Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 41, No. 5, 2014–2018, April 1970

Phase Diagram of Bismuth at Low Temperatures

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(Received 16 October 1969; in final form 3 December 1969)

The phase diagram of bismuth has been studied from 4.2° to 300°K at pressures up to 50 kbar. Pressure was generated using a piston-cylinder apparatus with AgCl as the pressure transmitting medium. Phase transitions were detected by observing the accompanying discontinuities in electrical resistance. The phase diagram thus determined is in fair agreement with previously published results of other authors. However, the new low-temperature phase of bismuth reported by Il'ina and Itskevich was not observed.

I. INTRODUCTION

The phase diagram of bismuth above room temperature has been investigated extensively.[1–7] The results of several authors are in reasonable agreement near room temperature. The recent results of Tikhomirova, Tonkov, and Stishov[6] have been selected as representative. As shown in Fig. 1, their results for the bismuth I–II and II–III phase boundaries can be represented by straight lines within experimental error. Below room temperature less is known due to the difficulty in obtaining hydrostatic pressures and the slow transformation rates of solid-solid phase transformations. In 1935 Bridgman[1] located the bismuth I–II and II–III transitions at 223°K and extrapolated to find the I–II–III triple point as indicated on Fig. 1. In 1961 Brandt and Ginzburg[8] observed the bismuth I–III transition at 77°K as shown on Fig. 1. Brandt and Ginzburg[8] also reported that Bi II and Bi III are metastable. In 1966 Il'ina and Itskevich[9] made a more extensive study of the phase diagram of bismuth at low temperatures. They reported the existence of a new phase below room temperature in a pressure region previously believed to belong to bismuth I. Their results are also shown in Fig. 1. Thus Fig. 1 is believed to represent all the information regarding the phase diagram at low temperatures published prior to the present study.

Because of the sparsity of data available for pressure calibration at low temperatures and in order to verify the existence of the new phase of bismuth reported by Il'ina and Itskevich[9] we decided to investigate the low-temperature phase diagram of bismuth. The data was collected using a new high-pressure, low-temperature system previously used in determining the critical field curve for superconducting bismuth III.[10] The system is described in detail elsewhere[11] and briefly below.

II. EXPERIMENTAL SETUP

The pressure-generating system is shown in Fig. 2. It consists of a hydraulic ram coupled to a compression member which presses on the high-pressure piston. The high-pressure cell is supported by a tension member which is also connected to the ram. The compression and tension members and the high-pressure cell are inserted into a Dewar which provides a suitable low-temperature environment. The high-pressure cell is depicted in Fig. 3(a). It consists of a $\frac{1}{8}$-in.-diam tungsten carbide piston A and a solar steel cylinder B. A few tungsten carbide cylinders were used but they failed at pressures above about 30 kbar. The bottom plug C is electrically insulated from the remainder of the cell by a threaded Bakelite ring E. The high-pressure chamber is shown greatly enlarged in Fig. 3(b). Pressure is contained by the piston, cylinder, bottom end plug and solar steel anti-extrusion rings A and B. Electrical insulation is provided by mica C and AgCl D. Current passes through the sample via gold wires E, the top piston, and the bottom end plug. The samples were rectangular parallelepipeds 0.029-in. wide, 0.036-in. high, and 0.75-in. long. Six samples were used of 99.999% purity material obtained from Semi-Elements, Inc. The samples were originally single crystals but became polycrystalline because of cycling through the phase transformations. Some deformation of the samples was observed at the end of each experiment indicating the presence of pressure gradients.

III. EXPERIMENTAL TECHNIQUES

Typical resistance versus pressure plots are illustrated in Fig. 4. The resistance was measured by passing a 0.15–1.0 A current through the sample and applying the resulting voltage drop to the Y axis of an X–Y recorder. The resistance observed included the sample resistance, the resistance of the piston, bottom plug, gold wires, and a contact resistance. A four-lead measurement was made at the top and bottom of the high-pressure cell. The resistance of the sample was approximately equal to the sum of all the other resistances and was of the order of milliohms at room temperature.

Temperature was measured with a copper–constantan thermocouple potted with GE 7031 glue in a hole in part D shown in Fig. 3(a). Temperatures near 4.2°K were measured with a carbon resistor similarly mounted. Temperature was varied by cooling slowly with liquid-nitrogen vapor blown into the bottom of the Dewar. The temperature measured at the bismuth transition on the up stroke was at most 6°K different from the temperature on the down stroke. Constant temperature baths of carbon dioxide in acetone, liquid nitrogen, and liquid helium were also used.

