# The Study of the Structural and Transformation Characteristics of the Pressure-Induced Polymorphs in Bismuth

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*It is known from the early work of Bridgman that the two lowest-pressure transitions (I-II and II-III) are accompanied by substantial and abrupt changes in resistivity and volume. However, unlike the temperature-induced allotropic transformations observed in such elements as lithium, cobalt, tin, and so forth, there is little actually known about many of the characteristics of the pressure-induced transitions. This current work involves an examination of the structural and transformation characteristics of the bismuth I-II and II-III transitions under hydrostatic pressures. The relationship of initial structure to the transformation pressure, rate, resistivity change, and resultant structure is discussed. It is shown that the transition pressure and transformation rate are independent of the presence of grain boundaries and associated anisotropy-induced deformation. An observed hysteresis in both the I-II and II-III transitions is shown.*

BISMUTH is one of the most interesting of the elements exhibiting pressure-induced polymorphs since it undergoes several allotropic transformations at pressures below 90,000 atm. It is known from the early work of Bridgman[1,2] that the two lowest-pressure transitions (I-II and II-III) are accompanied by substantial and abrupt changes in resistance and volume. However, unlike the temperature-induced allotropic transformations observed in such elements as lithium, cobalt, tin, and so forth, there is little actually known about many of the characteristics of these pressure-induced transitions. It is the purpose of this work to examine some of the structural and transformation characteristics of the bismuth I-II and II-III transitions under hydrostatic pressures.

Another interesting characteristic of bismuth is that, in its polycrystalline form, hydrostatic pressures of sufficient magnitude will induce severe progressive plastic deformation in the region of the grain boundaries.[3] This deformation, which has also been observed in several other metals, is attributed to the high degree of anisotropy in the linear compressibility of bismuth, resulting in shear stresses in the grain boundaries when it is exposed to hydrostatic pressure.

Most thermally induced allotropic transformations in metals, whether of the diffusionless athermal (martensitic) or isothermal nucleation and growth types, are dependent upon structure and prior history,[4] viz., grain boundaries, deformation, and so forth. One logically wonders then whether the transformation characteristics of the pressure-induced polymorphs in bismuth might also depend upon initial structure, particularly with respect to the presence of grain boundaries and associated plastic deformation.

In this investigation, the role of grain boundaries and plastic deformation on the characteristics of the bismuth I-II and II-III transitions will be established. The rather unique residual microstructural changes associated with these transitions will be presented and discussed. The occurrence of a measurable hysteresis in both the I-II and II-III transitions will be demonstrated. The type of transformation mechanism based on the observed transformation rate will be discussed.

## EXPERIMENTAL PROCEDURE

*A*) Apparatus. The hydrostatic pressure system utilized in this investigation is similar to that previously reported by Bridgman[1] and Birch and Robertson,[5] and has been previously described.[3]

For the purpose of this work, the pressure medium utilized was a 1:1 mixture of pentane and isopentane. Pressure measurement was by means of a manganin coil in conjunction with a Foxboro Recorder. The manganin coil was mounted in the bottom closure and inserted inside the pressure cavity. Based on calibration against a controlled clearance piston gage at approximately 10,000 atm, the estimated error in the pressure measurement was ±2 pct. Assuming the nonlinearity in the pressure coefficient of resistivity between 10,000 and 28,000 atm to be not greater than 1 pct, then the estimated error in the range of the I-II and II-III transitions was ±3 pct.

*B*) Specimen Material and Preparation. The bismuth utilized throughout this investigation was of

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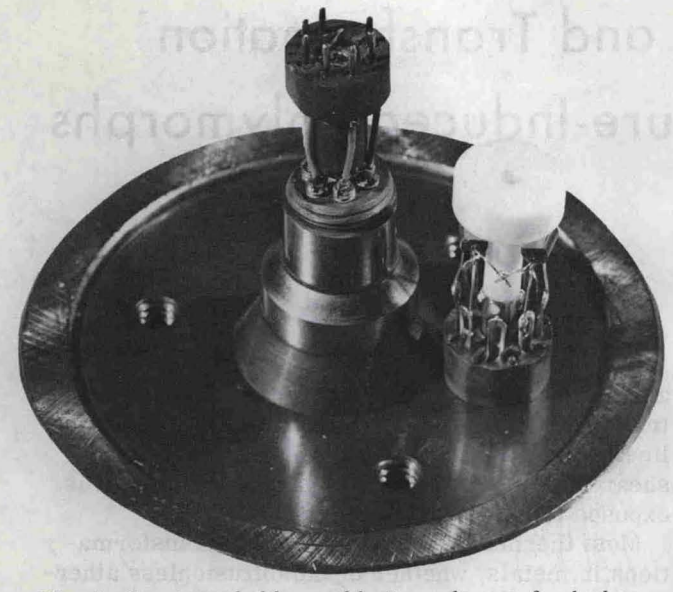

