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Phase Diagram of Bismuth to 130 000 kg/cm^2, 500°C

F. P. Bundy
Research Laboratory, General Electric Company, Schenectady, New York

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The phase diagram of Bi has been determined experimentally to 130 000 kg/cm^2 and 500°C. The observations of Bridgman, and others, to 30 000 kg/cm^2 and 270°C were generally verified. The new work indicates two new phases of solid Bi and several new triple points. The Bi VI$\rightarrow$VIII transition at room temperature and about 125 000 kg/cm^2 involves a sharp decrease in electrical resistance which can serve as a pressure calibration point in future work.

I. INTRODUCTION

THE sharp drop of resistance associated with the Bi I$\rightarrow$II phase transition at 25.3 kg/cm^2 and 25°C has been useful as a pressure calibration point in high-pressure work for many years. Availability at this Laboratory of superpressure apparatus capable of reaching pressures well above 100 000 kg/cm^2 at elevated temperatures, together with a need to know more about the temperature coefficients of various phase transitions, led to an exploration of the Bi phase diagram to 130 000 kg/cm^2 and 500°C.

Previous knowledge about the phase diagram of Bi resulted largely from the work of Bridgman,[1–4] and of Butuzov *et al.*[5] Figure 1 is a graph from Bridgman (reference 1) summarizing the data. Four solid phases and a liquid phase are shown. Of these Bi I has the highest electrical resistance, Bi II the lowest, while Bi III, IV, and liquid are intermediate.

In addition to the data shown in Fig. 1, Bridgman[2,4] also lists results of his compressibility measurements made prior to 1942. These measurements made at 25°C showed the following polymorphic transitions:

Transition	Pressure kg/cm^2	$\Delta V/V_0$
I$\rightarrow$II	25 300	0.0460
II$\rightarrow$III	27 000	0.0295
III$\rightarrow$IV	44 800	0.006
IV$\rightarrow$V	65 000	0.005
V$\rightarrow$VI	89 800	0.012

In reference 2 Bridgman states that he could not observe any consistent resistance changes associated with the last three listed volume transitions. Bridgman's phase nomenclature will be adopted in this paper.

In the course of the present work, which used changes of electrical resistance as indication of phase change, two more solid phases were identified and the course of the melting line was followed up to about 500°C. The large resistance change associated with the VI$\rightarrow$VIII transition at about 125 000 kg/cm^2 25°C, provides a useful new pressure calibration point for superpressure apparatus.

II. APPARATUS AND METHODS

Superpressure apparatus similar to that of Hall[6] was employed. Three different types of cells were used in the superpressure apparatus. In the initial and final series of experiments the simple cell shown in Fig. 2 was employed. In this, a 0.021-in. Bi wire was located on the axis. This was surrounded by a AgCl sleeve, which in turn was in an insulating "sample holder." The Bi wire was heated by passing an ac current through it. End caps of Ni to carry the current were only 0.005 in. thick to minimize heat loss to the electrodes at the ends of the chamber, thereby making the temperature of the Bi wire more uniform. A little gold foil at each end of the Bi wire seemed to improve electric contact and reduce chemical reaction there at elevated temperatures. Resistance was taken from the voltage-current ratio. The temperature of the Bi wire as a function of the heating power was calibrated by comparison with the thermocouple-determined values for unique phase points measured in the more complicated cells described below.

Figure 3 illustrates a cell which incorporates indirect heating and thermocouple arrangements. Heating was produced by passage of current through the carbon sleeve between the electrodes at top and bottom of the cell. The 0.021-in. Bi wire sample was located on the

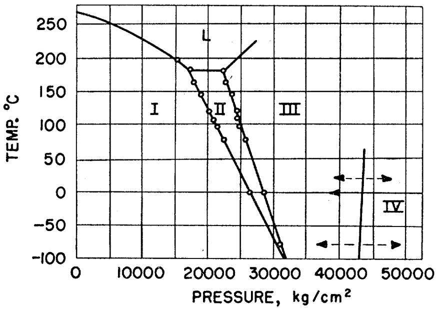

FIG. 1. Phase diagram of Bi (Bridgman).

