I. INTRODUCTION

In recent years powder x-ray diffraction experiments to 300 GPa have been successfully performed using a diamond anvil cell (DAC) and a third generation synchrotron as a source of the primary beam. In experiments at such high pressures, equations of state (EoS) of elemental metals are commonly used as pressure markers. The metals proposed for the pressure scale are Pt, Au, Ag, Cu, and Al. In particular, the EoS of Pt has been well studied to 660 GPa with a two-stage gas gun and by a first-principle theoretical treatment. These metals, except Al, have relatively low compressibility, limiting the precision of pressure determination. Further, the pressure scales provided by different materials remain to be compared.

Bismuth undergoes a number of pressure-induced structural phase transitions in a sequence: rhombohedral (R) → distorted simple cubic (dsc) → body-centered tetragonal (bct) → body-centered cubic (bcc). These transitions have been used as fixed points for pressure calibration at room temperature. In an earlier study using the Au pressure scale, the bcc Bi was found to be stable up to 145 GPa, with a high compressibility, limiting the precision of pressure determination. Further, the pressure scales provided by different materials remain to be compared.

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Because of its high compressibility, bcc Bi is a good choice for a pressure marker that will offer improved precision in pressure measurement. The bcc-Bi was found to be stable up to 222 GPa, the highest pressure reached in this study, and measure the EoS on the Pt pressure scale. A fit of the Vinet EoS to the volume compression data gave \( B_0 = 35.22 \) (19) GPa, \( B'_0 = 6.303(18) \), and 1 atm atomic volume \( V_1 = 31.60(4) \) Å³. Because of the high compressibility, the use of bcc-Bi as a pressure marker is expected to give improved precision in pressure measurement. The Pt and Au pressure scales were compared up to 145 GPa. The Au pressure scale gave lower pressure than the Pt pressure scale. The deviation between the two scales became noticeable at ~30 GPa and diverged with increasing pressure, reaching ~60 GPa at 222 GPa. A fit of the Vinet EoS to Au compression data on the Pt pressure scale gave \( B_0 = 166.34(77) \) GPa, and \( B'_0 = 6.244(33) \). © 2002 American Institute of Physics. [DOI: 10.1063/1.1515378]
III. RESULTS AND DISCUSSIONS

A. General

Figures 1(a) and 1(b) show typical diffraction patterns in two sets of experiments. The observed reflections were sharp without noticeable asymmetry and the number ranged between 4 and 6 for each sample. The lattice parameter \( a_{(hkl)} \) was calculated from each measured \( d \) spacing \( d_{(hkl)} \). The standard deviation in the lattice parameter \( \sigma(a) \) calculated from \( a_{(hkl)} \) values for each run was small for Bi and Pt ranging between 0.0002 and 0.0015 (Fig. 2). Gold data showed a larger standard deviation that ranged from 0.0008 to 0.0028. The bcc Bi was found to be stable up to 222 GPa, the highest pressure reached in the present study. At 222 GPa, \( V/V_0 = 0.4735(10) \). This observation is consistent with the findings of a theoretical study\(^\text{17} \) that predicted the stability of bcc Bi up to a compression of \( V/V_0 = 0.4 \).

B. Equation of state of bcc Bi

Figure 3 shows the measured atomic volumes of bcc Bi as a function of pressure on the Pt scale,\(^1\) together with the data from an earlier study\(^\text{12} \) conducted using the MoK\(\alpha\) radiation from a rotating-anode x-ray generator and the Au pressure scale.\(^2\) The present data from Bi-Pt-Au and Bi-Pt-Au...
The pressure by Holmes' Pt scale. The pressures estimated from the ruby-line shift below ~60 GPa lie between the Pt scale and the Au scale. The results of fitting the Vinet and Birch–Murnaghan (BM) equations to the volume compression data of Au on the Pt pressure scale are shown in Table I.

A comparison of the Pt and Au scales based on data in Fig. 4 depends on the assumptions that the samples of different materials placed together in a DAC experience equal pressures. Further, the pressure on the sample has been assumed to be hydrostatic while the pressure is known to non-hydrostatic at such high pressures. The influence of these assumptions on the comparison of the Pt and Au scales is considered in Sec. III D. It may be noted that the comparison between two Pt scales or two Au scales is independent of the present experimental data.

