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THE COMPRESSIBILITY OF BISMUTH AND ITS UPPER TRANSITION PRESSURE

A. A. GIARDINI* and G. A. SAMARA†

U.S. Army Electronics Laboratories, Fort Monmouth, New Jersey

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Abstract—We have measured the compression of bismuth to over 60 kbar under nearly hydrostatic conditions by the inductive coil technique. The over-all results are in close agreement with Bridgman's data, but some significant differences occur in the region of the transitions. The Bi_{I-II} and Bi_{II-III} transitions were clearly resolved with compressions, $-(\Delta V/V_0)$, of 0·064 to 0·122 and 0·124 to 0·160, respectively. Bridgman's extreme compressions across both transitions are 0·064 to 0·150. There was no evidence of either of the two transitions reported by Bridgman at 44 and 64 kbar.

The pressure value at which the upper bismuth transition occurs was re-examined by the use of a manganin gauge with integral calibrants and by a multiple event resistance cell. The results indicate that the transition occurs at a pressure no higher than 81–82 kbar in agreement with recent results. The observed volume change at this transition is approximately 1·5% which is in good agreement with Bridgman's value.

1. INTRODUCTION

BISMUTH (Bi) has been more thoroughly investigated under pressure than any other material, because it has a number of pressure-induced polymorphic transitions that have been widely used as pressure calibration points. These transitions were discovered by Bridgman using volumetric and electrical resistance measurements.[1–3] The values for the transition pressures at room temperature are: Bi_{I-II} 25·4 kbar, Bi_{II-III} 26·8 kbar, and the upper Bi ~ 80 kbar. The first two values are accurate to about ±1%; however, the third is much less accurately known.

The only detailed study of the compression of Bi is that of BRIDGMAN[1,2] who determined the vol. change up to 100 kbar using the piston-cylinder displacement technique. His data are reproduced in Fig. 2. The two small transitions at 44 and 64 kbar were not observed by Bridgman in his electrical resistance measurements[3] and have not been substantiated by other workers by either electrical resistance or differential thermal analysis[4] techniques.‡

Efforts by numerous workers to study the volume changes and crystal structures of the various phases of Bi by high pressure X-ray methods have so far failed to yield any useful results.

Because of the importance of Bi as a high pressure standard, it was felt desirable to re-examine its compression by an independent method, namely, our inductive coil technique.[5] We have measured the compression of Bi to 60 kbar under nearly hydrostatic conditions and also re-examined the pressure value of the upper transition. The results are presented and discussed below.

2. EXPERIMENTAL TECHNIQUES

The apparatus and inductive coil technique have been described elsewhere.[5] High purity (99·999%) Bi was used. For most experiments, the material was melted in a pyrex tube under an

* Present Address: Department of Geology, University of Georgia, Athens, Georgia.

† Present Address: Sandia Laboratory, Albuquerque, New Mexico.

‡ Bridgman detected the 44 kbar transition by shearing measurements also. (See ref. 9.)

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argon atmosphere. The castings were then compressed in a mold to an average pressure of 8·5 kbar, machined into cylindrical samples, and threaded. A number of samples were prepared by grinding the Bi and compressing it to either 20 or 35 kbar before machining and threading. All samples were of theoretical density (9·80 g/cm^3). The differences in the vol. changes for the differently prepared samples were within the scatter of the data.

The samples varied in size from 0·635 cm dia. × 0·635 cm long to 0·900 cm dia. × 1·300 cm long with from 18 to 32 threads/cm. Initial coil inductance (corrected for leads) varied from 0·63 to 7·82 μH. The largest samples were recovered with no more than $\pm 3\%$ change in dimensions after compression to 60 kbar. Small samples suffered less than $\pm 1\%$ deformation. Formvar coated copper wire (0·01 cm dia.) was used for the coils.

With relatively soft materials like Bi it is important to make the profile of the thread to conform as closely as possible to that of the coil wire. If the latter is not flush with the core initially, it will be forced deeper into the sample under pressure, thus yielding an enlarged vol. change. It was also found useful to place a thin sleeve of a material harder than silver chloride directly on the coil before enclosing the whole in a silver chloride jacket. The hard sleeve forces the coil to conform more reliably to the sample core under compression.

There was usually some scatter in the data in the initial stages of compression (below 10 kbar).* This is the region of gasket formation in the cubic apparatus. The scatter is most likely associated with the fact that Bi is relatively soft, and some readjustment in the fit of the coil on the core takes place. There is also some uncertainty in the pressure calibration of multianvil apparatus in this low pressure range. For these reasons the present data were matched with Bridgman's up to 20 kbar. This is the range to which Bridgman's data should be most accurate.

In order to re-examine the pressure value of the upper Bi transition, it was necessary to extend the 70 kbar range of our multianvil cubic apparatus. This was done by the use of tungsten carbide intensifier plates in the manner described previously.(7) The plates were in the form of truncated pyramids 0·865 cm thick and 3·30 cm long at the base.

Pressure was measured both by the recently developed manganin gauge with integral calibrants(8) and by multiple event resistance cells. The latter consist of small sections of Bi, Tl, and Ba wire cut in lengths inversely proportional to their respective resistivities and encapsulated in series in a silver chloride sleeve. The transition pressures of the calibrants were taken as 25·4, 37, and 59 kbar for Bi_{I-II}, Tl, and Ba, respectively.

3. RESULTS AND DISCUSSION

Compression

Bismuth was the test material most widely used in developing the inductive coil technique, and a large number of experiments were made on it. Many of these were made to test various refinements in the original technique, which rendered it more quantitative in measuring "long range" vol. compression as well as vol. changes accompanying polymorphic transitions.

A typical inductance vs. ram pressure curve is shown in Fig. 1. The experimental set-up is such that the coil collapses proportionately with the sample, and the inductance, L, is related to sample vol. by the relationship $L = V^{1/3}$.

Volume changes for the transitions are calculated from the inductances at the terminal points of each event. This is because the transformations in Bi are very nearly isobaric, and pressure gradients across the sample are negligible in our apparatus.(7) This is supported by the fact that there is always a sharp step separating the two transitions regardless of the range of applied load required to complete each transition. In cases where the Bi is not jacketed by silver chloride, the spread in the ram pressure required to complete each transition is over twice that shown in Fig. 1 (see for e.g. Fig. 3). This difference in load requirement is attributed to the "cave principle" which we described earlier.(7)

* In a number of experiments some large irreversible changes in inductance (usually an increase by several per cent) were observed in this low pressure region. These are attributed to mechanical difficulties associated with gasket formation during the initial stages of compression. Such experiments were rejected. Only experiments which showed the expected monotonic decrease of inductance with pressure in the low pressure phase were considered acceptable.