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[1] P. W. Bridgman, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957).

[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 228 (1952).

[3] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 438 (1942).

[5] Butuzov, Gonikberg, and Smirnov, Doklady Akad. Nauk S.S.S.R. **89**, 651 (1953) [translation: National Science Foundation-tr-76].

[6] H. T. Hall (to be published).

axis in the midspan region where the temperature was quite uniform. The Bi was surrounded by a sleeve of AgCl to give an approximate hydrostatic pressure field around it. The ends of the Bi wire were connected to the outside by 0.010-in. chromel and alumel wire. These wires served alternately for measurement of the resistance of the Bi circuit and to determine the temperature of the Bi element. (The emf generated by the chromel-Bi-alumel thermocouple would be the same as that of a simple chromel-alumel junction provided the temperature at both ends of the Bi would be the same. Deviations from this uniform temperature requirement could cause considerable error because of the large thermal emf coefficient of Bi.)

A third type of cell employed in this study is shown in Fig. 4. This cell provided an independent thermocouple as well as independent heating. 0.010-in. stainless steel wire connected the Bi to the outside for resistance measurement. The thermocouple was of 0.005-in. chromel-alumel. Such small wires of stainless steel, chromel and alumel were used to minimize heat loss from the heated zone. In spite of its complication and difficulty of assembly this type of cell worked very well, eight successful runs being obtained from the eight cells that were made up.

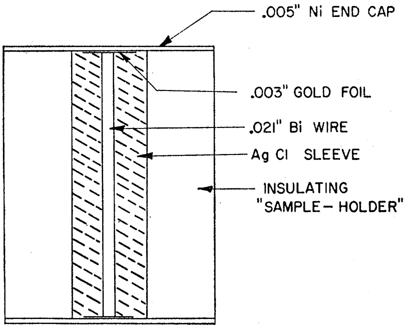

FIG. 2. Simple directly heated cell.

III. RESULTS

The results of the experiments are summarized in Fig. 5. The I, II, III and liquid areas obtained here agree quite well with those shown by the older data of Fig. 1. The new VII and VIII solid phases appear to be normal metals in that their melting points rise with increase in pressure and the liquid has a higher electrical resistance than the solids. Bi VII has a slightly lower resistance than III or IV at the same P, T conditions. Bi VIII has considerably lower resistance than VII, V, or VI. No certain changes of resistance could be observed at the pressures at which Bridgman had observed volume changes between III–IV, IV–V, and V–VI. The small dent in the low-temperature boundary of the Bi VII region is consistent with the presence of III–IV phase boundary indicated by Bridgman.

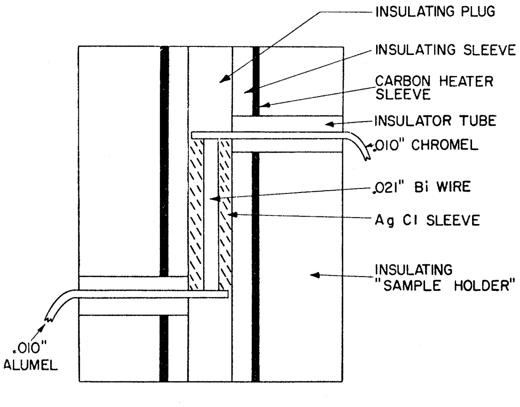

FIG. 3. Bi phase cell with indirect heating and chromel-Bi-alumel thermocouple.

The resistance change associated with crossing each of the phase boundaries in Fig. 5 is characteristic. Examples of each will now be presented.

Figure 6 shows a typical crossing of the Bi I⟶ Liquid line at 7800 kg/cm^2 pressure, as observed in the simple cell of Fig. 2. The complete transition does not occur sharply at a single heating power because under the conditions of direct heating the Bi wire is hotter at the center than at the ends. As soon as melting starts at the center of the wire the distribution of heat generation is altered because the new liquid phase has lower resistance than the solid. In this type of cell the resistance change tends to draw out if the new phase has lower resistance, and tends to be more abrupt if the new phase has higher resistance.

