

Paper to be presented at Symposium on the Accurate Characterization of the High-Pressure Environment, October 14-18, 1968, U. S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, Maryland.

CHARACTERIZATION OF THE BISMUTH I-II AND BARIUM I-II POINTS
UNDER HYDROSTATIC PRESSURE

by

R. J. Zeto, H. B. Vanfleet*, E. Hryckowian and C. D. Bosco
Institute for Exploratory Research
US Army Electronics Command, Fort Monmouth, New Jersey

* On Sabbatical leave from Brigham Young University,
Provo, Utah.

ABSTRACT

Hydrostatic pressure experiments were made which have new and important relevance to high pressure calibration in both liquid and solid pressure systems for the bismuth I-II and barium I-II points on the high pressure scale. The bismuth I-II transformations were characterized and the mechanism of the solid-state reactions was related to pressure calibration. The strain hysteresis commonly associated with the bismuth I-II point was shown to be invalid and was alternatively explained on the basis of a thermally activated nucleation and growth mechanism which was demonstrated to govern these transformations. With hydrostatic pressure initiation of the I-II transformation was observed as a function of kinetic times as long as 15 hours while pressure and temperature were maintained constant. The transformation behavior was a function also of the microstructure, purity and thickness of the sample. The bismuth I-II transformation was not necessarily sharp with respect to kinetic time. As long as 42 hours were observed for completion of the transformation with very thin samples. Under hydrostatic pressure the bismuth I-II equilibrium point was not midway between the initiation of the I-II and II-I transformations but was located appreciably closer to the former transformation. The bismuth I-II calibration point was correlated between liquid and solid pressure systems. For solid systems it was shown that the "apparent" hysteresis was completely one-sided toward

the low pressure side and that the equilibrium point coincided with the initiation of the I-II transformation which should be employed as the pressure calibration point. The bismuth I-II region of indifference was characterized with respect to nature of the sample and manner of measurement. An experimental technique was indicated by which the center of the region of indifference was reproducible within ± 5 bars. The barium I-II point was measured at 56.27 kbar on the basis of a manganin gage under hydrostatic pressure.

I. INTRODUCTION

The current high pressure scale is based upon fixed-point pressures of solid-solid phase transformations. Although the bismuth I-II point at 25.380 kbars at 25°C is fundamental to the high pressure scale and is universally employed for high pressure calibration, very little work has been done to characterize the nature of the I $\rightleftharpoons$ II phase transformations upon which the fixed-point calibration pressure is based. In view of experience and theory on the variable nature of solid-solid phase transformations such a characterization and relation to the calibration pressure is warranted both for hydrostatic pressure systems which calibrate on the equilibrium point and for solid pressure systems which calibrate on the initiation of the transformations. This is particularly important for ultimate accuracy of the bismuth I-II calibration point in the former pressure systems in which pressures can be measured with a sensitivity of 1 bar. The behavior of the phase transformations can certainly be expected to display an influence on the calibration point in terms of this degree of sensitivity of pressure. More practically important at the present time is the resolution in terms of phase transformation theory of the several different calibration procedures employed in solid pressure systems. During the last several years in the high pressure laboratory at Fort Monmouth an incomparable hydrostatic pressure capability was developed with a hexahedral press, and hydrostatic pressure experiments were made which have new and important relevance to high pressure calibration in both solid and liquid pressure systems for both the bismuth I-II and barium I-II points on the high pressure scale. In

view of the large amount of information which resulted from these experiments, the important results pertinent to pressure calibration and the goals of this conference are presented in the manuscript in summary form. More elaborate discussion and experimental detail will be orally presented and will be submitted to J. Phys. Chem. Solids in the near future.