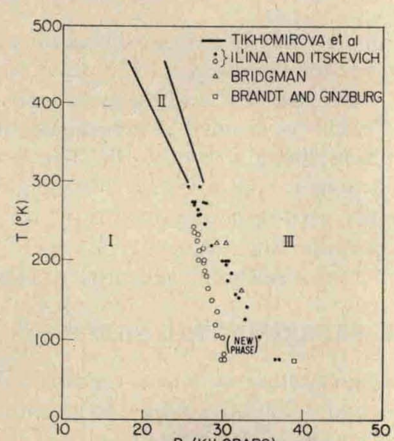

FIG. 1. The phase diagram of bismuth below room temperature. The open triangles refer to Bridgman's data (Ref. 1). The solid lines are straight lines drawn through the data of Tikhomirova *et al.* (Ref. 6). The open square is a point determined by Brandt and Ginzburg (Ref. 7). The circles represent a replotting of the data of Il'ina and Itskevich (Ref. 9).

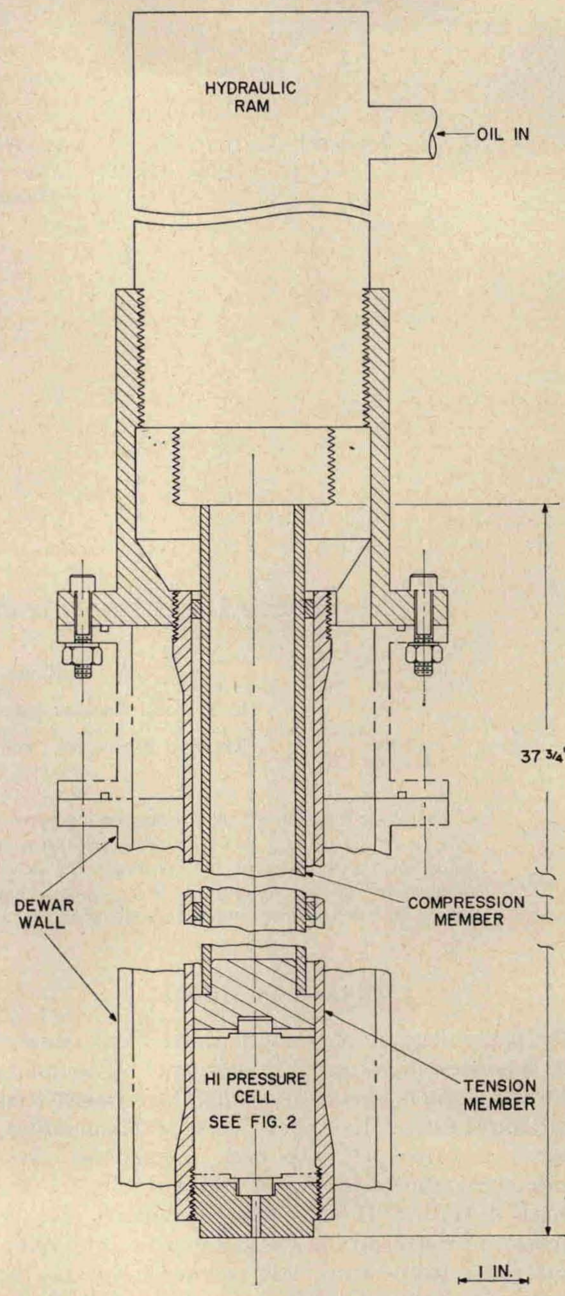

FIG. 2. A cross sectional view of the high-pressure generating system used at low temperatures. Cross-hatched members are 304 stainless steel.