D. Analysis of stress state

The stress state of the sample compressed in a DAC is generally non-hydrostatic. The stress state at the center of the sample possesses an axial symmetry and is described by the axial (σ\(_{\alpha}\)) and radial (σ\(_{\rho}\)) components. The equivalent hydrostatic pressure is given by

\[ \sigma_{H} = (\sigma_{\alpha} + 2\sigma_{\rho})/3. \]

Criteria for yielding of the sample material under compression suggests the following relation:

\[ \tau = (\sigma_{3} - \sigma_{1})/2 = \tau_{y}, \]  

(2)

for different materials placed together in a DAC experience equal pressures. Further, the pressure on the sample has been assumed to be hydrostatic while the pressure is known to non-hydrostatic at such high pressures. The influence of these assumptions on the comparison of the Pt and Au scales is considered in Sec. III D. It may be noted that the comparison between two Pt scales or two Au scales is independent of the present experimental data.

C. Comparison of Au and Pt pressure scales

For a comparison of the Pt and Au pressure scales, we plot in Fig. 4 the pressures calculated from volume compression data of Au using the Jamieson's scale and the Anderson scale against the pressure obtained from the volume compression of Pt using the Holmes' scale. The pressures estimated from the Jamieson's Pt scale are also given for comparison. The x = y line helps in visualizing the deviation of the various pressure scales from the Pt scale. The pressure obtained from the Jamieson's Pt scale is ~3% smaller than the pressure from the Holmes' scale in the entire pressure range. The discrepancy between the Jamieson's Au scale and the Holmes' Pt scale becomes noticeable at ~30 GPa and increases with increasing pressure reaching ~20 GPa at 150 GPa. The Anderson's Au scale shows a marginally better agreement with the Holmes' Pt scale. The pressures estimated from the ruby-line shift below ~60 GPa lie between the Pt scale and the Au scale. The results of fitting the Vinet and Birch–Murnaghan (BM) equations to the volume compression data of Au on the Pt pressure scale are shown in Table I.

![FIG. 4. A comparison of different pressure scales. The error bar is of the size of the symbols.](image-url)
where $\sigma_F$ is the yield stress and $r$ the shear strength of the sample material at $\sigma_F$. Equations (1) and (2) give

$$\sigma_F = \sigma_3 - 2r/3. \tag{3}$$

Consider the compression of a mixture of the sample and the pressure marker. Quite generally, the sample and the pressure marker develop stress states in accordance with Eqs. (1) and (2) with appropriate values of $t$. Some assumption connecting the stress states in the two has to be made to derive the sample pressure from the pressure computed using the measured volume compression and the EoS of the marker. Assumption that the marker and the sample experience equal pressures (continuity of pressure) is most likely to be valid when the experiments are done on intimate mixture of the sample and the marker, both in powder form. In the present experiments, the sample and the marker are in the form of foils. This configuration favors the continuity of $\sigma_3$ across the crystallites of the sample and the marker. Equation (3) suggests the following relation between the pressures in the sample and the marker:

$$\sigma_F(t) = \sigma(m) + 2[t(m) - t(t)]/3. \tag{4}$$

The second term on the right-hand side of Eq. (4) gives the difference between the sample pressures calculated assuming the $\sigma_3$ continuity and the $\sigma_F$ continuity.

We now examine the effect of the nonhydrostatic stress on the volume compression data. The measured rf-spacing under nonhydrostatic compression is given by

$$d_{n}(hkl) = d_{p}(hkl)[1 + (1 - 3\cos^2\phi)Q(hkl)], \tag{5}$$

where $d_{p}(hkl)$ is the d spacing under $\sigma_F$, $\phi$ is the angle between the diffracting plane normal and the load axis of DAC, and $Q(hkl)$ is a term containing the single-crystal elastic compliances and $t$. For the cubic system

$$Q(hkl) = \{\alpha/3\}[2G_{\mu}^2(hkl)^{-1} - (1 - \alpha^{-1})(2G_{\nu})^{-1}], \tag{6}$$

