

Nonexistence of the Diatomic β -Tin Structure

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(Received 1 July 1997)

Many high-pressure phases of the III-V and II-VI semiconductors have been believed to have the diatomic equivalent of the (tetragonal) β -tin structure. Recent work has shown this to be incorrect in several cases. It is now shown that the same is true of all the remaining possibilities—AlSb, HgSe, InP, and GaP. The phases concerned all have orthorhombic structures of the $Cmcm$ type. The apparent nonexistence of the β -tin structure has important implications for the structural systematics. [S0031-9007(97)04474-8]

PACS numbers: 61.50.Ks, 62.50.+p

The start of structural studies of group IV, III-V, and II-VI semiconductors under pressure was marked by Jamieson's discovery in 1963 [1] that the first transition in silicon and germanium is to the tetragonal β -tin structure previously known only in elemental tin. Very soon afterwards, he carried out the first diffraction studies of the high-pressure transitions in AlSb, GaSb, and InSb, which have the cubic zinc-blende structure at ambient pressure [2]. He concluded that they all transform to a β -tin-like structure in which the metal and Sb atoms are probably ordered onto different sites—that is to say, with the metal atoms at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the Sb atoms at $(0, \frac{1}{2}, \Delta = \frac{1}{4})$ and $(\frac{1}{2}, 0, \Delta + \frac{1}{2} = \frac{3}{4})$. This is generally referred to as simply “ β -tin,” but where it is necessary to make the distinction we will call this the “diatomic β -tin” structure (henceforth d - β -tin) as against the true, monatomic β -tin structure (m - β -tin) of Si and Ge. Site-disordered binary systems can also be regarded as having the m - β -tin structure.

Subsequent work confirmed the β -tin phase in AlSb [3], GaSb [4], and InSb [5], and revealed the same zinc-blende (ZB) to β -tin transition also in GaP [6]. In his pioneering work, Jamieson [2] found different behavior in InP and InAs, with the ZB phase transforming to an NaCl structure. This was later shown to be true also of all the II-VI systems, except the Hg chalcogenides—where there is the NaCl phase but it is preceded by a cinnabar phase [7]—and ZnTe [8]. However, when the NaCl phase was taken through a further transition at higher pressures, it was found in nearly all cases to transform to β -tin—in InP [9], InAs [10], CdTe [11], and probably HgSe and HgTe [7]. The majority of III-V and II-VI systems thus appeared to exhibit a transition from fourfold coordinated ZB directly to quasisixfold coordinated β -tin, or first to NaCl and then to β -tin. This perception has steadily grown since Jamieson's early work, and β -tin has come to occupy a central role in the high-pressure structural systematics of the III-V and II-VI semiconductors.

However, recent results on GaSb [12], InAs [13], InSb [14], CdTe [15], and HgTe [16] have shown that their supposed β -tin phases do not, in fact, have that structure. This is very surprising, and suggests the whole nature of

the systematics may be in question. We have therefore undertaken studies of all the remaining possibilities—in AlSb, HgSe, InP, and GaP—and can now show conclusively that their supposed β -tin phases are also incorrect interpretations. In this Letter, we present these results and discuss the remarkable conclusion that then follows: *there is, as yet, no evidence for the d - β -tin structure in any of the III-V or II-VI systems*—despite much theoretical work apparently establishing its stability.

First, we will rehearse the already established new results on GaSb, InSb, CdTe, HgTe, and InAs. They were all obtained following the introduction of angle-dispersive x-ray (ADX) powder diffraction using an image-plate detector [17], which yields data of considerably greater resolution and sensitivity than were previously available.

GaSb was long believed to transform from ZB to β -tin at ~ 7 GPa [4]. Image-plate data revealed several features not consistent with β -tin [12] that are well fitted by a site-disordered (and thus quasimonatomic) orthorhombic structure, with $Imma$ symmetry, found also in Si and Ge [18]. This is a distorted β -tin structure, in which the z -coordinate, Δ (see above), differs significantly from $\frac{1}{4}$ —rising from 0.31 at 7 GPa to 0.37 at 35 GPa [12]. The supposed β -tin InSb-II phase has been shown to have an orthorhombic $Immm$ structure which differs significantly from β -tin in having an 8% difference between the a and b lattice parameters and a Δ value of 0.5 [14,19]. These give rise to peak splittings, other non- β -tin peaks, and d -spacing misfits to β -tin that were already evident—and sometimes remarked upon—in earlier studies [14].

