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Phase Diagram of Bismuth at Low Temperatures

ELVIN M. COMPY
U. S. Naval Research Laboratory, Washington, D. C. 20390
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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 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 purity 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.

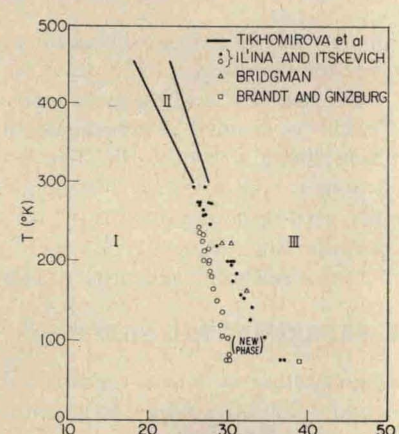

FIG. 1. The phase diagram of bismuth below room temperature. The open triangles refer to Bridgman's data (Ref. 1). The solid lines are straight lines drawn through the data of Tikhomirova *et al.* (Ref. 6). The open square is a point determined by Brandt and Ginzburg (Ref. 7). The circles represent a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

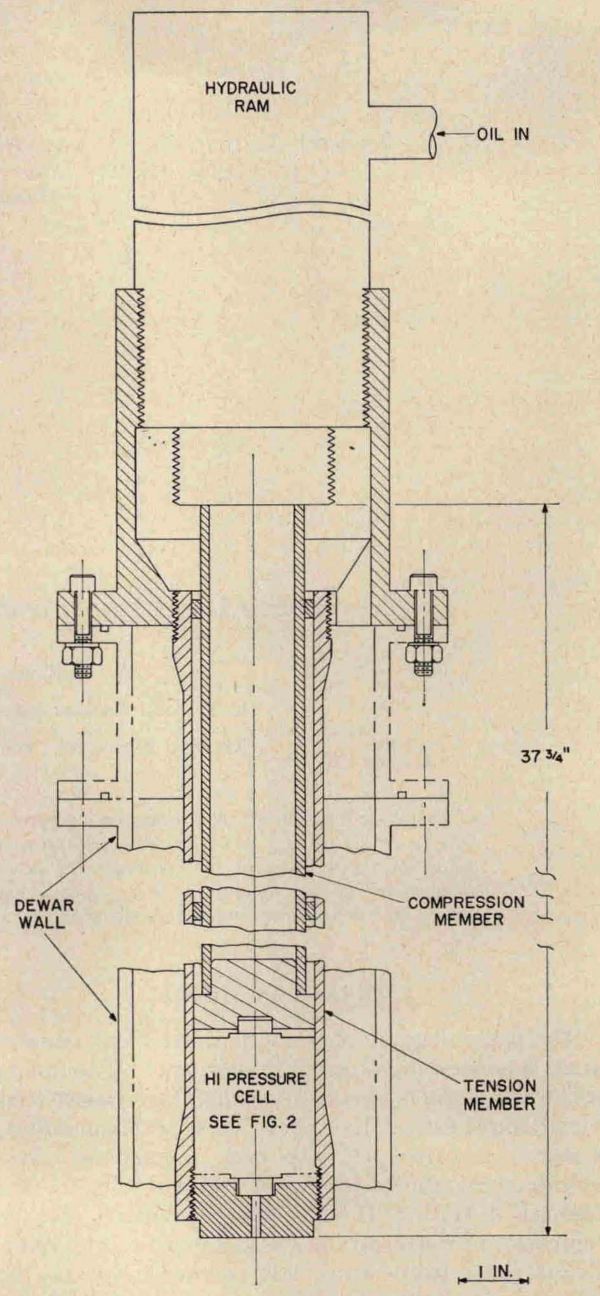

FIG. 2. A cross sectional view of the high-pressure generating system used at low temperatures. Cross-hatched members are 304 stainless steel.