To place the results of the present paper in context it is helpful to briefly review the present concept of the bismuth I-II and II-I transformations. A perusal of the literature reveals that the general nature of these transformations, whether examined by means of electrical resistance, volume change or x-ray measurements in either liquid or solid pressure transmitting systems, can be schematically depicted as in Figure 1 for the vicinity near the calibration point. With increasing pressure on a sample composed completely of bismuth-I, the I-II transformation initiates at a pressure corresponding to A. After sufficient overpressurization to completely convert all bismuth-I to bismuth-II, decreasing pressure causes the II-I transformation to initiate at a pressure corresponding to B which is substantially lower than A. Both transformations occur isobarically in liquid systems but may have to be pressurized to completion in solid systems. Thus the transformations to completion, C and D, exist as illustrated for solid systems but are vertical for liquid systems. The pressure interval between points A and B is commonly denoted as a hysteresis for the transformations. In liquid systems this pressure interval has been reported to have an average value of about 0.71 kbar (Ref. 1), whereas in solid systems the value is observed to be much larger and is of the order of kbars due to the attendant and additional hysteresis of the pressure transmitting medium, e.g., pyrophyllite or AgCl. The transformations

can be made to reverse over a much smaller pressure range near the equilibrium pressure if the hysteresis is entered, either by reducing pressure during the I-II transformation or by increasing pressure during the II-I transformation, so that both phases are in intimate contact. In his liquid system Bridgman (Ref. 2) measured a pressure range of about 60 to 100 bars within which the transformation would not perceptibly run in either the I-II or the II-I direction and denoted this pressure range as the region of indifference. It is generally assumed, primarily because of a lack of data, that the equilibrium pressure, E , is situated halfway between the pressures at which the I-II and II-I transformations occur when measured either at the hysteresis or at the region of indifference. Several investigators (Ref. 3, 4), however, have stated that such an occurrence might not be true with respect to the hysteresis, but in fact might be located at a higher pressure, E' .

II. EXPERIMENTAL

The basic apparatus was a hexahedral press with 2000-ton capacity rams and a cubic pressure chamber 2.25 inches on an edge. Hydrostatic pressures were generated within a stainless steel cell which contained an equal-volume liquid mixture of normal- and iso-pentane. The stainless steel cell was situated within a pyrophyllite cube. As force was applied to the pyrophyllite cube the cell experienced the uneven solid pressures within the cubic volume, but the sample within the stainless steel cell was exposed only to those forces transmitted by the liquid. The original hydrostatic pressure cell (Ref. 5) was improved to increase its reliability and useable high pressure volume (7/16 in. dia. x 1 in. length) and to give 10 electrical leads for measurement from the hydrostatic pressure chamber. This capability of volume and leads permitted four-terminal measurements, simultaneous comparison of several samples in the same experiment, and simultaneous measurement of manganin and samples. For example, one experiment comprised a manganin coil, mercury (for calibration of the coil), and four different bismuth samples. Four-terminal measurements were always made on manganin and also on the samples whenever possible. The resistance of the manganin coil was measured with a Leeds and Northrup Model 8069 G-2 Mueller Bridge with a sensitivity of ± 0.1 mohm which for our coils was equivalent to about ± 0.5 bar. Quantitative experiments were conducted with a properly seasoned and calibrated (mercury L-I and bismuth I-II points at 25°C) manganin gage. Relative pressures from an uncalibrated manganin coil sufficed for the examination of qualitative features of the mechanism of the bismuth I-II and II-I transformations. The sample

parameters investigated were purity (six nine's vs. two nine's), micro-structure (single crystal vs. polycrystal), and thickness (0.040 in. dia. vs. 0.013 in. dia.). Samples were monitored with a sensitivity of at least 0.1 per cent either by means of a Keithley Model 150A microvolt-ammeter with the output recorded on a Varian Model G-11 strip chart recorder, or directly by means of a four-channel Model 240 Brush oscillograph-recorder. In order to avoid heating the samples, the current level was adjusted such that the power through the sample was kept at approximately 1.54×10^{-5} watts. Temperature was measured to 0.001 C by means of a platinum resistance thermometer immersed in a well of water which made contact through a brass plug with the anvil bearing on the pressure cell. Temperature corrections to 25°C were applied for the resistance of manganin and for the temperature coefficient of 50 bars/deg. C for the bismuth I-II point.