CdTe was thought to transform from an NaCl phase to β -tin at 10 GPa, and then to orthorhombic $Pmm2$ at 12 GPa [11]. In fact, the 10 GPa transition is to the orthorhombically distorted NaCl structure, with $Cmcm$ symmetry, first found in ZnTe [8], and this is stable to at least 28 GPa [15]; the proposed $Pmm2$ structure can be understood as a subcell. In their study of HgTe, Huang and Ruoff [7] identified a β -tin-like phase between 12 and 38 GPa; they suggested that $\Delta = 0$ gives the closest fit to their data, but it is not evidently different from the fit with the β -tin value of $\Delta = \frac{1}{4}$. In any case, there are various other misfits and discrepancies, and they are all

accounted for very well by a strongly first-order transition from NaCl to the same $Cmcm$ structure as in CdTe [16]. Vohra *et al.* [10] reported a transition from the NaCl phase of InAs to β -tin at 17 GPa. But non-NaCl peaks become clearly visible at pressures as low as 9 GPa in the image-plate ADX data, and grow in intensity with pressure increase [13]; these peaks are obscured by nonsample lines in the energy-dispersive x-ray (EDX) data [10]. Though there are some small unexplained features in the ADX patterns [13], the transition appears to be very similar to the continuous NaCl to $Cmcm$ transition in CdTe. There is no transition at 17 GPa, and—again—no β -tin phase.

We now turn attention to the new studies of AlSb, HgSe, InP, and GaP. Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury, using an image-plate area detector [17]. The incident wavelength was ~ 0.45 Å. Finely ground samples were made from starting material of 99.99+% purity, and—except GaP—loaded with 4:1 methanol:ethanol as a pressure medium and chips of ruby for pressure measurement; GaP was loaded without any medium because of its high sensitivity to water. (AlSb was tested with and without methanol:ethanol. There was no difference, except that sharper diffraction peaks were obtained *with* the medium.) Profile refinements were carried out with the program GSAS [20].

Jamieson's identification [2] of the first high-pressure phase of AlSb as β -tin at ~ 10 GPa was amended to NaCl by Yu *et al.* [4] and to orthorhombically distorted NaCl—with a transition pressure of 7.7(5) GPa—by Baublitz and Ruoff [21]. However, the most recent study by Greene *et al.* [3] returned to the β -tin interpretation. Figure 1 shows our diffraction pattern in this phase at 14.7 GPa, and it is plainly not β -tin which—among many other things—cannot account for two of the lowest-angle lines. These lines appear to have been beyond the range of the EDX data of Greene *et al.*;

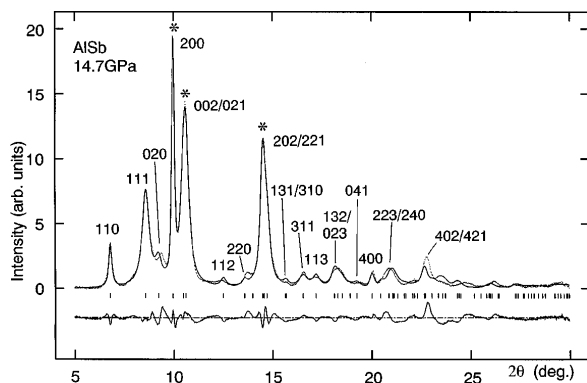


FIG. 1. Rietveld refinement fit of the $Cmcm$ structure to a profile from AlSb at 14.7 GPa. Tick marks show the positions of all reflections allowed by symmetry. Reflections giving rise to visible peaks are indexed; overlapping ones are separated by an oblique line. The difference between the observed and calculated profiles is displayed below the tick marks. Asterisks mark reflections visible in the data of Ref. [3].

