Pressure Calibration to 60 kbar Based on the Resistance Change of a Manganin Coil under Hydrostatic Pressure

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The relative resistance change of a properly seasoned manganin coil was measured at the center of the region of indifference for the bismuth II–III, thallium II–III, and barium I–II phase transformations in a hydrostatic system. The equilibrium pressures for these transformations were obtained from the relative resistance change of manganin which was calibrated with pressure by means of the mercury L–I and bismuth I–II transition pressures. Equilibrium pressures corrected to 25°C of 26.861±0.042, 36.569±0.153, and 56.273±0.521 kbar were determined for the bismuth II–III, thallium II–III, and barium I–II phase transformations, respectively. Only the barium I–II point deviated from the presently accepted high pressure scale. On the basis of the manganin pressure gauge, either the presently accepted value of the barium I–II point is too high by about 2.5 kbar or the pressure coefficient of manganin resistance changes sharply between 37 and 59 kbar. A two-point quadratic calibration curve was satisfactory for pressures to 37 kbar.

INTRODUCTION

The manganin pressure gauge is widely used in liquid hydrostatic pressure systems. The electrical resistance of a coil of manganin wire was employed as a pressure gauge by Bridgman[1] after the suggestion of Lisell.[2] Subsequent investigations[3–7] characterized the properties and seasoning techniques for manganin coil pressure gauges. The electrical resistance change with pressure was found to deviate from linearity between about 8 and 25 kbar and to have good stability after the proper seasoning. In his work to 30 kbar Bridgman employed the freezing point of mercury at 0°C and the bismuth I–II phase transformation for a two-point pressure calibration of the coil, while Babb[6] has suggested the melting curve of mercury.

In our laboratory, we have recently developed the capability of containing fluid hydrostatic pressures to 60 kbar in a hexahedral high-pressure apparatus.[8] In the present study the hydrostatic transformation pressures of bismuth II–III, thallium II–III, and barium I–II were measured according to a manganin resistance gauge. Because of the fundamental importance of these fixed points to the high pressure scale, the purpose of this investigation was to compare the thermodynamic pressure values determined in hydrostatic pressure apparatus to the currently accepted values for these transformations, particularly for thallium and barium.

For most high-pressure apparatus, particularly in the solid media systems, the direct calculation of pressure is not possible and a calibration based on fixed-point pressures is necessary. This type of calibration is based on knowing the pressure at which sharp polymorphic phase transformations occur, their occurrence being noted by abrupt changes in volume and/or electrical resistance of the calibrant. High-pressure calibration to 60 kbar is presently based upon the polymorphic transformation pressures of bismuth, thallium, and barium. With suitable corrections for friction and distortion of the pressure vessel in simple piston-cylinder devices, pressure can be directly calculated from applied force per unit piston area. In this way, Bridgman[3,9] determined the pressures at which these materials exhibited polymorphic transformations as detected by volume measurements. These fixed-point pressures as corrected by Kennedy[10] are currently accepted as calibration standards of the high-pressure scale although Bridgman only examined the bismuth I–II transformation in terms of a calibration point for high-pressure measurement.[3] The determinations for bismuth and thallium by Kennedy and La Mori[10] using rotating piston technique and volume measurements, and for thallium by Boyd and England[11] using electrical resistance measurements, are in close agreement with Bridgman's values. There is presently some uncertainty with regard to Bridgman's value of 58.8 kbar at 25°C for the barium point, however.

Supporting Bridgman's value is the measurement of 58.5 kbar recently reported by Vereshchagin et al.,[12] who used a rotating free-piston technique. Also, Drickamer's[13] value of 133 kbar for the iron transformation, which was based on the accepted value of the

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barium I–II point, agreed quite well with the shock measurements[14] at 131 kbar. It is questionable, however, if static equilibrium measurements can be compared with shock data. The shock measurements are known to have a high shear component, and corrections for sample hysteresis and temperature must be made that increase the uncertainty of the measurements.