III. THE BISMUTH I-II POINT UNDER HYDROSTATIC PRESSURE

A. The Apparent Hysteresis

The hysteresis has important relevance to pressure calibration in solid pressure systems which comprise the bulk of pressure apparatus in current use. Two calibration procedures are generally employed in these systems: in one procedure only the I-II transformation pressure is measured and the calibration point is associated with point A in Figure 1, and in the other procedure both the I-II and II-I transformation pressures are measured and the calibration point is associated with point E in Figure 1. Obviously these are different calibrations, and pressures reported on the basis of the one type of calibration will be different than those pressures based on the other type of calibration. To resolve this discrepancy it

has been suggested (Ref. 4) that the former calibration method should add a pressure corresponding to one-half of the hysteresis width, i.e., A-E in Figure 1. In any case, all of this type of calibration in solid pressure systems depends upon the hysteresis (both for bismuth and for the pressure medium) exhibiting a fixed and reproducible value.

Two publications (Ref. 1, 4) associate a real hysteresis with the bismuth I-II point, but each also implies the possibility of a thermally activated nucleation and growth mechanism. Since a fixed strain mechanism and a thermally activated mechanism are mutually exclusive of one another, and in view of the obvious importance of the hysteresis for solid pressure calibration, it was considered desirable to conduct hydrostatic pressure experiments to determine the mechanism of the I-II and II-I transformations and the basis of the hysteresis. Actually, results published in the literature appeared to indicate a nucleation and growth type of mechanism. Also, our general experience with multiple cycles in the hydrostatic system failed to reproduce a closed loop with respect to resistance or to reproduce either boundary with respect to pressure and cast additional doubt on a fixed strain basis for the nature of the hysteresis A-B as represented in Figure 1. It was of particular interest to determine whether or not this pressure hysteresis was real, i.e., if the initiation of the transformations beyond the equilibrium point was dependent upon a fixed strain energy which would yield a fixed pressure interval A-B. The alternative explanation of this pressure interval as being due to a thermally activated nucleation and growth mechanism requires that the pressure interval A-B be time dependent.

Experiments made under hydrostatic pressure showed that the hysteresis A-B of Figure 1 was not a real strain hysteresis but was time dependent according to a thermally activated nucleation and growth mechanism.

By holding a sample comprised completely of bismuth-I at constant pressure and temperature below that represented by point A in Figure 1, the I-II transformation initiated as a function of kinetic time. The observation of waiting periods prior to initiation of the I-II and II-I transformations at constant temperature and pressure within the apparent hysteresis has been noted numerous times for the I-II transformation and also for point B and the II-I transformation. Furthermore the pressure coefficient of the waiting periods for the I-II transformation, for example, was consistent with a thermally activated nucleation and growth mechanism; longer waiting periods were observed for lower pressures toward the equilibrium pressure. For the I-II transformation, point A was located with a very slow pressurization rate of 1 bar/minute and then on different cycles pressure was maintained constant at various lower values. Waiting periods as long as 15 hours at constant pressure and temperature were measured prior to initiation of the I-II transformation. The waiting periods can be explained as a direct consequence of the kinetic time for nucleation of the new phase in a solid state transformation. In the vicinity of 150 to 200 bars over the equilibrium pressure, the pressure coefficient of the waiting periods appeared to be very large, about -6 minutes/bar. The waiting periods for the II-I transformation did not vary in a consistent manner with hydrostatic pressure. The initiation pressure of this transformation appeared to be dependent on the pressure with which the I-II transformation was overpressurized.

Hydrostatic pressure experiments in which several different samples were simultaneously examined and recorded showed very clearly that the

transformation behavior was a function of sample purity, microstructure, and thickness. At constant pressure and temperature, appreciably different waiting periods for initiation of the I-II transformation were observed for different samples. Also, the times required for complete transformation to bismuth-II varied not only from sample-to-sample but also as a function of the holding pressure. Slower transformation rates were observed for lower holding pressure in accordance with a nucleation and growth mechanism. Dramatically slow transformation rates were measured for very thin samples. For example, a bismuth strip sample 0.0004 in. thick required about 42 hours for complete transformation, whereas under the same conditions in the same experiment a bismuth strip sample 0.011 in. thick transformed completely in 1 hour. In the literature, "sharpness" of the transformations is sometimes invoked as a criteria for "hydrostaticity" of pressure, but the role of kinetic time in a solid-solid transformation must not be overlooked. Even though the transformations occur isobarically in a hydrostatic pressure system the transformations may be very sluggish with respect to kinetic time. The slow transformation rates are further support for a thermally activated nucleation and growth mechanism. The fastest initiation and transformation rates were observed with thick (0.040 in. dia.) polycrystalline samples.