where

$$[2G_{\mu}^2(hkl)^{-1} - 3S^2(hkl)]^{-1} = [S^2 - 3S \Sigma(hkl)]^{-1},$$

$$S = S_{11} - S_{12} - S_{44}^*,$$

and

$$(2G_{\nu})^{-1} = S(S_{11} - S_{12} - 3S \Sigma(hkl)) + S_{44}^*.$$ \tag{7}$$

The term $\alpha$ lies between 0 and 1. Recently it was shown \[^{21}\] that for the cubic system $\sigma_F(hkl)$ versus $3(1 - 3\cos^2\phi)Q(hkl)$ plot (gamma plot) for the data recorded under the conventional DAC geometry can be approximated very closely to a straight line with a slope and an intercept, respectively,

$$M_1 = -a \sigma_F(\alpha S/3), \tag{11}$$

and

$$M_0 = a \sigma_F[1 + (\alpha/3)[1 - 3\cos^2\phi]x[(S_{11} - S_{12}) - (1 - \alpha^{-1})(2G_{\nu})^{-1}]]. \tag{12}$$

A very good estimate of $\alpha S$ can be made from such plots by using the relation

$$\alpha S = 3M_1/M_0. \tag{13}$$

In the following discussion we use $\alpha = 1$. This choice for $\alpha$ gives the lowest estimate of the nonhydrostatic compression effect. The neglect of the nonhydrostatic compression effect results in an underestimation of the volume strain by

$$\Delta \epsilon_n(V) = 3[(1 - 3\cos^2\phi)Q(hkl)] \times (\sigma_F/\sigma_0)^3. \tag{14}$$

where $\{ \}$ denotes the average value for all the observed reflections. The gamma plots for the Au data showed a good straight-line trend and $\Delta \epsilon_n$ values were determined using Eq. (13). The $\Delta \epsilon_n$ values at high pressure were estimated using Birch equations \[^{22}\] and the single-crystal elasticity data. \[^{23}\] The $t$ values obtained from these data are shown in Fig. (5a). These values are in good agreement with the $t$ values observed in earlier studies discussed elsewhere. \[^{24}\] A fair degree of correlation is found between $t$ and $\sigma_F(a)$. This is expected as the neglect of the nonhydrostatic compression effect contributes to $\sigma_F(a)$. On correcting $\sigma_F(hkl)$ for the nonhydrostatic compression effect using the procedure suggested
earlier, $\sigma(a)$ reduces considerably. The volume strain is under-estimated by an amount given by Eq. (14). The data in Figs. 5(a) and 5(b) suggest that $t = 0.40 \pm 0.06$ GPa and $\Delta P = 2.0 \pm 0.3$ GPa at 150 GPa. Extrapolations of these data using a logarithmic equation suggest that $t = 0.5 \pm 0.07$ GPa and the resulting $\Delta P = 2.7 \pm 0.3$ GPa at 222 GPa. A linear extrapolation of the data above 50 GPa gives practically the same result.

The gamma plots for Pt data from the Bi-Pt-Au set of experiments did not show straight-line trends ($R^2 \leq 0.4$). Such a situation can arise if the slope of the line is small in comparison with the standard deviation in the lattice parameter. The lack of the straight-line trend in the gamma plot does not always imply the hydrostatic stress state in the sample. A small (zero) slope indicates nearly hydrostatic (hydrodynamic) pressure, while a large (nonzero) slope indicates nonhydrostatic pressure. However, the stress state may be significantly nonhydrostatic if a small (zero) slope arises from a small (zero) $S$. The estimate of $t$ can be made in such a case by making use of the fact that $t$ scales with the shear modulus of the sample material. The 1 atm shear modulus of Pt is 63 GPa in comparison with 28 GPa for Au. Ignoring the influence on $t$ of the presence of Au and Bi in the cell, for Pt is expected to be $\sim 2.2$ times larger than the value for Au. Since $S = 0.02204$ (GPa)$^{-1}$ for Pt, it is small (zero). The stress state is assumed then Eq. 4 suggests that the $y$ values derived. These are the same runs wherein the Pt data gave good gamma plots. The sign of the slopes in these plots suggests that $S$ is positive for bcc Ba. A detailed analysis of the bcc Bi data is not possible as the elastic moduli and the pressure derivatives of bcc Ba are not known. An extrapolation using the Birch equation suggests that, at any pressure below 250 GPa, the bulk modulus of bcc Ba remains less than the bulk modulus of Au. Assuming, though not justifiably, that the Poisson’s ratios for bcc Ba and Au are equal, the shear modulus of bcc Ba at any pressure below 250 GPa is expected to be less than that of Au. This would suggest that the magnitude of $t$ in bcc Ba is not very different from that in Au.