they detected only the three strongest lines (marked by asterisks) as visible features in patterns dominated by peaks from a gold pressure marker and Sb fluorescence [3]. The calculated profile in Fig. 1 is from a site-ordered $Cmcm$ structure with $a = 5.353(1)$ Å, $b = 5.788(1)$ Å, $c = 5.086(1)$ Å, $y(\text{Al}) = 0.599(1)$, and $y(\text{Sb}) = 0.163(1)$. The main reflections are indexed on this cell, which is very similar to the cell proposed by Baublitz and Ruoff [21]. There are small misfits in a few (weak) peak positions, but these do not appear to fit *any* lattice. This is a problem we have encountered in several III-V and II-VI phases, and is likely to arise from nonhydrostatic (deviatoric) stress or stacking faults. Otherwise, the profile fits well to all the known features—and the relative intensities—of a $Cmcm$ pattern. We thus conclude that $Cmcm$ —or a very similar structure—is the most probable interpretation. Refinement of a mixed-phase ZB/ $Cmcm$ pattern at 8.1 GPa shows the $Cmcm$ distortions to be already fully developed at the transition, with $a = 5.448(1)$ Å, $b = 5.847(9)$ Å, $c = 5.150(1)$ Å, $y(\text{Al}) = 0.55(4)$, and $y(\text{Sb}) = 0.15(1)$; and $a = 5.9344(2)$ Å for ZB, giving $\Delta V/V_0 = 19.5(2)\%$.

In their first study of the transition from the NaCl phase III of HgSe to phase IV, starting at 28 GPa, Huang and Ruoff reported the phase-IV structure as orthorhombic [22]. Later they reinterpreted the same data (with some differences in analysis) in terms of the same two β -tin-like structures as they considered for HgTe [7]. As in that case (above), the observed intensities fit equally well with the β -tin value of $\Delta = \frac{1}{4}$. However, neither of these structures accounts for five peaks—labeled A, B, C, D, and F by Huang and Ruoff [7]—which were attributed to a second, hexagonal phase (A and B) and various other uncertain causes (C, D, and F) [7]. (The previous, orthorhombic interpretation fitted all of these “extra” lines, except that “A” was not included [22].) Figure 2 shows a site-ordered $Cmcm$ fit to our data collected at 35.6 GPa. The general similarity to the AlSb pattern in Fig. 1 is clear. There are also small misfits as in AlSb (in 020 and 220), and some additional ones.

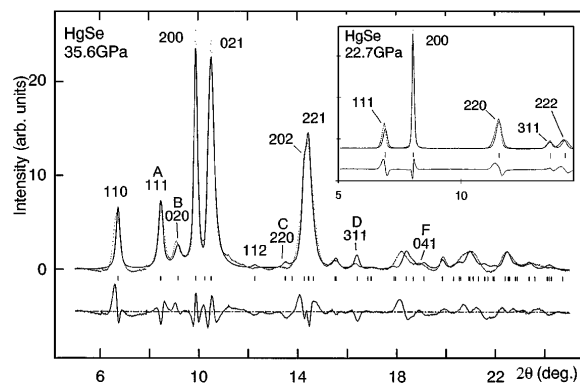


FIG. 2. As Fig. 1 for HgSe at 35.6 GPa. “A” to “D” and “F” label the same features as in Fig. 4 of Ref. [7]. The best fit to a profile from the NaCl phase at 22.7 GPa is shown in the inset.

We again attribute these to microstructural effects, for which there is direct evidence in the NaCl phase (of the same sample), as shown in the inset. A *Cmcm* (or *Cmcm*-like) structure is clearly the most probable interpretation, particularly since *Cmcm* fits so well (at a much lower pressure) to HgTe [16]. Features A, B, and D are well accounted for, and C and F probably are—as indexed. (There is also the lowest-angle reflection, 110, which would have been under the fluorescence peaks in the earlier studies.) The fit in Fig. 2 gives $a = 5.153(1)$ Å, $b = 5.559(1)$ Å, $c = 4.972(2)$ Å, $y(\text{Hg}) = 0.644(1)$, and $y(\text{Se}) = 0.141(2)$. The transition from the NaCl phase is first order, as in HgTe [16], with a (small) $\Delta V/V_0$ of 0.9(5)%.