In recent years, the experimental results of Stark and Jura,[15] Giardini and Samara[16] and others have indicated discrepancies between Bridgman's value for the transformation pressure of the bismuth III–V (upper bismuth point) and calibration curves based on his transformation pressure for the barium I–II point. Jeffery et al.,[17] using a tetrahedral press and x-ray techniques along with Decker's[18] theoretical equation of state for NaCl, have published results indicating that the accepted pressures for the barium I–II and the bismuth III–V transformations are about 10% and 20% high, respectively. They originally placed the barium I–II point at 53.3 kbar at 25°C, but a revised value of 54.4 kbar was subsequently obtained from more recent and more accurate NaCl compressibility data.[19] Although Kennedy and La Mori originally published a provisional value of 59.6 kbar for the barium I–II point,[10] recent and detailed measurements showed a lower value of 55.0 kbar for high-purity barium and 54.7 kbar for less pure barium.[20]

Most high-pressure measurements above 40 kbar depend upon a calibration curve based on the barium I–II point. The importance of this point for accurate high-pressure measurement is clearly evident, particularly for pressures greater than 60 kbar that require extrapolation of the calibration curve. The present investigation constitutes the first examination of the thallium and barium transformations with hydrostatic pressure and, therefore, provides an independent and valuable determination of the equilibrium pressure of these important calibration points on the high-pressure scale.

EXPERIMENTAL

Two experiments were carried out with a 2000-ton hexahedral press and a modification of the hydrostatic pressure cell originated by Barnett and Bosco.[8] The pressure transmitting medium was a 1:1-volume mixture of normal and isopentane which equalized pressures within the capsule by viscous flow in times of the order

of seconds at 50 kbar and of minutes at 60 kbar.[21] The cell was modified to increase its reliability and volume, and to increase the number of electrical leads from 6 to 10. In one experiment, the region of indifference of bismuth, thallium, and barium was measured, and in the other experiment the manganin coil was calibrated with mercury and bismuth.

For the first experiment, the sample assembly consisted of three calibration samples and a seasoned 80-Ω manganin coil (B. and S. gauge No. 26, cotton wrapped, from Driver–Harris Company). The calibration samples, each about 16 mm in length, were: single-crystal bismuth (1 mm sq, 99.9999% pure from Electronics Space Products Inc.), polycrystalline thallium (1 mm diam Standard Grade from Fisher Scientific Company), and polycrystalline barium (0.25 by 3 mm flat strip, 99% pure from A. D. Mackay Company). The manganin coil was initially temperature seasoned by alternately heating at 150°C and quenching with liquid nitrogen. The coil showed essentially no drift in resistance after a pressure treatment of 25 kbar for 40 days in a previous experiment. Four-lead measurements were employed to monitor the phase transformations and to measure the resistance of the manganin coil. A constant current of about 20 mA was maintained through each sample with a 6-V battery and a large external resistor. Separate leads were employed to measure the electrical potential of the samples on a Keithley model 150 A microvoltammeter, the output of which was recorded on a Varian model G-11 strip chart recorder. In this manner, a sensitivity to detect between 0.03% and 0.1% transformation was obtained. 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 mΩ, which for our coils was equivalent to about ±0.6 bar. Temperature was monitored by a mercury thermometer on the press.

On decreasing the pressure of the above experiment, a blowout occurred and the calibrants and manganin coil were lost. In another experiment, a second manganin coil, from the same spool and with about the same physical dimensions, characteristics, and seasoning cycle as the coil that was lost, was calibrated using the freezing point of mercury and the bismuth I–II phase transformations in a similar pressure cell at room temperature. The temperature in this run was monitored much more accurately using a calibrated chromel-alumel thermocouple that was bolted to the hydraulic cylinder of the press, which, in turn, made direct contact with the stainless steel pressure cell.

The experimental procedure for the determination of the equilibrium pressures was similar for each transformation. After the initiation of a transformation, pressure was reversed and adjusted until a condition was achieved in which there was a low fractional trans-

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TABLE I. Manganin relative resistance and pressures calculated according to Eq. (1) for the region of indifference of mercury, bismuth, thallium, and barium calibrants below 60 kbar.

Phase transformation	Temperature (°C)	Manganin ($\Delta R/R_0$)	Equilibrium pressure (kbar)	Width of region of indifference (kbar)
Mercury Liq-I (run No. 2)	20.36±0.15	0.027241	11.627±0.035[a]	...
Bismuth I–II (run No. 2)	20.34±0.15	0.058850	25.599±0.028[b]	0.035
Bismuth I–II (run No. 1)	23.0±0.5	0.058545	25.462±0.028	0.035
Bismuth II–III (run No. 1)	23.5±0.5	0.061733	26.899±0.042	0.040
Thalium II–III (run No. 1)	23.5±0.5	0.082806	36.533±0.153	0.006
Barium I–II (run No. 1)	22.0±0.5	0.124417	56.228±0.521	2.320