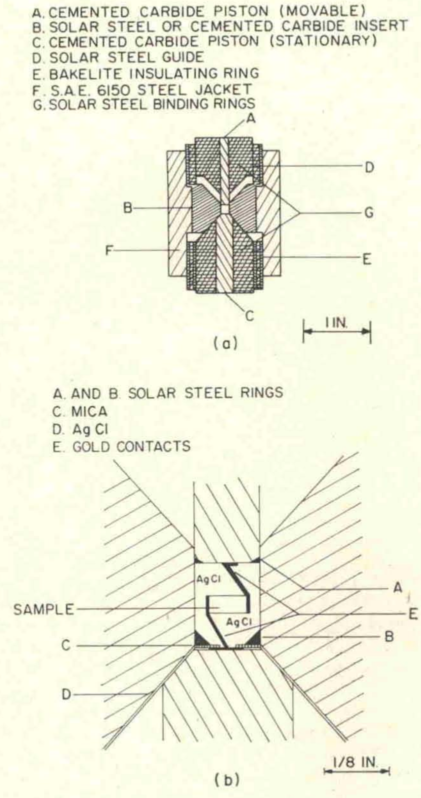

FIG. 3. (a) The piston-cylinder device which contains the high pressure at low temperatures. A thermocouple and a carbon resistor are located in holes drilled into part D. Four-lead resistance measurements are made between the top of piston A and the bottom of piston C. (b) A magnified view of the high-pressure sample chamber. All electrical contacts are pressure contacts. Electrical insulation is provided by mica C and AgCl D.

Sample pressure was monitored with a strain-gauge pressure cell in the hydraulic line of the ram shown in Fig. 2. The output voltage of the pressure cell was applied to the X axis of the X–Y recorder, thereby giving a continuous plot of resistance versus pressure which is invaluable in detecting transitions. No attempt was made to use extremely slow pressurization rates. Pressure was typically applied at a rate of about 1 kbar/min. Several runs were made with much slower pressurization rates but no appreciable difference was noted in the observed transition pressures.

The sample pressure must be deduced indirectly from the pressure in the hydraulic line. It cannot be calculated simply as applied force divided by piston area because of losses due to friction in the hydraulic ram, friction between the piston and cylinder in the high-pressure cell, and friction between the AgCl medium and the cell walls. The sample pressure is inherently nonhydrostatic because of the use of a solid pressure-transmitting medium and uniaxial loading. However, we may reasonably assume that the axial pressure gradients are much larger than the radial gradients and neglect the latter in what follows. Thus for the increasing pressure stroke we represent the pressure as being constant in horizontal strata parallel with the piston face and decreasing downward from a maximum just below the piston. The neglect of data obtained on the decreasing pressure stroke is reasonable due to the metastability of bismuth II and III as reported by Brandt and Ginzburg.[8] Also this has become common practice among high pressure investigators using solid pressure transmitters, e.g., Il'ina and Itskevich.[9]

By considering the balance of forces on a thin disk of the AgCl we obtain

$$(\pi D^2/4)dP = \pi D S dx, \tag{1}$$

where D is the i.d. of the high-pressure cell, and S is the shear strength of the AgCl. The expression on the left of Eq. (1) represents the downward force due to the pressure differential across the disk, and the expression on the right of Eq. (1) represents the upward resistance offered by the shearing of the AgCl at the cell wall. The disk being considered is located a distance x below the piston face.

According to Bridgman[12] the shear strength of AgCl increases approximately linearly with pressure. Thus

$$S = S_0 + \alpha P, \tag{2}$$

where the material parameters S_0 and α are independent of pressure but vary with temperature. Inserting (2) into (1) and integrating yields

$$P(x) = [(P_A - P_F + S_0/\alpha)\exp(-4x\alpha/D)] - S_0/\alpha. \tag{3}$$

We have used the boundary condition that at the piston face, $x=0$, $P=P_A-P_F$. P_A is the applied pressure calculated from the hydraulic pressure neglecting all

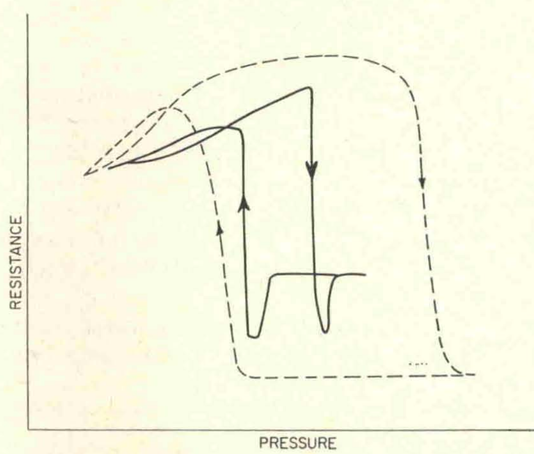

FIG. 4. Tracings taken from X–Y recorder plots showing electrical resistance as a function of applied pressure, both in relative units. The solid lines indicate a resistance versus pressure run at 249°K and the dashed line represents a run at 77°K. Note the difficulty of determining the beginning of the transition at 77°K. For this reason the pressure on the increasing stroke at half the discontinuity is used as the transition pressure.

losses, and P_F represents the losses due to friction in the hydraulic ram plus those due to friction between the piston and cylinder in the high-pressure cell.