Figure 7 shows typical resistance *vs* pressure behavior for the I–II and II–III solid transitions at room temperature. This demonstrates that the AgCl sleeve

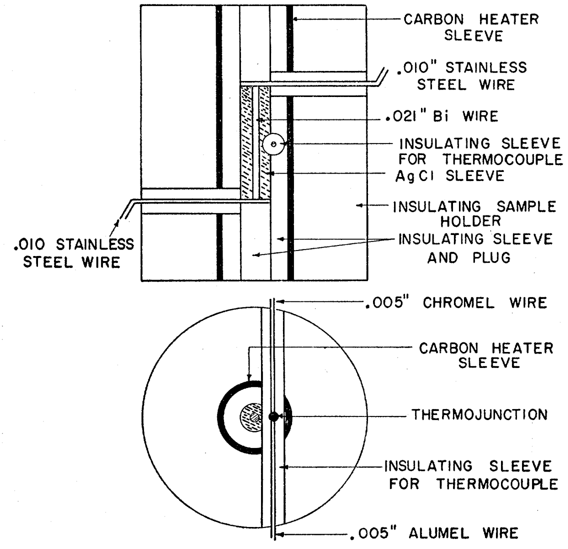

FIG. 4. Bi phase cell with indirect heating and independent thermocouple.

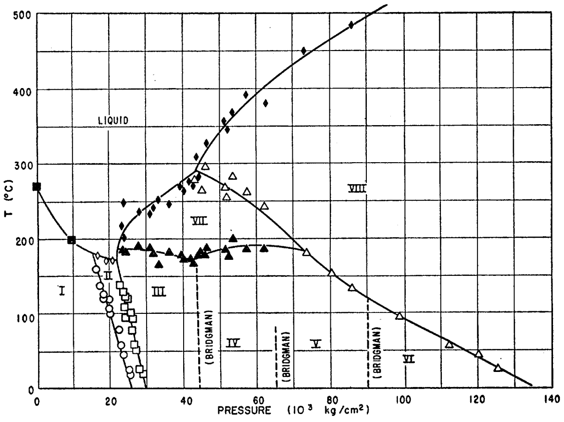

FIG. 5. Phase diagram for Bi.

around the Bi is "fluid" enough to allow the transitions to be very sharp. The resistance change between Bi I and II is the largest of any known in the Bi system. Its magnitude, sharpness, and reversibility make it an ideal pressure calibration point.

Figure 8 shows the change of resistance associated with the II to liquid transition as observed in the cell of Fig. 4. The relatively high resistance indicated on the *R* scale in this case is due to the small stainless steel connecting wires. The resistance of the Bi II wire itself is a little less than 0.02 ohm. The increase of *R* upon melting is about 0.015 ohm, which is a large fractional change. The liquid shows some tendency to supercool about 5° before freezing sets in.

Figure 9 shows examples of the resistance behavior of the cell of Fig. 2 as a function of heating power at various pressures above 26 000 kg/cm². Three characteristic changes were found. First, the small decrease associated with going over to VII from III, IV, or V. Second, the large sharp increase from VII or VIII to liquid. Third, the medium, moderately sharp drop from VII, V, or VI to VIII. It is interesting to note how this latter transition suddenly appears between 44 000 and 46 500 kg/cm² and how, as the pressure is increased, the temperature at which it occurs gets lower. Finally, at 25° it takes place at about 125 000 kg/cm². This transition is reversible and is large and sharp enough to serve as a good pressure calibration point for superpressure apparatus.

