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bcc arsenic at 111 GPa: An x-ray structural study

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The crystal structure of arsenic has been studied in a diamond anvil cell by energy dispersive x-ray diffraction with a synchrotron source to 122 GPa, where $V/V_0 = 0.513$. The phase sequence on compression is: $\alpha \rightarrow$ sc $\rightarrow$ As(III) $\rightarrow$ bcc. As(III) may have the α-Np structure. The equilibrium transformation pressures, P_e, between sc/As(III) and As(III)/bcc are 48 ± 11 and 97 ± 14 GPa, respectively. There is no measurable volume discontinuity between the phases. The equation of state was measured and the BE2 parameters are in good agreement with literature values.

I. INTRODUCTION

The foundation of modern semiconductor technology is a wealth of fundamental knowledge about Si, Ge, and GaAs. This includes the crystal structure vs pressure relations. Si has been compressed to 250 GPa, Ge and GaAs to over 100 GPa.[1–3] It is logical to extend this scale of investigation to the components Ga and As because they are the building blocks of the increasing important ternary systems such as $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$. We have performed a high pressure diamond anvil cell (DAC) experiment on arsenic to determine the transition pressure to an expected bcc phase, and extend the room temperature phase diagram to over 100 GPa.

Pressure-induced structural phase transitions of the group-V elements are also of intrinsic interest. Bi and Sb transform to bcc at pressures of 7.7 (Ref. 4) and 28 GPa (Ref. 5), respectively. It is expected that As will also transform to the bcc structure at high pressure. At room temperature and pressure As has the α or rh(2) structure.[6] The α to sc transition was first reported at $31 < P_t < 37$ GPa,[7] and more recently as $P_t = 25 \pm 1$ GPa.[8] The 45 GPa work of Kikegawa and Iwasaki was the highest experimental pressure reached on As before this study.[7] There has been one theoretical study predicting a sc to bcc transition at 70.9 GPa.[9] Although there have been many other calculations on As, they have concentrated on the $A7$ (or α) and sc phases.[10–16]

II. EXPERIMENT

The sample was a commercial As powder of 99.99% purity and −325 mesh. A DAC of the controlled displacement type was used as the pressure vessel.[17] Single beveled diamond anvils with 100 μm flats were used. The sample chamber was a 50 μm diameter hole drilled in a rhenium gasket pre-indented to 29 μm thickness. A small flake of gold powder to be used as a pressure marker was placed on the top of the sample chamber after loading and compaction of the As powder into the hole. No pressure medium was used; the state of stress in the sample was nonhydrostatic.

Energy dispersive x-ray diffraction (EDXD) experiments were performed at the Cornell High Energy Synchrotron Source (CHESS) to measure the crystal structure of the As sample. Further details of the experimental techniques and apparatus are given in Refs. 17, 18. The size of the incident x-ray beam into the DAC was collimated to 20 μm × 20 μm with a set of tungsten apertures for pressures up to 100 GPa on up-loading, and to 10 μm × 10 μm for the remainder of the experiment. These apertures and other modifications for 10^2 GPa scale EDXD work are described in Refs. 19, 20.

The diffraction angle was calibrated with a gold foil; 2θ angles of 16.018° and 16.923° were used. The typical collection time for a spectrum was over 0.5 h. The pressure for each spectrum was determined from the isothermal equation of state (EOS) of gold by Jamieson *et al.*[21] from the x-ray measured gold cell volume. The sample cell volume was also obtained from each x-ray spectrum in the α, sc, As(III), and bcc phases.

III. RESULTS

Diffractometer analysis of the as-purchased powder showed a mixture of α and amorphous phases. After compaction in the DAC only α remained, although there were a few extra diffraction lines attributed to defect-type structures. These extra lines decreased in intensity with increasing pressure. The 24 GPa spectrum was entirely α. At the next pressure step to 37 GPa the sample was entirely in the sc phase. This is consistent with the reported $\alpha \rightarrow$ sc transition pressure of 25 ± 1 GPa of Ref. 8.

A diffraction spectrum of As in the sc phase at 37 GPa is shown in Fig. 1, and a list of the calculated and observed d spacings and integrated diffraction intensities is displayed in Table I. The agreement of the d spacings is excellent, but the integrated intensities have only fair agreement. This is typical for DAC EDXD experiments in which the sample is also the pressure medium so that deformation under loading often exacerbates texturing and preferred orientation to give a less than ideal powder diffraction pattern. This should be compared to a case where a quasihydrostatic pressure was obtained by

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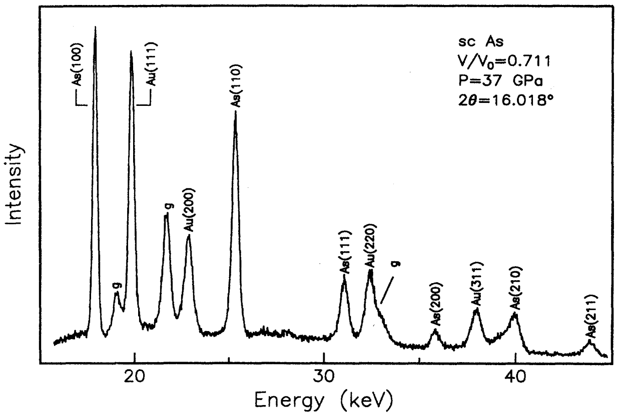

FIG. 1. EDXD diffraction spectra of As in the simple cubic structure. Peaks labeled As, Au, and *g* are from the arsenic sample, gold pressure marker, and rhenium gasket, respectively.