The sample pressure was calculated from (3) by inserting the value of x appropriate to the sample position and the value of P_A observed at the midpoint of the phase transformation. The midpoint of the transition was taken to be that pressure at which the sample resistance had changed by one-half the discontinuity associated with that transition. This procedure avoided the difficulty of determining the beginning or end of the transition which became poorly defined at low temperatures (see Fig. 4).

In order to evaluate Eq. (3) we need to know the shear strength of AgCl as a function of temperature and pressure. Bridgman[12] measured the shear strength of AgCl up to 50 kbar at room temperature and Towle[13] measured the shear strength of AgCl down to 77°K at atmospheric pressure. By combining these data with the melting curve of Deaton[14] and the empirical shear strength equation of Towle[15] we were able to calculate the values of the parameters α and S_0 at all the temperatures required. Some representative values are given in Table I. Finally the frictional term, P_F, was determined by normalizing our room-temperature results on the bismuth I–II transition pressure to the value 25.5 kbar. This value for the bismuth I–II transition pressure at room temperature was agreed upon at the "Symposium on the Accurate Characterization of the High-Pressure Environment" held at the National Bureau of Standards in 1968. Within experimental error it also agrees with the result obtained by Heydemann[16] in his accurate measurements. The value of P_F thus determined was typically 2 kbar and was assumed to be independent of temperature.

IV. RESULTS

The resulting phase diagram is shown in Fig. 5. There is good agreement with extrapolations of the data of Tikhomirova *et al.*[7] and also with the two points determined by Bridgmen[1] at 223°K. There is also good agreement with Brandt and Ginzburg's[7] result at 77°K. Ignoring for the moment the question of a new phase of bismuth we find fair agreement between our phase diagram and Il'ina and Itskevich's.[9] There is

TABLE I. Representative values for the material parameters S_0 and α [see Eq. (2)] used in determining the sample pressure are given for several temperatures.

T(°K)	S_0 (bar)	α
300	300	0.0205
200	520	0.0273
100	870	0.036
4.2	1520	0.0473

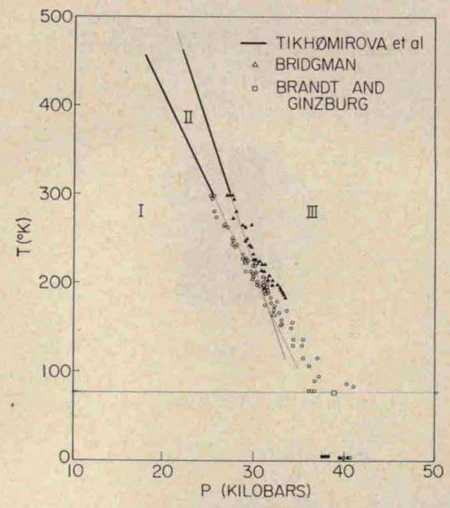

FIG. 5. The phase diagram of bismuth below room temperature as determined by the present author. The open circles represent the bismuth I–II or I–III phase boundaries. The closed triangles belong to the bismuth II–III phase boundary; however, the data points below about 225°K should not be used as an indication of the actual phase boundary because of the large uncertainty discussed in the text. The closed circles at 4.2°K represent one run in which the hysteresis loop was exceptionally small due to extrusion of some of the AgCl pressure-transmitting medium as described in the text. The open triangles refer to Bridgman's data (Ref. 1). The solid lines are straight lines drawn through the data of Tikhomirova *et al.* (Ref. 6). The open square is a point determined by Brandt and Ginzburg (Ref. 7).

