Ordered Superstructure of InSb-IV

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The crystal structure of InSb phase IV has been determined at 5 GPa using angle-dispersive powder-diffraction techniques. The proposed solution is a site-ordered orthorhombic superstructure, spacegroup *Cmcm*, composed of six NaCl-like planes stacked along the c axis and alternately displaced approximately $\pm 0.1b$. Two of the planes are flat, and the others are slightly puckered due to a small relative displacement of the In and Sb atoms along the c axis. The results add a remarkably complex example to growing evidence that (generally much simpler) *Cmcm*-type structures are common to most of the more ionic II-VI and III-V semiconductors under pressure.

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Indium antimonide has long been one of the most studied of the III-V semiconductors under pressure. Intensive investigations of its properties in the 1960s revealed unusually complex behavior below 10 GPa [1]. The first transition from the ambient zinc blende phase was found to be either to tetragonal InSb-II at ~2 GPa at temperatures just above room temperature (or with rapid pressure increase at room temperature, due to slight sample heating) or to orthorhombic InSb-IV at ~3 GPa; a further transition to another orthorhombic (or hexagonal) phase was reported at 9 GPa [1,2]. InSb-II was found to have the diatomic equivalent of the β-tin structure, and InSb-IV a very simple (orthorhombic) structure having atoms at (0,0,0) and $(0,\frac{1}{2},\alpha)$ in spacegroup $Pmm2$, with α in the range $\frac{1}{4}$ to $\frac{1}{2}$ [1–3]. Vanderborgh *et al.* obtained a best-fitting value of 0.38 [3].

Sensitive angle-dispersive data from an image-plate detector have recently enabled us to show that there are in fact two different reproducible paths from the zinc blende phase to the equilibrium high-pressure phase [4,5]. Either there is a transformation at ~2.1 GPa to a mixture of a previously undetected phase ($P2$) and InSb-II, which then transforms to nearly single-phase InSb-II before recrystallizing to InSb-IV with only a very slight (~0.1 GPa) further increase in pressure, or there is a direct transformation from zinc blende to InSb-IV at a significantly higher pressure of ~3.0 GPa [6]. To achieve complete transformation to InSb-IV through $P2$ and InSb-II, it was found necessary to heat the sample to ~100 °C. Anomalous dispersion effects at the In K edge showed the structures of InSb-II and InSb-IV to be site ordered, but the $P2$ structure was not. $P2$ appears to have a tetragonal β-tin structure [7]. InSb-II does *not* have the β-tin structure previously reported, but a body-centered orthorhombic structure with In at (0,0,0) and Sb at, or very close to, $(0,\frac{1}{2},\frac{1}{2})$. All the readily visible peaks of the InSb-IV pattern are well fitted by the $Pmm2$ structure with $\alpha = 0.387(1)$—in close agreement with Vanderborgh *et al.* [3]. However, the sensitivity of our data revealed a large number of superlattice reflections not accounted for by the $a_p \times b_p \times c_p$ $Pmm2$ cell, and a $2a_p \times 3b_p \times 2c_p$ cell is required to index all these additional reflections. In separate work, the superlattice reflections have been found to remain up to the known transition at 9 GPa; all the features of the apparent additional phase V reported by Vanderborgh *et al.* [3] above 6 GPa can be accounted for by the mixture of $P2$, phase II, and phase IV, usually obtained when phase IV is produced (via $P2$ and phase II) without heating the sample [4,5]. InSb-IV thus emerges as the true equilibrium phase of InSb above 2.2 GPa at room temperature and also up to at least 100 °C; it is stable up to the next transition at ~9 GPa [8].

These new results reveal the remarkable new phenomenon among simple semiconductor systems of a superlattice structure that is the stable phase over a substantial range of P and T. We have now solved this complex structure. The results show that it is based on zigzag stacking of NaCl-like planes and that it is closely related to a similar but simpler structure (with the same spacegroup symmetry) recently observed in some II-VI and III-V systems.

The solution of the InSb-IV structure is made difficult by its relative complexity and the relative weakness of the superlattice reflections—the strongest of them has only ~1% of the intensity of the main reflections, and the full structure solution requires the measurement of intensities at least an order of magnitude weaker still. To improve the signal-to-noise on these very weak superlattice reflections and also to check the reproducibility of their intensities, two new samples of InSb-IV were prepared, and powder profiles were recorded with counts an order of magnitude greater than in the previous work. This required counting times of ~8 h. The samples were prepared as previously described [4]. Finely ground powder from starting material of 99.9999% purity was loaded into Merrill-Bassett diamond anvil cells, with 4:1 methanol:ethanol as a pressure transmitting fluid and chips of ruby for pressure measurement [9], and taken through the transition to InSb-IV at 100 °C. After cooling to room temperature, the sample pressure was adjusted to