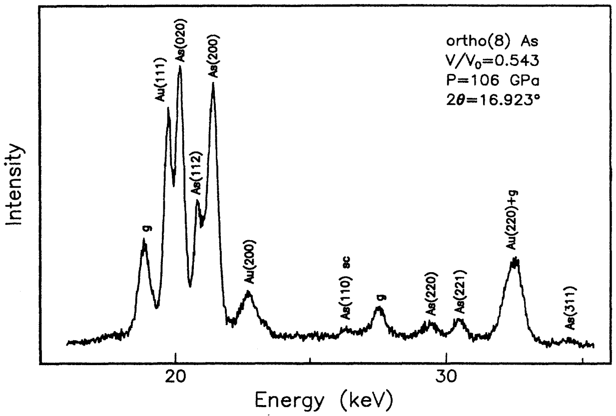

FIG. 2. EDXD diffraction spectra of As in the intermediate As(III) phase, labeled ortho8, structure. Peaks labeled As, Au, and *g* are from the arsenic sample, gold pressure marker, and rhenium gasket, respectively.

use of a pressure medium (see Table I of Ref. 17). The small area of the solid state detector also provides poor averaging over the powder diffraction rings, sampling less than 1% of the circumference.

The As remained in the sc phase to at least 47 GPa, consistent with Ref. 7. Upon further loading to 59 GPa the diffraction spectrum was dramatically different in the pattern and intensities of the sample diffraction lines, indicating a structural phase transformation. This new phase is designated As(III) and a spectrum at 106 GPa is displayed in Fig. 2. The region between 18 and 24 keV contains diffraction from the As sample, gold pressure marker, and Re gasket. Furthermore, the atomic volumes of Re and As are quite close in the pressure range of the As(III) phase. Nevertheless, we have tentatively identified As(III) to have the α-Np crystal structure, an orthorhombic lattice with an eight-atom basis. This structure may be viewed as a considerably distorted body-centered form.[6]

This intermediate As(III) phase continued upon further loading to 106 GPa. Upon further loading to 111 GPa the diffraction pattern was a mixture of As(III) and bcc As. The spectrum at 111 GPa had a sharp peak corresponding to the (211) of bcc which was not present at the previous pressure of 106 GPa. Figure 3 shows the bcc As phase at 122 GPa, the highest pressure of this study. A list of the calculated and observed d spacings and integrated diffraction intensities for the bcc phase at 122 GPa is displayed in Table II. The agreement of the d spacings is excellent, but the integrated intensities have only fair agreement, similar to the sc case discussed above. We note that neptunium transforms at high temperature to a bcc phase.[6]

TABLE I. List of the observed and calculated interplanar spacings (d) and intensities (I) of As in the simple cubic structure at 37 GPa. The calculation of relative intensities is discussed in Ref. 17.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(100)	2.482	2.483	100.0	76.5
(110)	1.756	1.755	97.9	100.0
(111)	1.433	1.433	29.3	35.8
(200)	1.241	1.241	8.8	14.8
(210)	1.113	1.110	23.3	34.2
(211)	1.013	1.013	7.9	20.6

A series of down-loading spectra were then taken, and combined with the up-loading data we calculate the equilibrium transformation pressures P_e between sc/As(III) and As(III)/bcc to be 48 ± 11 and 97 ± 14 GPa, respectively. Here P_e is estimated as $P_e = (1/2)(P_\uparrow + P_\downarrow)$, where $P_\uparrow$, and $P_\downarrow$ are the respective up-loading and down-loading transformation pressures between the phases.

The equation of state (EOS) for the α, sc, As(III), and bcc phases is plotted in Fig. 4. These data were fitted to the two-parameter Birch EOS (BE2):

$$P = \frac{3}{2}B_0(x^{7/3} - x^{5/3})\left[1 + \frac{3}{4}(B_0' - 4)(x^{2/3} - 1)\right], \qquad (1)$$

where $x = V_0/V$, B_0 is the isothermal bulk modu-

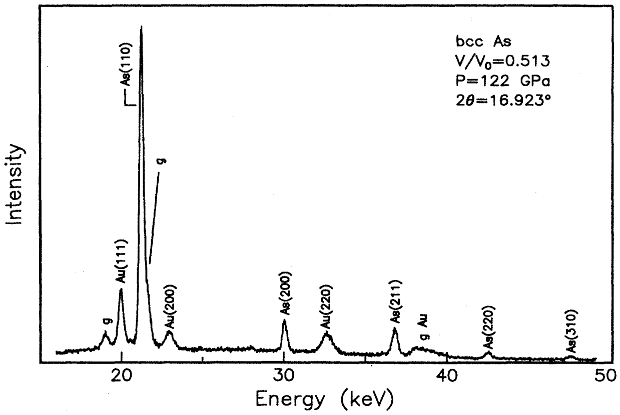

FIG. 3. EDXD diffraction spectra of As in the bcc structure. Peaks labeled As, Au, and *g* are from the arsenic sample, gold pressure marker, and rhenium gasket, respectively.