some disagreement regarding the II–III phase line and the I–III phase line. This could be due to the fact that we assume corrections to transition pressures due to AgCl pressure-transmitting medium are much greater than the corrections associated with the metastability of bismuth II and III as reported by Brandt and Ginzburg[8] and also Il'ina and Itskevich.[9] Corrections due to metastability would certainly lower our transition pressures, especially at low temperatures. This could improve agreement between our results and those of Il'ina and Itskevich, but considering the scatter in our data, the agreement would still be questionable. In any case the agreement observed between our results and those cited above indicates that our method of determining the sample pressure is satisfactory. This is reassuring considering that the hysteresis loops associated with pressure cycling were about 8 kbar at 300°K, 22 kbar at 77°K, and 40 kbar at 4.2°K. One notable exception occurred during one run at 4.2°K. A loud crack was heard accompanied by a large change in sample resistance. Subsequent pressure cycling at 4.2°K produced a pressure hysteresis loop width of only 15 kbar for the phase transition. Later examination revealed that a large amount of AgCl had extruded up out of the cell, but that the sample and electrical leads had remained intact. The extrusion greatly reduced the length of the AgCl column which had previously caused a frictional loss along the wall of the cylinder and hence, greatly reduced the width of the hysteresis loop. Because the length of the AgCl column was not known in this case the transition pressure was estimated by averaging the transition pressures on the increasing and decreasing pressure strokes. These points are shown as solid circles in Fig. 5 and can be compared with the open circles obtained by applying Eq. (3) to another run where there was no extrusion. The agreement is very good. Further evidence supporting our analysis of the sample pressure is the fact that the bismuth II–III transition at room temperature agrees very well with extrapolations of the data of Tikhomirova *et al.*[7] However, it should be noted that there seems to be some disagreement between various authors regarding the pressure for the bismuth II–III transition.

It is important to point out that the data for the bismuth II–III transition pressures below about 225°K are very uncertain and are included in the phase diagram only to indicate that the bismuth II–III transition was actually observed at these temperatures. The uncertainty is due to the fact that the separation in pressure between the I–II and II–III transitions is approaching zero. When this separation in pressure becomes smaller than the pressure difference across the sample, a condition arises wherein phases I, II, and III are present in the sample simultaneously. This gives rise to a decreasing contribution to the total resistance by the II phase as pressure is increased beyond this point. This effect tends to obscure the bismuth II–III transition because the total resistance is the quantity determined in the experiment. As a result the triple point could only be obtained by an extrapolation from higher temperatures. If this is done the triple point is found to be in approximate agreement with Bridgman's[1] extrapolated result as shown in Fig. 5. The data also seems to indicate that the slope dT/dP, along the phase boundary becomes infinite at $T=0$°K as required by Clausius–Clapyron equation for a first-order phase transition.

No evidence was found of the new phase of bismuth reported by Il'ina and Itskevich.[9] This is surprising in view of the similarity of the apparatus; their system as well as ours employed AgCl as a pressure transmitting medium in a piston-cylinder device. Direct comparison of isothermal tests can be made. They associated the existence of a new phase with a dip in the R–P curve (see Fig. 1 in Ref. 9) which we did not observe. The only resistance changes we observed were those normally attributed to the familiar phase transitions of bismuth as shown in Fig. 4. The disagreement could possibly be attributed to differences in pressurization rates. This author used pressurization rates of 1 to 2 kbar/min; the pressurization rates used by Il'ina and Itskevich were not reported. Furthermore there appear to be some inconsistencies between Il'ina and Itskevich's[9] data and their interpretation of their results. For example, in one isobaric run at 28 kbar they did not observe resistance discontinuities associated with the "new phase"-II and II–III transitions as they raised the temperature to about 275°K. (See Fig. 4, Ref. 9.) These transitions should have been observed according to their phase diagram (see Fig. 2, Ref. 9). Also they show a large resistance discontinuity in an isobaric run at 28 kbar (see Figs. 3 and 4, Ref. 9) as temperature is raised, which they associate with the I-"new phase" transition and a small resistance discontinuity which they associate with the "new phase"-II transition. This appears to contradict runs at 77° and 200°K as pressure is increased, wherein small resistance discontinuities are attributed to the I-"new phase" transition and large resistance discontinuities are attributed to the "new phase"-II transition. (See Fig. 1, Ref. 9.) These apparent inconsistencies in the work of Il'ina and Itskevich[9] and our failure to obtain evidence of a new phase of bismuth suggests that another more conclusive experiment be done. The experiment would require a hydrostatic system, slow pressurization rates, temperatures below 289°K and pressure between 25 and 30 kbar. These temperatures and pressures are implied by extrapolating Il'ina and Itskevich's[9] data to find the I-"new phase"-II triple point at 25 kbar, 298°K.

In summary the phase diagram of bismuth at low temperatures was determined and compared with previously published phase diagrams. The question of a new phase of bismuth was answered tentatively in the negative. Further experimentation to conclusively determine the existence of the new phase was suggested.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Perry B. Alers for his help and encouragement during the early experimental stages of this work, and Dr. Laird C. Towle for valuable assistance in the preparation of this paper.

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