[a] Reference 22.
[b] Reference 10.

formation of one phase to the other at the same time that the sample contained about equal amounts of the two phases. After the pressure stabilized due to pyrophyllite flow around the pressure cell, the pressure was progressively moved through the equilibrium value in increments of about 25 bars or less. At each pressure the transformation rate was recorded for a period of 20–25 min. The constancy of pressure within 1 or 2 bars was verified by a pressure measurement at the beginning and at the end of each recorded trace of the transformation rate. The rate reversed as the pressure passed through the equilibrium value, but was invariant and essentially zero over a small pressure interval. The equilibrium pressure was then approached from the opposite pressure direction. Transformation rates were similarly measured at small increments of pressure until the transformation again reversed itself. Temperature drifts of the press of as much as 0.15°C/h limited the useful transformation rates to values greater than about $1 \times 10^{-4}\%$/sec. This general procedure was followed through at least two complete cycles for each phase transformation.

In all cases the manganin resistance was corrected to the temperature at which the atmospheric pressure resistance R_0 was measured. The temperature coefficient of the manganin resistance at ambient pressure and near room temperature was accurately determined by means of Mueller Bridge measurements of a coil situated in a well regulated and thermostated oil bath. The resistance/temperature plot was concave downward with a peak at about 25°C and a temperature coefficient of resistance of 3.8×10^{-6}/°C.

RESULTS

The relative resistance range in which the calibrant transformation rate was preceptibly constant, regardless of pressure direction, was noted as the width of the region of indifference. The equilibrium pressure was determined from the manganin relative resistance corresponding to the center of the region of indifference. The manganin relative resistance values and the pressures at the region of indifference of each calibrant are shown in Table I. All of the equilibrium pressures were obtained from a second order calibration curve in the form of Eq. (1),

$$P = A(\Delta R/R_0) + B(\Delta R/R_0)^2. \qquad (1)$$

The coefficients $A = 419.774 \pm 2.819$ kbar and $B = 258.509 \pm 56.322$ kbar were determined from the accepted pressures and the measured relative resistance change of the manganin coil for the mercury and bismuth transformations in Run No. 2. The equilibrium pressures listed in Table I for these two transformations are the accepted values obtained from the mercury melting curve of Zhokhovskii[22] and the bismuth I–II temperature coefficient of Bridgman.[3] The associated uncertainty in these equilibrium pressures was taken as the uncertainty stated in the literature value plus the uncertainty evaluated from the temperature coefficient of each transformation due to temperature uncertainties and variations during Run No. 2. These limits of uncertainty of the mercury and bismuth points were

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TABLE II. Comparison of the presently accepted equilibrium pressures of bismuth, thallium, and barium by Bridgman with the values determined from Run No. 1 on the basis of manganin and corrected to 25°C.

| Phase transformation | Equilibrium pressure | | Discrepancy $[P_A - P \text{ (Manganin)}]$ (kbars) |
	From manganin (kbars)	Accepted value[a] (kbars)	
Bismuth I–II	25.368±0.028	25.380±0.020	0.012
Bismuth II–III	26.861±0.042	26.965±0.180	0.104
Thallium II–III	36.569±0.153	36.690±0.100	0.121
Barium I–II	56.273±0.521	58.8	2.5

[a] Presently accepted pressure values taken from Refs. 9 and 10.

employed to determine the uncertainty of the coefficients A and B of the manganin calibration curve. For the remaining transformations in Table I, the listed uncertainty in the equilibrium pressure was calculated from the calibration curve. By comparison, sources of experimental errors such as the sensitivity and temperature correction of the manganin resistance measurement, the limit of detection of the equilibrium pressure within a finite pressure region of indifference, and systematic errors, were all considered negligible, since the calculated uncertainty of the equilibrium pressures were larger than the respective region of indifference, except for barium, which is discussed later. The values for the region of indifference in Table I were taken as the pressure interval between the experimental transformation rates of $\pm 3 \times 10^{-4}\%$/sec. The tabulated values for the region of indifference reflect only the uncertainty in the precision of the pressure measurement and do not include any uncertainty due to the calibration curve. For the mercury L–I transformation, the region of indifference was so small that it was completely masked by the temperature variations in the system. The temperature coefficient of bismuth,[3] thallium,[23] and barium,[20] were employed to adjust the equilibrium pressures of Run No. 1 to 25°C, and the comparison of these values with the presently accepted equilibrium pressures is shown in Table II.