TABLE II. List of the observed and calculated interplanar spacings (d) and intensities (I) of As in the body-centered-cubic structure at 122 GPa. The calculation of relative intensities is discussed in Ref. 17.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(110)	1.984	1.983	100.0	100.0
(200)	1.402	1.403	13.3	21.8
(211)	1.145	1.145	13.5	37.3
(220)	0.992	0.992	3.4	8.7
(310)	0.887	0.887	2.3	8.8

lus at zero pressure, and B_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure.[22] The resulting values of the two parameters are $B_0 = 56 \pm 3$ GPa and $B_0' = 3.7 \pm 0.2$, in good agreement with the most recently measured values of $B_0 = 58 \pm 4$ GPa, $B_0' = 3.3 \pm 0.4$, measured to 30 GPa.[8]

Beister *et al.* have also determined that there is no detectable volume discontinuity between the α and sc phases to the limit of their experimental uncertainty of 0.5% in $\Delta V/V_0$.[8] Our EOS data are too sparse to make such quantitative statements about $\Delta V/V_0$ for the sc to As(III) transition. However, the fact that our B_0 and B_0' agree well with the values of Beister *et al.* is qualitative evidence that any such volume discontinuity is less than a few percent. Our spectrum at 111 GPa indexed as a mixture of As(III) and bcc with the same atomic volume within the experimental error of less than 1%.

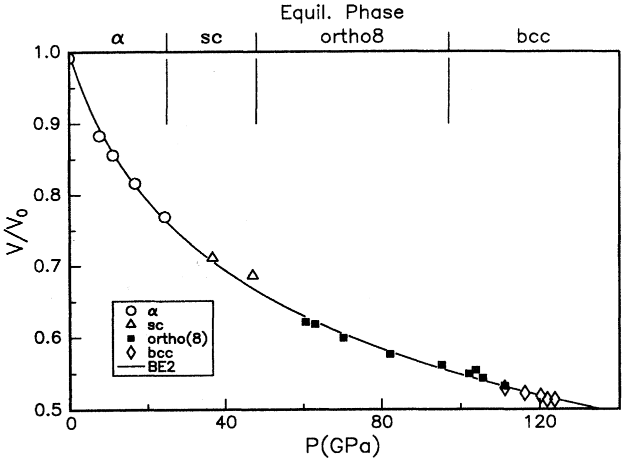

FIG. 4. Equation of state for As. V/V_0 is the measured atomic volume divided by the zero pressure atomic volume. Also shown are the regions of phase equilibrium vs pressure; the As(III) phase is labeled ortho8. The BE2 fit has parameter values of $B_0 = 56(3)$ GPa and $B_0' = 3.7(0.2)$.

IV. DISCUSSION

Our measured $P_e = 97 \pm 14$ for As(III)/bcc differs considerably from the value of 70.9 GPa predicted by Sasaki, Shindo, and Niizeki (SSN).[9] However, SSN were calculating the P_e between the sc and bcc phases, not between As(III) and bcc, and so their value for that transition may indeed be correct. This interpretation is consistent with the P_e for As(III)/bcc being larger than the P_e between the sc and bcc phases.

The observed phase sequence for As is $\alpha \rightarrow$ sc $\rightarrow$As(III)$\rightarrow$bcc. This is in agreement with the general sequence of structures (with variations for each element) for the group-V elements suggested by Young: diatomic $\rightarrow$ covalent $\rightarrow$ rh(2) or sc(1) $\rightarrow$ complex $\rightarrow$ bcc.[23] Bi, Sb, and now As all have complicated phases between rh(2) and/or sc and bcc. This suggests that phosphorus may also have a more complicated phase between the high pressure sc and a higher pressure bcc phase. Experimentally, the sc phase of P remains stable to 70 GPa, with indications of another transformation in the 80–100 GPa range.[24]

The transition pressures P_t, to bcc for the sequence Bi, Sb, As are 7.7, 28, and 97 GPa; i.e., P_t is 3.5× the preceding member of the column. Based on this empirical observation we speculate that P_t for phosphorus to bcc is 340 GPa. A pseudopotential calculation by Sasaki *et al.* predicts a (sc) to bcc transition pressure of 135 GPa for P.[27] However, since it is likely that there is an intermediate phase between sc and bcc P, the calculated P_t of Sasaki *et al.* is more probably a lower bound on P_t.

It would be interesting to perform further experiments on As(III) to confirm and refine its crystal structure. This may be possible with DAC synchrotron angle dispersive x-ray diffraction experiments, similar to some of the recent work of Nelmes and co-workers.[25,26]

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