The detailed data frequently showed sudden small changes of resistance. At the beginning of this work such changes were often confusing since no one knew what phase changes to expect. Before any change of resistance was finally accepted as indicating a phase change, it was required to satisfy the following criteria: (1) It had to be repeatable under the same conditions. (2) It had to show up consistently with a reasonable trend in the general *P*, *T* vicinity. (3) It had to be reversible in a manner consistent with the characteristics of the cell.

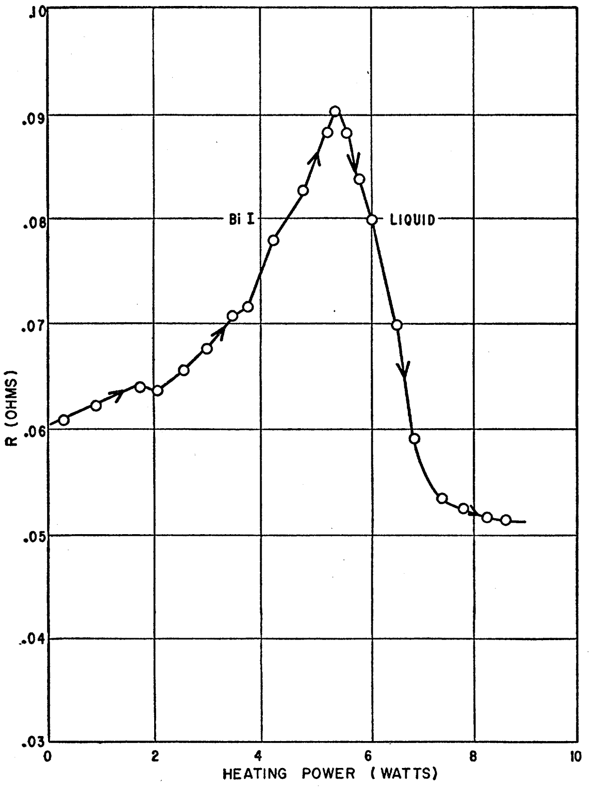

FIG. 6. Resistance change upon melting Bi I at 7800 kg/cm².

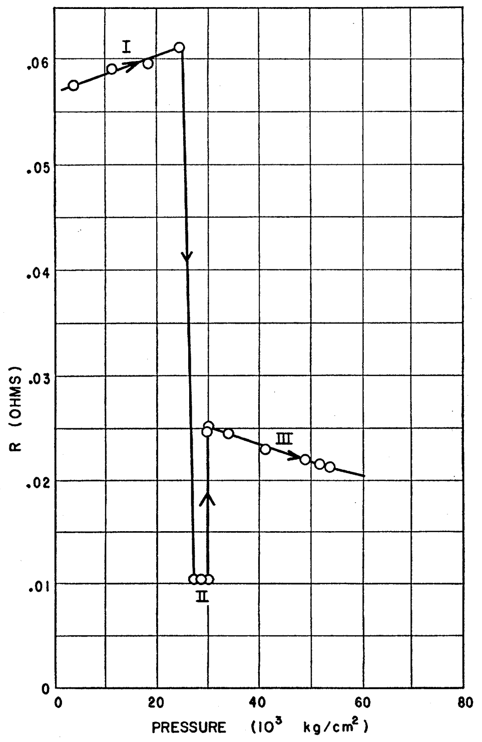

FIG. 7. Resistance changes associated with Bi I–II and Bi II–III at 25°C.

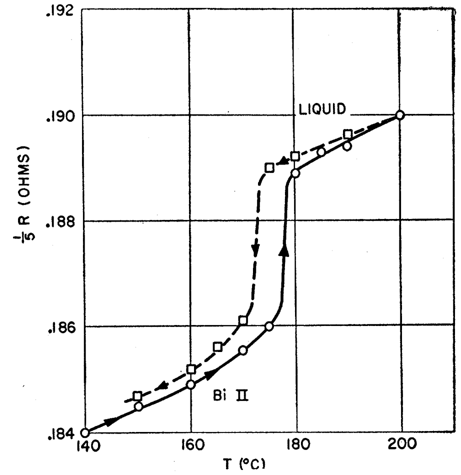

FIG. 8. Resistance change associated with Bi II → liquid.