Since the manganin coil from Run No. 1 was destroyed before it was calibrated, it was necessary to demonstrate that the same calibration curve applied to the two different manganin coils before confidence could be placed in the pressures obtained in Run No. 1. The validity of this procedure was revealed by the excellent agreement of the bismuth I–II point in Table II, since the accepted value was directly related to the bismuth calibration point of the manganin coil in Run No. 2. It was realized that the correspondence at the bismuth

I–II point for the two coils did not insure good correspondence over the whole pressure range, but our experience indicated that any differences would be well within the experimental error. It was therefore concluded that the calibration curve for the manganin coil of Run No. 1 insignificantly differed from the coil of Run No. 2.

DISCUSSION

The comparison of equilibrium pressures for the calibrant transformations in Table II showed that the manganin pressures were all lower than Bridgman's values. The discrepancies of 0.104 kbar for bismuth II–III and 0.121 kbar for thallium II–III were in good agreement and within the experimental error. The presently accepted value of the barium I–II point was clearly outside the uncertainty of the manganin calibration curve, however.

The pentane–isopentane pressure medium evidently did not solidify within the pressure range to 60 kbar as had been previously supposed by Bridgman.[24] It has been shown that this pressure medium is still relatively fluid in this pressure range.[21] Even if the manganin coil had been strained as a result of solidification or viscous flow, the measured equilibrium pressures shown in Table II would be high and the discrepancy with the accepted values would be even greater.

Alternative manganin calibration curves were investigated in an attempt to resolve the discrepancy of the barium I–II point. Quadratic equations of the form of Eq. (1) were tried, but with different coefficients A and B determined from various combinations of calibration points, e.g., Hg–Tl, Bi–Tl, Hg–Ba, Bi–Ba, and Tl–Ba. It was found that if the barium I–II point was excluded, the data were adequately fitted to a quadratic equation. In these cases, the presently accepted barium point was still higher and was outside the uncertainty

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of the manganin curve. All attempts to fit a quadratic equation by forcing agreement with the barium point yielded results in which the calibration curve deviated from the accepted pressures for one or more of the other calibrations points by amounts large in comparison to their error flag.

It is known that the manganin pressure gauge deviates from linearity between about 8 and 25 kbar. Since it was not certain that the quadratic relationship between pressure and the resistance of manganin would persist in the pressure range from 25 to 60 kbar, a third order calibration equation of the form of Eq. (2) was investigated,

$$P = C(\Delta R/R_0) + D(\Delta R/R_0)^2 + E(\Delta R/R_0)^3. \quad (2)$$

The mercury L–I, bismuth I–II, and thallium II–III points were employed to determine the coefficients C, D, and E, which were found to have the values $419.8\pm$ 7.2, 259.2 ± 291.3, and -4.7 ± 2739.0 kbar, respectively. The barium I–II equilibrium pressure was found to be 56.36 ± 1.66 kbar, which was again lower, by about 2.4 kbar, than Bridgman's value, which was still outside the uncertainty of the calibration curve. Third order equations of the form of Eq. (2) were investigated with different coefficients determined by forcing agreement with the barium I–II point. In all cases, untenable coefficients were obtained—second-order coefficients changed sign and there was an order of magnitude uncertainty in second and third order coefficients. Even in Eq. (2) the uncertainty of the second- and third-order coefficients was unusually large due to the relatively large uncertainty in the thallium point. It was noted, however, that the fit for the third-order equation yielded an equation in which the contribution from the third-order term was insignificant.

On the basis of the above discussion it was evident that a two-point quadratic calibration curve was satisfactory for pressures to 37 kbar with a manganin pressure gauge. All of the manganin calibration curves indicated that the presently accepted value of 58.8 kbar for the barium I–II point is high by about 2.5 kbar. For the presently accepted value of this calibration point to be correct, the only alternative interpretation of the present data requires that the manganin resistance–pressure curve change sharply above 37 kbar. Based on this data, therefore, it was concluded that for pressures above 37 kbar either the accepted equilibrium pressure for the barium I–II transformation is high by about 2.5 kbar or the curvature of the manganin calibration curve changes quite sharply between 37 and 58.8 kbar. In this pressure range, there is a deviation of about 0.2%/kbar between the currently accepted calibration curve and the quadratic manganin relationship. A lower value for the barium point is in agreement with both Jeffery et al.,[17] and Kennedy,[20] although our result based on manganin is in closer agreement with the value of Kennedy.

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