The evidence for an NaCl to β -tin transition at 19 GPa in InP rests only on weak lines reported at the top pressure, just before gasket failure, in the study by Menoni and Spain [9]. We find that the NaCl phase remains stable until 28(1) GPa, above which pressure the continuous transition shown in the inset of Fig. 3 occurs. These changes have all the characteristics of the continuous NaCl to *Cmcm* transition first observed in CdTe [15]. The site-ordered *Cmcm* fit in Fig. 3 to data collected at 45.6 GPa gives $a = 4.879(1)$ Å, $b = 5.088(2)$ Å, $c = 4.923(3)$ Å, $y(\text{In}) = 0.658(1)$, and $y(\text{P}) = 0.143(2)$; unlike all other *Cmcm* phases found previously, the unit cell is close to tetragonal. Apart from some difficulty with the very broadened 111 reflection, the fit is very good.

Yu *et al.* reported that the transition from the ZB phase at 22 GPa in GaP was *not* to a β -tin structure [4]. But a more detailed study soon after by Baublitz and Ruoff [6] concluded that it was β -tin, and this was supported by Hu *et al.* [23] who also reinterpreted the data of Yu *et al.* as a mixture of ZB and β -tin. However, the data in Fig. 6 of Baublitz and Ruoff show a reflection not allowed in β -tin—as the authors recognized—and there are clear shoulders that are also not accounted for on the low-angle side of the “ β -tin” 200 and 220 peaks. All these features are reproduced in our data, as shown in inset (ii) of Fig. 4 for a pattern collected at 37.3 GPa, well above

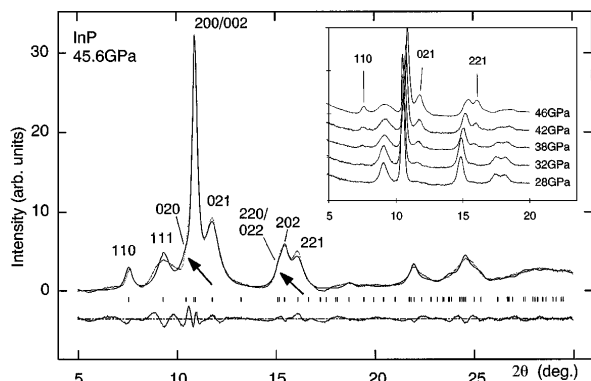


FIG. 3. As Fig. 1 for InP at 45.6 GPa. Arrows mark weak shoulders that indicate the orthorhombic splitting. The continuous growth of the *Cmcm* 110, 021, and 221 reflections above 28 GPa is shown in the inset.

a transition pressure of 26(1) GPa (see also Ref. [23]); in addition, we detect a very weak 110 reflection. The calculated profile in Fig. 4 is with a site-disordered *Cmcm* structure, which gives a good fit to all the features with $a = 4.707(2)$ Å, $b = 4.949(1)$ Å, $c = 4.701(3)$, $y(\text{Ga/P}) = 0.647(3)$, and $y(\text{Ga/P}) = 0.159(3)$. The lack of long-range site ordering is made evident by the weakness of 110 and the absence of 111—as shown by the site-ordered “fit” in inset (i). The pattern is otherwise very similar to that of InP in Fig. 3, and GaP is like InP in having a unit cell close to tetragonal. A mixed-phase ZB/*Cmcm* sample at 29.4 GPa gives $\Delta V/V_0 = 14.0(2)\%$.

So, it can be shown conclusively that none of the III-V or II-VI phases previously thought to have the β -tin structure in fact does so. All these phases have various lower-symmetry structures: site-disordered *Imma* in GaSb, site-ordered *Immm* in InSb (InSb-II), site-disordered *Cmcm* in GaP, and site-ordered *Cmcm* (or *Cmcm*-like) in AlSb, InP, InAs, CdTe, HgTe, and HgSe. The site-disordered *Imma* structure has since also been found in InSb (phase P5 [19]), and what may be the only known true β -tin structure has been discovered in the new, site-disordered P2 phase of InSb [14]. P2 has so far been obtained only in mixed-phase samples with InSb-II, which makes it difficult to be certain that there is no departure from tetragonal symmetry. However, there is known to be a true β -tin phase in InSb when it is brought down to ambient pressure from above 2 GPa at low temperature (77 K) [14], and it seems likely that this is the same phase as P2. Other recent work has shown GaAs-II to have the *Cmcm* structure [18]—probably site-disordered as in GaP; as noted, there is a (site-ordered) *Cmcm* phase in ZnTe [8]; and NaCl to (site-ordered) *Cmcm* transitions have also been found in CdSe and ZnSe [18]. The corrected interpretations of the supposed β -tin phases are thus in accord with the new systematics emerging from several other III-V and II-VI systems.