All evidence from these hydrostatic pressure experiments was consistent with a thermally activated nucleation and growth mechanism. The hysteresis which is generally associated with the bismuth I-II point is not a real strain hysteresis but is actually an apparent hysteresis due to a large activation energy for nucleation and/or growth and the sluggish rates of

a solid-solid phase transformation. This apparent hysteresis is variable with respect to kinetic time, pressurization rate, and sample characteristics. The assumption that the bismuth I-II equilibrium point is centered within the apparent hysteresis is also invalid. The relationship of the equilibrium point within the apparent hysteresis for liquid pressure systems was determined and is illustrated in Figure 2. The apparent hysteresis A-B was found with a slow and constant pressurization rate and was then entered as described earlier for the measurement of the region of indifference within which is the equilibrium and calibration point. The region of indifference was not at all midway between the initiation pressures of the I-II and II-I transformations but was located appreciably toward the I-II side. The calibration point, E, was about 150 bars below point A which corresponded to about $1/3$ of the pressure interval A-B in the liquid system. The transformations to completion, C and D, are represented as vertical lines since each transformation occurred isobarically. The initiation pressure of the II-I transformation, point B, was not reproducible on different pressure cycles and after completion of this transformation the initial bismuth-I resistance was not recovered. Additional evidence of the variable nature of point B is shown in the next section.

Superficially these results have serious and detrimental implications for pressure calibration in solid pressure systems since without the "hysteresis" there is no stable fixed point upon which to pin a calibration. Consider, however, a nucleation and growth mechanism in the context of general experience with the kinetics of solid-solid phase transformations. The observed waiting periods at constant pressure and temperature may be

associated with induction times for the nucleation of the new phase. It is known that scratching or grinding a material will reduce and remove an induction period, lower the activation energy for nucleation, and facilitate the nucleation rate of the new phase. Clearly a scratching and grinding effect on the bismuth sample can be expected from the solid pressure medium and this would tend to eliminate the waiting periods observed under hydrostatic pressure. Theoretically, then, it would be expected that initiation of the I-II transformation in a solid pressure system should take place at a pressure which corresponds, or at least is close to, the real equilibrium point. Evidence that this correlation is valid is presented in the next section.

B. Correlation of the Calibration Point Between Liquid and Solid.

An experiment was designed to test the transformation hypothesis just mentioned in the previous section. An experiment in the hydrostatic pressure cell was conducted with two identical bismuth samples: one sample was directly exposed to the pentane-mixture pressure medium and the other sample was completely embedded in an epoxy solid (about 0.040 in. wall thickness) which in turn was directly exposed to the same pentane-mixture pressure medium. These samples were simultaneously examined in the same experiment and gave a direct comparison of the bismuth I $\rightleftharpoons$ II transformations for a specimen subjected to a hydrostatic pressure and one subjected to a solid pressure transmitting medium. The samples were first pressure cycled with a slow, constant pressurization rate of about 15 bars/minute in order to determine the apparent hysteresis for both samples. In cycling the samples, pressure was taken well beyond

the bismuth II-III transformation in order to insure the presence of only one or the other of phase I and II at the initiation of the transformations. The true equilibrium pressure was then measured with the sample which was directly exposed to the hydrostatic pressure medium.

The correlation of the bismuth I-II equilibrium point within the apparent hysteresis for liquid and solid pressure transmitting media is schematically illustrated in Figure 3. The equilibrium point, E, measured with the sample in the liquid medium corresponded within a few bars to the pressure, A_S , at which the bismuth I-II transformation initiated in the sample which was embedded in the solid pressure transmitting medium. Verification of the theory of the mechanism of the transformation was obtained and these results provided striking correlation between liquid and solid pressure systems for pressure calibration at the bismuth I-II point. The hysteresis observed in solid pressure systems is completely one-sided towards the II-I transformation. In solid pressure systems calibration should be conducted with a slow pumping rate and should be fixed to the initiation of the bismuth I-II transformation.