In the interpretation of the resistance curves like those shown in Figs. 6 to 9, an important question is what value of P and T to choose in those cases in which the transition drags out somewhat. Transitions at constant pressure, caused by increasing the heating power in the Bi wire (Figs. 6 to 9) begin at the hottest place along the wire sample. Since the temperature *vs* heating power calibration of the wire was made in terms of the hottest place on the wire, the beginning of the resistance change was selected for the P, T point of the transition.

In the pressure-produced transitions at constant T the transitions may drag out because of pressure gradients in the cell, slow plastic flow of the wall material in following volume changes of the Bi, or slow phase reaction for kinetic reasons. In such cases our convention has been to select the press load (or nominal chamber pressure) corresponding to the most rapid rate of change of R. In the present work, in those cases in which dR/dP starts high and remains constant for a moderate ΔP interval the initial break point has been selected. This is the case for the VII, V, or VI to VIII transitions whether caused by a ΔT or by a ΔP.

The absolute pressure calibrations used in this work were based on the values given by Bridgman for the Bi I–II and the Ba I–II transitions at 25°C. These are 25 300 kg/cm^2 and 80 000 kg/cm^2, respectively. These two transitions, as observed in the cell of Fig. 2, are shown in Fig. 10. Bridgman's accurate work on Bi was done under truly hydrostatic conditions, and he believes the absolute value of the quoted transition pressure is accurate to a fraction of a percent. His work[7] on Ba was done in very thin disk samples squeezed between faces of Carboloy cemented carbide anvils. The Ba was in the form of a thin ribbon embedded between disks of AgCl. In this setup he could measure the total force and total area with considerable accuracy, but various corrections had to be made for radial pressure gradients within the disk sample. He used the Bi I–II transition as a fiducial point in this anvil apparatus from which corrections could be made to the force/area value of the calculated pressure. He found that in this kind of apparatus his calibration line would not extrapolate linearly to zero pressure for zero load. His value of 80 000 kg/cm^2 for the Ba I–II transition is thus based on the accurate Bi I–II transition and logical corrections to the force/area ratio. He estimates his value for the Ba transition to be correct on an absolute basis within a "few percent."

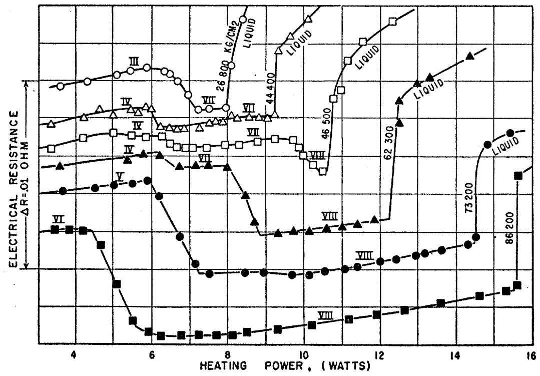

FIG. 9. Resistance changes associated with various phase changes in Bi.

Figure 11 shows the pressure calibration of the superpressure apparatus used in part of the present work. Note that this calibration, like Bridgman's, does not extrapolate linearly to zero. Considering the absolute

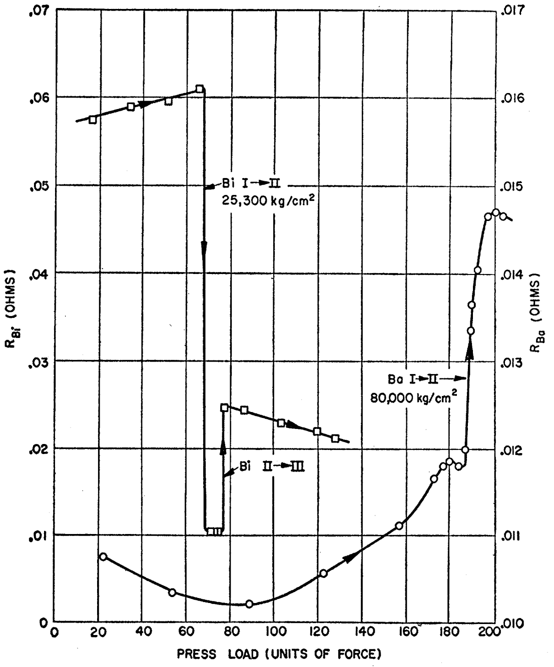

FIG. 10. Pressure calibration of cell by Bi and Ba transitions.