Fig. 1—Specimen holder and bottom closure for hydrostatic pressure system.

high-purity single-crystalline stock having the following detectable impurity levels:

Pb - 0.6 ppm
Fe - 0.9 ppm
Cu - 0.1 ppm
Cd - 0.3 ppm

In order to minimize variations in impurity content between the single and polycrystalline specimens, the polycrystalline samples were produced from the original single crystals by remelting into a 3/4-in. billet and extrusion at 220°C to a 0.17-in. diam. The smaller grain size samples were prepared directly from the as-extruded material. For the larger grain size, the as-extruded material was subjected to an annealing treatment of 220°C for 5 hr. It was attempted to obtain polycrystalline samples by progressive compressive deformation of the single crystals with intermediate annealing. Although moderate grain sizes could be obtained in this manner, this technique was abandoned in favor of the former.

The specimens were 0.16 in. in diam and 0.22 in. long. Prior to pressurization, a plane parallel to the longitudinal axis of the specimen was metallographically prepared by electropolishing using a saturated KI solution with 2 pct by volume of concentrated HCl.

*C*) Resistance Measurement. Electrical resistance as a function of pressure was measured by means of a conventional potential-drop method using a K-3 type potentiometer and recording oscillograph. Two specimens were connected in series to a current source, and the potential drop across each was measured separately. The arrangement of the two specimens in the sample holder is shown in Fig. 1 along with the bottom pressure closure. For the pressure run, the sample holder was simply connected to the seven-anode insulating block of the

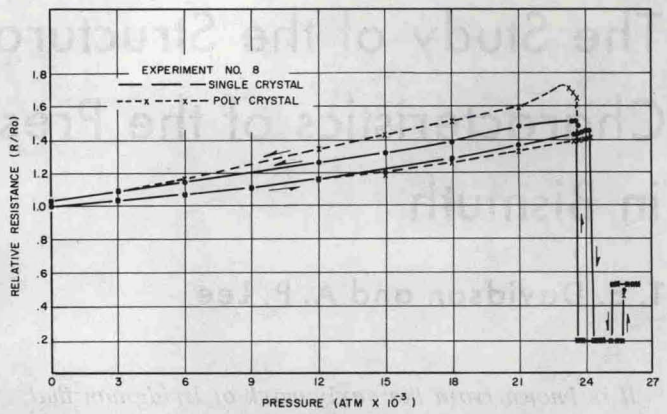


Fig. 2—Relative resistance vs pressure.

closure. There is a total of seven electrical leads emerging through the bottom closure with two being used for the current through the specimens, four for voltage measurements, and the remaining one for the manganin coil inserted inside of the insulating block.

*D*) Procedure. In all experiments, pressure was increased by 3000-atm increments up to 21,000 atm and a 2000-atm increment to 23,000 atm with a 5- to 10-min hold period between each pressure change to permit stabilization of the pressure and voltage readings due to thermal effects. Beyond 23,000 atm, four different procedures, consisting of *a*) 100-, *b*) 250-, and *c*) 500-atm increments with 5-min stabilization periods, and *d*) continuous pressurization at the rate of 50 atm per min, were utilized. The depressurization rate closely approximated the procedure used for increasing pressure.

## RESULTS AND DISCUSSION

*A*) Transition Pressure. In order to establish the effect of initial structure on the transition variables, a single crystal and a polycrystalline sample, connected in series in the manner previously described, were simultaneously exposed to the pressure. Typical relative resistance vs pressure curves utilizing this procedure are shown in Fig. 2.

As is demonstrated in Fig. 2, the I-II and II-III transitions, upon increasing pressure, occur isobarically with the transformation pressure being independent of initial structure. Similarly, the III-II transition, upon decreasing pressure, is also isobaric and structure-insensitive. However, the II-I transition is not completely isobaric, but exhibits some sluggishness near the completion of transformation. This deviation from isobaric conditions is small, usually not exceeding 300 atm.

Under the condition of this experiment, there is a substantial hysteresis in both the I-II and II-III transitions. The magnitude of this hysteresis is independent of structure, but somewhat dependent upon pressurization rate as is shown in the following tables.
The single value of the pressures and pressure difference shown is the average for all tests (only