This phenomena was investigated in another experiment in which a AgCl pressure transmitting medium was employed. The same effect was clearly evident although it was less pronounced than for bismuth in epoxy. Comparison of the transformation curves from initiation to completion of the transformation, C, revealed a dependence on the nature of the pressure transmitting media. This observation was consistent with a thermally activated nucleation mechanism in which nucleation of the new phase was accelerated by the pressure medium which was more non-isotropic, i.e., from pentane to

AgCl to epoxy. Initiation of the I-II transformation occurred at the highest pressure, A_L , for the bismuth sample in the liquid medium. The II-I transformation, D, was very fast in all cases but the initiation of this transformation, B, occurred at a much lower pressure when the II-I transformation was preceded by the II-III transformations in the pressure cycle. In this case the equilibrium point, E, was located about the same pressure interval below A_L as when the II-III was not included in the pressure cycle, but A_L -E became only about 1/6 th of the apparent hysteresis A_L -B.

C. The Region of Indifference Equilibrium Point.

The region of indifference comprises the equilibrium point and is employed for pressure calibration in hydrostatic pressure systems. According to Bridgman (Ref. 2) the region of indifference is measured as the pressure range over which the transformations can be made to run in opposite directions when starting from a pressure at which no transformation is perceptible. The region of indifference is determined with about equal amounts of both phases I and II present in the sample. Nucleation is no longer a consideration as the apparent hysteresis and the transformations can be made to reverse over a pressure range less than 100 bars. Although hydrostatic pressure systems comprise the minority of pressure apparatus in current use, there are an increasing number of laboratories utilizing these systems in which small pressure changes of about 1 bar can be measured with a manganin pressure gage. This precision cannot be utilized for pressure calibration with a comparable accuracy, however, since the equilibrium point has not been characterized with respect to

the purity, microstructure, and thickness of the sample, the width of the region of indifference, the pressure direction of measurement, and the variation of the equilibrium point with respect to the relative proportions of bismuth-I and bismuth-II present in the sample. The pressure calibration point must be evaluated and considered in the context of the solid-solid phase transformation upon which it is based. General experience with high temperature transformations shows that transformations in the solid state are influenced by these factors mentioned above. Characterization of the I-II equilibrium point is therefore important for the ultimate accuracy of hydrostatic pressure calibration, particularly in terms of the current techniques which measure pressure with a sensitivity of 1 bar. Hydrostatic pressure experiments were made to bear on such a characterization. The technique which was experimentally employed to investigate the region of indifference was as follows. The sample potential was recorded for 15 minute intervals at constant pressure. After the completion of an individual sample trace, pressure was altered either up or down in increments of 5 to 8 bars and the sample potential was again monitored for about 15 minutes at each pressure. The rate traces of sample potential vs. time were zero within the region of indifference; positive for the II-I transformation, and negative for the I-II transformation. The manganin resistance was measured at the beginning and at the end of each trace and was monitored on the recorder simultaneously with the sample trace. Pressure was constant within 1 bar over the duration of each rate record of the sample. The I-II and II-I boundaries of the region of indifference were noted as the pressure at which the sample rate trace deviated from zero in the negative and positive direction,

respectively. The equilibrium pressure was then taken at the center of the region of indifference. By this procedure and with the sample and manganin sensitivity employed, 20 bars was commonly measured for the width of the region of indifference. This is the smallest region reported to date.

With respect to the equilibrium point the question arises as to the existence of a pressure region or a single pressure value over which or at which the transformation will reverse. Theoretically there cannot be a single value of pressure for the equilibrium point. The bismuth I-II point is based on a solid-solid phase transformation in which strain energy is a thermodynamic variable. In the phase rule sense, this extra degree of freedom means that the transformation must occur over a range of pressures at constant temperature instead of at a single pressure as normally expected for a pure compound. While greater sensitivity than that employed in the present investigation might reveal a region of indifference less than 20 bars, the region of indifference will nevertheless not be zero. The small value of 20 bars, however, is favorable for utilization of the bismuth I-II transformation for high pressure calibration. In terms of this discussion, the nature of the region of indifference is based on the strain energy resulting from the volume change between phases I and II and this is really the strain hysteresis for the bismuth I-II point.