5.1(1) GPa in both cases. Angle-dispersive data were collected at Synchrotron Radiation Source (SRS), Daresbury, at x-ray wavelengths of 0.4635 and 0.4445 Å (close to the In K edge at 0.4439 Å). One sample was oscillated ±3.5° about a vertical axis during both exposures to check for any evidence of incomplete powder averaging. After structure solution, the final structural parameters, including lattice parameters, were obtained from Rietveld refinement [10] of the full integrated profiles, using the program MPROF [11]. All other details of the experimental procedures and data analysis were as described previously [4] and elsewhere [12].

No detectable differences were found between the profiles obtained with the oscillated and stationary samples. Figure 1 shows the profile obtained from the stationary sample at 0.4445 Å near to the In K edge. Inset (i) shows some low-angle superlattice reflections measured near to (n) and far from (f), the In K edge, and inset (ii) shows many further superlattice reflections in a higher angle part of the profile. Indices are given for a few principal reflections and—in inset (i)—for some of the superlattice reflections, based on a unit cell with $a = 2a_p$, $b = 2c_p$, and $c = 3b_p$ (where the $Pmm2$ unit cell is $a_p \times b_p \times c_p$). The b and c axes of the full unit cell have been interchanged, compared with our previous account [4,5] to give a standard setting of the spacegroup (see below). Thus the strongest of the superlattice reflections, shown in inset (i), was previously indexed (121) but is now (112).

Inspection of the profiles, measured both near to and far from the In K edge, revealed that reflections with $h + k =$ odd in all (hkl) and $l =$ odd in $(h0l)$ were systematically absent. The lattice symmetry is thus C-face centered (it was previously described as B-face centered [4], before the interchange of b and c), and the additional absence condition restricts possible spacegroups to $Cmcm$, $C2cm$, and $Cmc2_1$. Only the very weak (110) reflection shown in inset (i) of Fig. 1 rules out two other spacegroups, $C2cb$ and $Cmca$. Comparison with the $Pmm2$ structure and density considerations show that the unit cell must contain 12 In and 12 Sb atoms. The fact that the true structure is only a small distortion from $2 \times 3 \times 2$ $Pmm2$ unit cells stacked together (as shown by the systematic weakness of the superlattice reflections), taken together with the face centering and the site ordering, indicates that the structure is composed of six almost equispaced, flat (or nearly flat) NaCl-like planes stacked along the long axis (the c axis). The relationship to the $Pmm2$ subcell also means that atoms in adjacent planes must be in positions differing by $\alpha/2 \sim 0.2$ along the b axis. There is only one way in each of the possible spacegroups to satisfy these requirements: atoms in the $4(c)$ and $8(f)$ special positions of $Cmcm$ or in the three different $4(a)$ special positions of $Cmc2_1$ or in the $4(b)$ special position and $8(c)$ general position of $C2cm$. In the case of $Cmcm$, the $4(c)$ position puts atoms in mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. (Since both species must lie in the mirror planes, these planes are flat.) These planes are $c/2$ apart and so must be related by the $\alpha/2$ displacement. This is satisfied by placing In at $0, y \sim 0.1, \frac{1}{4}$ [and related $4(c)$ positions] and Sb at $0, y \sim 0.6, \frac{1}{4}$. The atoms in the $8(f)$ positions must then be close to planes at $z = \frac{1}{12}, \frac{5}{12}, \frac{7}{12}$, and $\frac{11}{12}$, and those in the planes at $\frac{1}{12}$ and $\frac{5}{12}$ must have approximately the same y coordinates as the atoms on the $z = \frac{3}{4}$ mirror plane. This implies either In at $0, y \sim 0.4, z \sim \frac{1}{12}$ and Sb at $0, y \sim 0.9, z \sim \frac{1}{12}$, or the same positions with In and Sb interchanged. The former assignment gives a larger number of unlike nearest neighbors and was tested first.