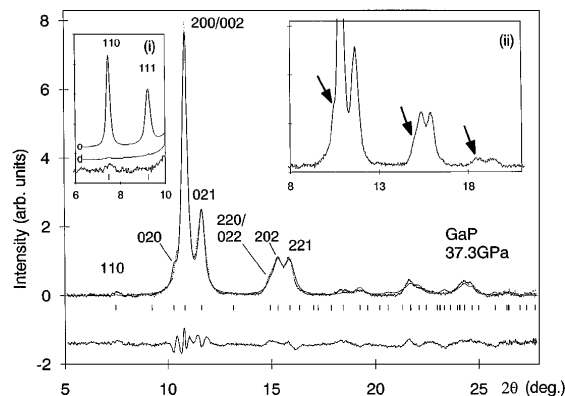


FIG. 4. As Fig. 1 for GaP at 37.3 GPa, except that the fit is with a site-disordered *Cmcm* structure. The best fit with a site-ordered *Cmcm* structure, “o”, is compared with the site-disordered fit, “d”, for the low-angle region in inset (i). Part of the pattern is enlarged in inset (ii), and arrows mark the non- β -tin features also visible in Fig. 6 of Ref. [6].

Except in the site-disordered *Imma* phases of GaSb and InSb, and the P2 phase of InSb, the structural differences from β -tin are not small; only in the three quasimonatomic cases do the structures come close to β -tin. It is to be noted that even truly monatomic β -tin is an unusual structure; apart from tin itself, it exists over just 2 GPa in Si and is found over a large pressure range only in Ge [18]. It is otherwise unknown. And the (site-ordered) diatomic β -tin structure does not appear to exist at all; not only have we shown its nonexistence (so far) in the III-V and II-VI systems under pressure, but a search of databases [24] reveals no known examples in *any* binary system under any conditions.

Yet theoretical and computational work has long appeared to show that the *d*- β -tin phase *should* exist [4], with a calculated energy significantly less than the NaCl structure in many cases [25]. Even in the most recent work, *d*- β -tin has still emerged as a possible equilibrium phase in some cases in which the *Cmcm* and *Immm* structures have now been included in new calculations: for example, in GaAs—where the *d*- β -tin energy is marginally less than that of the *Cmcm* structure at very high pressures [26], and in GaP—where the *d*- β -tin energy is clearly less than that of *Cmcm* above 20 GPa and a transition from *Cmcm* to *d*- β -tin is predicted [27]. But there is no evidence of the phase in GaAs [18], and Fig. 4 shows GaP still in the *Cmcm* phase at 37 GPa. The nonexistence of *d*- β -tin thus appears to be significant, suggesting some impediment to its formation. Its structure is quite different from *Cmcm*, and there may be kinetic hindrance to a transformation between them. A possibly more significant factor is that the known site-ordered high-pressure phases—NaCl, *Cmcm*, and *Immm*—have a structural feature in common; they are all made up of flat NaCl-like layers, differing only in the stacking. The *d*- β -tin structure is a strong departure from that. In their calculations of a *Cmcm*-like structure for GaAs, Zhang *et al.* [28] concluded that the Fermi surface is anisotropic, with a corresponding difference between more metallic bonding in the NaCl planes and more covalent bonding linking the planes. An interesting sidelight comes from the fact that β -tin-like structures are formed only in the quasimonatomic site-disordered phases—*Imma* GaSb and InSb, and P2 InSb—in which truly NaCl-like planes cannot be defined.

We thus conclude that diatomic β -tin, one of the apparently key structures in the high-pressure systematics of the III-V and II-VI semiconductors, has, in fact, never yet been found to exist; that calculations show it may nonetheless be an equilibrium structure in some cases; and that why it has not yet been observed is likely to prove an interesting and significant question.

We thank H. Liu for assistance with some of the experimental work, and A. A. Neild and G. Bushnell-Wye for technical support. This work is supported by a grant from the Engineering and Physical Sciences Research Council, by funding from the Council for the Central Laboratory

of the Research Councils, and by facilities made available by Daresbury Laboratory. M. I. M. acknowledges a fellowship from the Royal Society.

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