The nature of the region of indifference with respect to pressure direction of measurement was investigated with a polycrystalline bismuth sample of six nine's purity and 0.040 in. dia. Since the determination of an equilibrium point should be made by approach from each side of the equilibrium, there are two possible ways in which the region of indifference may be measured: (1) I-II in the up-pressure direction and II-I in the down-pressure direction, and (2) I-II in the down-pressure direction and the II-I in the up-pressure direction. Four determinations were made by each method with 45 to 55 percent bismuth-I present in the sample for each determination, and the results favored the former procedure as employed by Bridgman. The width of the region of indifference determined in this manner was 20 ± 6 bars whereas a region of indifference of 27 ± 12 bars was determined by the latter procedure. The average of each set of four determinations gave the same absolute value for the center of the region of indifference for each method of measurement.

If the region of indifference is a strain hysteresis as mentioned above, then this region could be a function of the relative proportions of bismuth-I and bismuth-II present in the sample. Consequently measurement of the equilibrium point for high pressure calibration might likewise be a function of the phase composition of the sample. To examine this phenomena the region of indifference was measured at

bismuth-I proportions between about 20 and 80 percent with a polycrystalline sample of six nine's purity and 0.040 in. dia. In this percentage range the widths of the region of indifference, about 20 bars in each case, overlapped. For bismuth-I proportions between about 20 and 60 percent the centers of the region of indifference were within about 5 bars of each other, however there appeared to be a definite bias, about 10 bars, towards lower pressures for the measurements at higher proportions of bismuth-I. This effect was also observed for different samples with larger grain size (single crystal) and less purity (two nine's). In terms of the sensitivity of our pressure and sample measurements this bias appears to be real although it is difficult to make such a conclusion with certainty for such small pressure values in view of possible and unknown systematic errors of measurement. Investigation of this point by other laboratories seems desirable. In any case it appears that highest reproducibility (several bars) of the calibration point is achieved when the pressure is adjusted so that about 50 percent of phase I exists in the sample when the region of indifference is measured.

As indicated above, the region of indifference was investigated as a function of the purity (six nine's vs. two nine's), microstructure (single crystal vs. extruded polycrystal), and thickness (0.040 in. dia. vs. 0.013 in. dia.) of the sample. The center of the region of indifference was reproducible within ± 3 bars with respect to

microstructure and thickness. Surprisingly, but favorable for pressure calibration, there was very little difference between six nine's and two nine's purity, the center of the region of indifference being about 10 bars higher for the less pure sample. The widths of the region of indifference overlapped for all samples. The most noticeable effect of these sample characteristics was that the width of the region of indifference became about twice as large as a function of sample thickness from 0.040 in. dia. to 0.013 in. dia., even though the center of the region was the same in each case. This width of the region was even 50 percent larger (about 70 bars) when measured by method (2) rather than by method (1) mentioned earlier. For all samples except the latter, the width of the region of indifference was about 20 bars.

The results described above have the following relevance to hydrostatic pressure calibration with the bismuth I-II point. First of all the calibration point is reproducible at least within 50 bars regardless of pressure direction of measurement, proportion of bismuth-I in the sample (between 20 - 80 percent), and sample characteristics (within the sample variation investigated) of purity, microstructure and thickness, except for the wide region for very thin samples. With the exception noted, all of these factors displayed their influence within ± 25 bars of the calibration point. The influence of these factors on the nature of the I-II transformations has been assumed

to be negligent in previous high pressure calibration, but these factors have a basis in phase transformation theory and in experience with high temperature transformations and it is comforting to have experimental verification of the extent of their influence. These results further indicate that the absolute reproducibility and accuracy for pressure calibration could be reduced to about ± 5 bars for the center of the region of indifference and to about ± 13 bars for the complete width of the region of indifference by employing a pressure and sample sensitivity comparable (or better) than that in this work and if the calibration is conducted starting with a pure single crystal sample about 0.040 in. dia. and by measuring the region of indifference after the manner of Bridgman with about 40-60 percent bismuth-I present in the sample.