E. Systematic errors in pressure

The two factors discussed in the preceding section introduce systematic errors in the pressure estimation. The neglect of the nonhydrostatic compression effect results in an underestimation of pressure. A limited analysis suggests that the magnitude of error in all the samples is nearly equal and increases with increasing pressure, reaching $\sim 3$ GPa at 150 GPa. Thus, $\sigma_P \sim 2\%$ larger than the pressure calculated from the measured volume strain and the EoS. The correction for the nonhydrostatic effect does not alter Fig. 4 significantly which is constructed assuming the pressure continuity between Pt and Au samples. On the other hand, if the continuity of $\sigma_P$ is assumed then Eq. 4 suggests that the $y$ coordinate of the Au datum at $v = 150$ GPa in Fig. 4 will increase by $\sim 5$ GPa and $y$ coordinates of other points will increase proportionately. This will bring the line for Au closer to the $x-y$ line but not enough to bring about a good agreement between the Pt and Au pressure derivatives. A good agreement between the two scales requires an increase of $\sim 20$ GPa in the pressure scale. Such a situation can arise if the slope of the line is small in comparison with the standard deviation in the lattice parameter. The lack of the straight-line trend in the gamma plot does not always imply the hydrostatic stress state in the sample. A small (zero) slope indicates nearly hydrostatic (hydrodynamic) pressure, while a large (nonzero) slope indicates nonhydrostatic pressure. However, the stress state may be significantly nonhydrostatic if a small (zero) slope arises from a small (zero) $S$. The estimate of $t$ can be made in such a case by making use of the fact that $t$ scales with the shear modulus of the sample material. The 1 atm shear modulus of Pt is 63 GPa in comparison with 28 GPa for Au. Ignoring the influence on $t$ of the presence of Au and Bi in the cell, for Pt is expected to be $\sim 2.2$ times larger than the value for Au. Since $S = 0.02204$ (GPa)$^{-1}$ for Pt, it is small (zero). The stress state is assumed then Eq. 4 suggests that the $y$ values derived. These are the same runs wherein the Pt data gave good gamma plots. The sign of the slopes in these plots suggests that $S$ is positive for bcc Ba. A detailed analysis of the bcc Bi data is not possible as the elastic moduli and the pressure derivatives of bcc Ba are not known. An extrapolation using the Birch equation suggests that, at any pressure below 250 GPa, the bulk modulus of bcc Ba remains less than the bulk modulus of Au. Assuming, though not justifiably, that the Poisson’s ratios for bcc Ba and Au are equal, the shear modulus of bcc Ba at any pressure below 250 GPa is expected to be less than that of Au. This would suggest that the magnitude of $t$ in bcc Ba is not very different from that in Au.

F. Random errors in pressure

In the Bi-Pt-Au runs the highest pressure as determined from the volume compression of Pt was $145.2 \pm 0.8$ and $150.5 \pm 0.22$ GPa from the bcc Bi compression data. The errors indicated correspond to $\sigma(a)$. The highest pressure in the Bi-Pt runs was estimated to be $222.0 \pm 1.0$ GPa from the bcc Bi compression data.
The Jamieson's pressure scale are consistently lower than the corresponding values estimated from Pt data. The highest pressure is estimated to be 128.9 ± 1.5 GPa. Large error in pressure arises from the volume--compression measurements being 0.1% at low pressure and 0.5% at the highest pressure. The Au pressure scale systematically underestimates pressure in comparison with the Pt pressure scale. Because of similar considerations the Pt pressure scale has been preferred in a recent study on the EoS of stishovite.

IV. SUMMARY

The bcc Bi is stable up to the highest pressure (222 GPa) reached in this study. Because of its high compressibility, bcc Bi promises to offer high precision in pressure measurement. The uncertainty introduced by the errors in volume--compression measurements being 0.1% at low pressure and 0.5% at the highest pressure. The Au pressure scale has been preferred in a recent study on the EoS of stishovite.

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