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Phase Diagram of Bismuth at Low Temperatures

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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 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 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

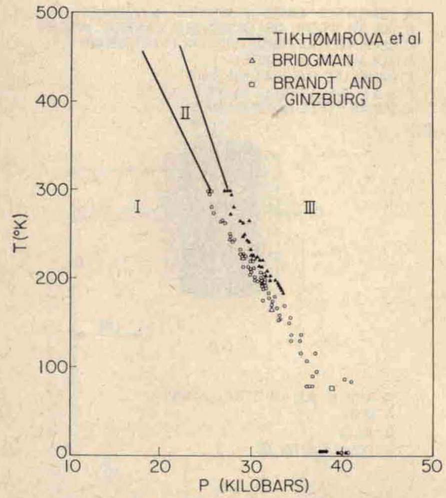

FIG. 5. The phase diagram of bismuth below room temperature as determined by the present author. The open circles represent the bismuth I–II or I–III phase boundaries. The closed triangles belong to the bismuth II–III phase boundary; however, the data points below about 225°K should not be used as an 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).

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