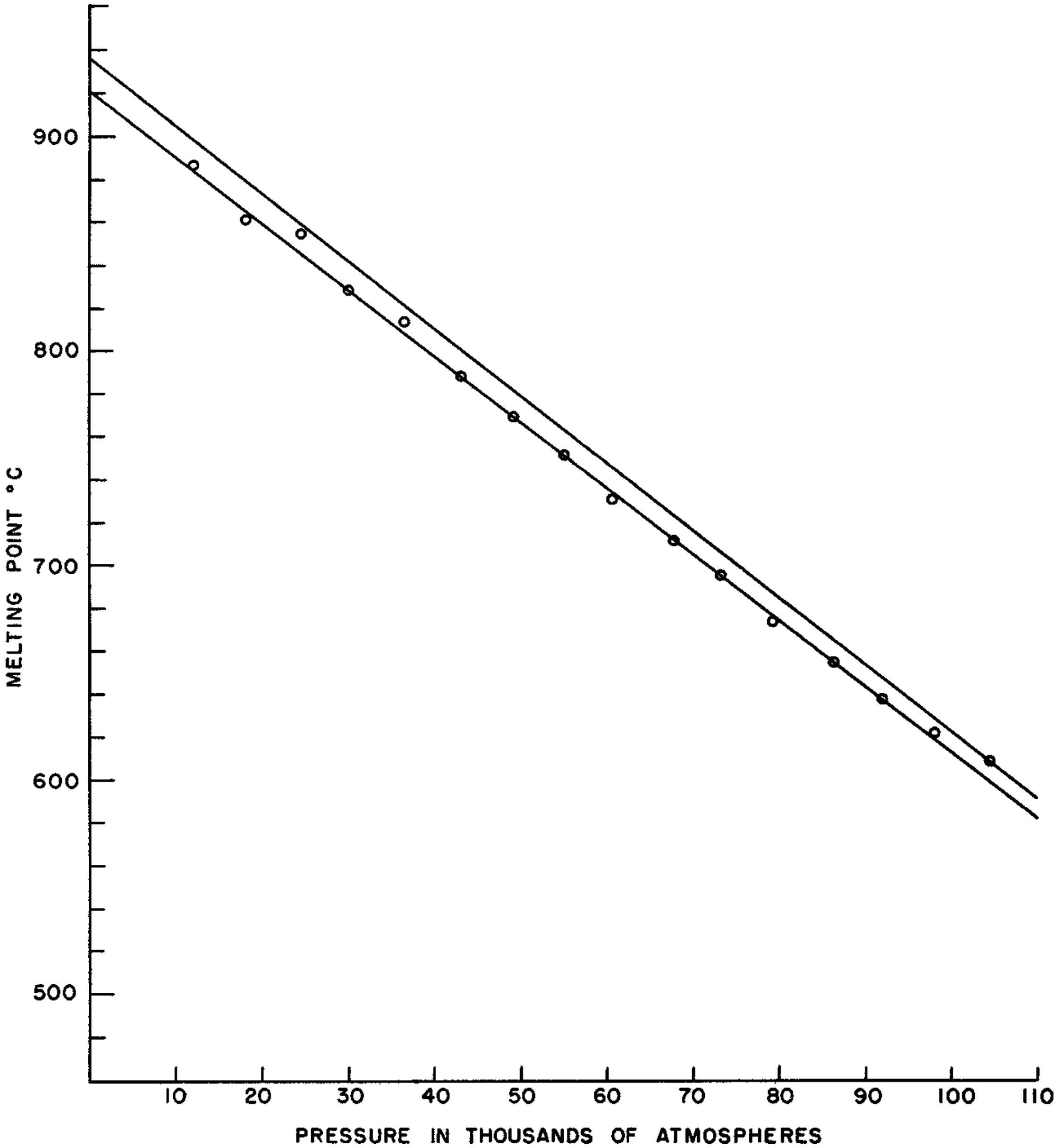

Fig. 4 Sample of melting point data. Lower line - as obtained. Upper line - corrected.

more than the equivalent of 3°C by the pressures and temperatures used in the germanium melting point experiments.

DISCUSSION

R.G. Sulman and D.M. VanWinkle[iii] 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°C as the melting point, 5 percent 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 percent volume change is probably an estimate and if changed to 6.7 percent would bring their calculation into line with the results of this work.

The linear dependence of melting point of pressure up to 100,000 atmospheres indicates that no new solid phases are formed, and 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 of the order of ten times 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 found by Bridgman for many substances.[iv]

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 (at pressures to 100,000 atmospheres). 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.[v] 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 100,000 atmospheres. The melting point decreases linearly from 936°C at one atmosphere with a slope of $-(3.25 \pm 0.10) \times 10^{-3}$ degree C/atmosphere. 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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[i] H. Tracy Hall, GE Research Lab. Rept. No. RL-1064.
[ii] Esther Conwell, I.R.E., 1336 (November 1952).
[iii] J. Appl. Phys., 24, 224 (1953).
[iv] P.W. Bridgman, The Physics of High Pressure, G. Bell and Sons (1949). See Chapter VII.
[v] Ibid., Chapter III.