IV. The Barium I-II Point Under Hydrostatic Pressure

Most high pressure measurements above 40 kbar depend upon a calibration curve based on the barium I-II point. The importance of the point for accurate high pressure measurements is clearly evident, particularly for pressures greater than 60 kbar. The barium I-II point has been measured (Ref. 6, 7, 4, 8) with piston-cylinder devices and rotating free-piston techniques and with tetrahedral apparatus and x-ray techniques in conjunction with equation-of-state. In view of the present

uncertainty associated with the calibration pressure for this transformation, the hydrostatic pressure cell described earlier was employed to provide an independent measurement of the barium I-II point, this one with hydrostatic pressure and based on a calibrated manganin pressure gage.

Pressure is hydrostatic to the extent that the viscosity of the pressure medium permits a fast relaxation time for bulk stresses. The pressure-transmitting medium in the hydrostatic pressure cell was a 1:1 volume mixture of normal- and iso-pentane in which pressures equalized by viscous flow through a prescribed capillary tube in times of the order of seconds at 50 kbar and of minutes at 60 kbar (Ref. 5). An approximate value of 10^8 poise at 60 kbars has been measured for this pressure medium (Ref. 9). The pressures generated at the barium I-II point were hydrostatic within this context.

The relative resistance change, $\Delta r/r_0$, of a properly seasoned manganin coil was calibrated with pressure by means of a quadratic equation.

$$P = A (\Delta r/r_0) + B (\Delta r/r_0)^2 .$$

whose coefficients A and B were determined by a two-point calibration with the accepted pressures and the measured relative resistance change of the manganin coil for the mercury L-I (Ref. 10) and bismuth I-II (Ref. 11) transformation at 25°C. At the barium point slow pressurization rates were employed and adequate time for pressure equilibrium was

allowed. The manganin relative resistance associated with the region of indifference of the barium I-II transformation was measured and the pressures corresponding to the width of the region of indifference were calculated from extrapolation of the manganin calibration curve. Using this same experimental and extrapolation technique, good agreement was obtained for measurement of the thallium II-III calibration point.

The width of the barium I-II region of indifference was 2.32 kbars according to manganin. This width is appreciably larger than the region of indifference measured with this same technique for bismuth I-II and thallium II-III, and is probably a reflection, at least to some extent, of the decreasing degree of "hydrostaticity" of the pressure medium. Nevertheless the pentane-mixture pressure medium is certainly more hydrostatic than the solid systems employed for the barium I-II point, and the present measurement of the region of indifference is the smallest reported for this transformation. According to the usual procedure the equilibrium pressure was determined from the center of the region of indifference and was 56.27 kbars. This value is 2.5 kbars lower than the presently accepted value of 58.8 kbars employed for high pressure calibration. Based on this data, therefore, either the presently accepted equilibrium pressure for the barium I-II transformation is high by about 2.5 kbars or the curvature of the manganin curve changes quite sharply between 37 and 59 kbars.

Several other recent measurements of this transformation have indicated that this calibration point should be lowered. Both of these measurements, 54.4 kbar (Ref. 4) and 55.0 kbar (Ref. 8), are still lower than the value obtained on the basis of manganin.

The results presented earlier for the comparison of the bismuth I-II point in solid and liquid pressure media have an interesting and potentially significant implication for measurement and calibration at the barium I-II point. If the mechanism of the barium I-II transformation is one of thermally activated nucleation and growth then, analogous to phase transformation theory and verification in the case of bismuth I-II, in solid pressure systems one would expect the real equilibrium point to be closer to initiation of the barium I-II transformation than to the average of the I-II and II-I initiation pressures, particularly in view of the very wide pressure interval measured between these transformations in the solid systems.

Acknowledgement

Grateful acknowledgement is expressed to Dr. H. H. Kedesdy for his encouragement during the course of this work, to Mr. G. E. Tomes for his able assistance with the experiments, and to Mr. F. J. Becker for his expert machining of the materials needed for the experiments.

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Figure Captions

- Figure 1. Schematic representation of the relative resistance of bismuth for increasing and decreasing pressure in the vicinity of the I-II calibration point.
- Figure 2. Schematic representation of the relative resistance of bismuth for increasing and decreasing pressure in the vicinity of the I-II calibration point under hydrostatic pressure.
- Figure 3. Location and comparison of the equilibrium point in solid and liquid pressure transmitting media for the bismuth I $\rightleftharpoons$ II transformations.