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[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 199 (1952).

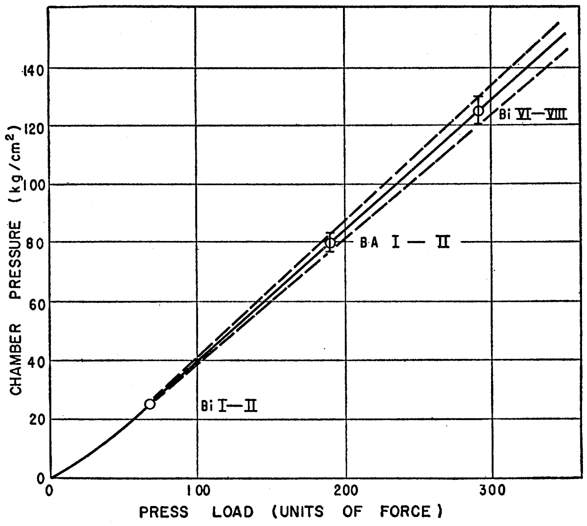

FIG. 11. Chamber pressure *vs* press load for superpressure apparatus.

accuracy of the Ba point, the calibration extrapolated to higher pressures can have an absolute accuracy of a few percent at the best. As far as the apparatus is concerned a linear extrapolation of the calibration is justified because it behaves elastically for many dozens of runs to these extremely high loadings.

IV. CONCLUSIONS AND DISCUSSION

The phase diagram of Bi has been extended more fully from 30 000 kg/cm² to over 125 000 kg/cm². Two new solid phases of Bi appeared. These have melting points which rise with increase of pressure. The sharp drop of electrical resistance from Bi VI→VIII at room temperature provides a new convenient pressure calibration point at about 125 000 kg/cm².

The now known triple points are listed in Table I. The pressures listed are estimated to be accurate to about ±1000 kg/cm² at the lowest pressures and within a few percent at the highest pressures. The temperatures listed are estimated to be correct within ±5°C in the 150°C region and about ±10°C in the 400 to 500°C region.

Techniques developed during the course of this work will be quite useful in other superpressure work. The methods could well be used in extending the known phase diagrams of other elements such as Ba, Tl, Pb, etc.

It is difficult to make any comparisons between the results reported here and those reported in very recent publications by Walsh *et al.*[8] and by Duff and Minshall[9] from shock-wave measurements in Bi. In the shock-wave work the observations depend upon compressibility and changes of volume between phases, whereas in the present work the observations depended upon electrical resistance. It is possible that the transition to phase VIII which is manifested by a considerable decrease in electrical resistivity has very little volume change associated with it, and hence would not show up clearly in the shock-wave experiments.

TABLE I. Triple points of Bi.

Triple point	P kg/cm²	T(°C)
I, II, liquid	15 500	180
II, III, liquid	21 700	170
III, VII, liquid	22 700	185
III, IV, VII	43 300(?)	170
VII, VIII, liquid	43 300	290
V(?), VII, VIII	71 000	190

V. ACKNOWLEDGMENTS

The author wishes to acknowledge the careful work of Sherman Reed in making the intricate cell parts, and the capable assistance of Roy Tuft in helping with the many experimental runs required.

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[8] Walsh, Rice, McQueen, and Yarger, Phys. Rev. **108**, 196 (1957).

[9] R. E. Duff and F. S. Minshall, Phys. Rev. **108**, 1207 (1957).