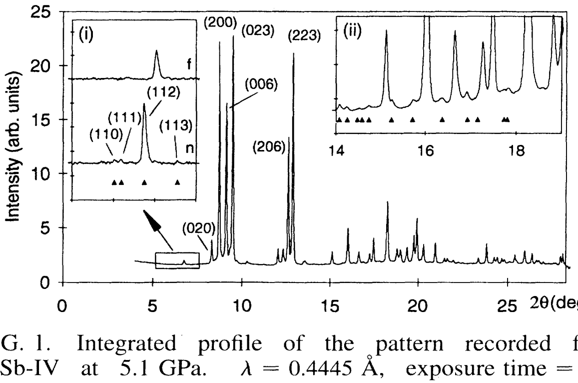

FIG. 1. Integrated profile of the pattern recorded from InSb-IV at 5.1 GPa. $\lambda = 0.4445$ Å, exposure time = 8 h. Inset (i) shows an enlarged view of the low-angle region of the profile recorded at 0.4635 Å, far (f) from the In K edge, and at 0.4445 Å, near (n) the In K edge (0.4439 Å). Inset (ii) shows an enlargement of a higher-angle part of the profile. The positions of the most prominent superlattice reflections are indicated by ▲ in both insets. The two profiles in inset (i) are on a common intensity scale.

Refinement of the trial structure in $Cmcm$ proceeded satisfactorily to give a good overall fit to the observed profiles (both near to and far from the In K edge [13]) with variable coordinates $y \sim 0.12$ and 0.62 for the In and Sb atoms in the $4(c)$ positions, and $y \sim 0.40$ and 0.91 and $z \sim 0.09$ and 0.08, respectively, for the $8(f)$ positions. Tests showed that a better fit was obtained with the atoms constrained to be exactly 0.5 apart along y in both positions. Thus, there is no detectable distortion from a NaCl arrangement in the x and y directions, except for the (significant) difference between the a and b lattice parameters. However, the small difference in the z coordinates *is* requires: Constraint of the In and Sb atoms to the same z coordinate gave a poorer overall fit and made the (110) and (111) reflections much stronger than observed, relative to the (112) reflection. The $8(f)$ planes are thus slightly, but significantly, puckered. A test was also made of exchanging the In and Sb sites in the $8(f)$ positions (the second choice above). This had a similar effect to that just described on the fit and the relative intensities. Puckering of the planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ is allowed by refining in the three $4(a)$ positions of $Cmc2_1$, but this gives only very small shifts from the coordinates obtained in *Cmcm* and no clear improvement in overall fit. Finally, refinement in the 4(b) and 8(c) positions of *C*2*cm* allows relative displacements along x (all the atoms are at $x = 0$ and $x = \frac{1}{2}$ in the other two spacegroups). This refinement proved unstable even with a very heavy damping factor, and no significant departures from $x = 0$ were found. There is thus no evidence for the reduced symmetry of $Cmc2_1$ or *C*2*cm*, and so final refinements were carried out in *Cmcm*, with the initial assignment of the In and Sb sites.

Since the difference in y(In) and y(Sb) had been shown not to be significantly different from 0.5 for either site, this constraint was applied in the final refinements. The refinable coordinates thus reduced to y(In) for each site and z(In) and z(Sb) for the 8(f) site. Other variables in the refinement were a scale factor, the a, b, and c lattice parameters, two isotropic thermal-motion parameters (one for each atomic species), four peak-shape parameters, and a preferred-orientation parameter. The best fit to the observed profile was obtained with $a = 5.847(1)$, $b = 6.140(1)$, and $c = 16.791(1)$ Å and coordinates $y(\text{In}) = 0.120(1)$ and 0.410(1) in the 4(a) and 8(f) sites, respectively, and $z(\text{In}) = 0.089(1)$ and $z(\text{Sb}) = 0.081(1)$ in the 8(f) sites. The fit to the main reflections is qualitative, as shown for the *Pmm*2 average structure in Fig. 13 of Ref. [4], with small but significant improvements. And now all the superlattice reflections are also accounted for, as illustrated for some of them in Fig. 2. The observed and calculated positions agree to within ±0.01° (2θ) except, perhaps, for the group of reflections around 17.8° (2θ). However, the apparent displacement in that case is partly attributable to a discrepancy between observed and calculated intensities, and the misfit in position alone is only 0.02° (2θ) or less. Some other intensity misfits are evident, but the agreement in better than 30% for most of the observable features in Fig. 2, which is very satisfactory for such weak reflections being fitted simultaneously with main reflections up to 500–1000 times stronger. In addition, there are 14 (very weak) reflections over the whole profile in which there is a detectable difference between measurements made near to and far from the In K edge, and the refined structure correctly predicts all of these. The inset of Fig. 2 shows some examples.

A drawing of the proposed structure is presented in Fig. 3. A *Pmm*2-like subcell is outlined at A, and it can be seen how the structure is related to an aggregate of true *Pmm*2 cells, with $\alpha \sim 0.4$ (referred to the *Pmm*2 cell). Based on total-energy calculations by Zhang and Cohen [14,15], Vanderborgh *et al.* proposed that the true unit cell of InSb-IV is twice the size of the *Pmm*2 cell along x and y (in the setting in Fig. 3) and that the atoms are ordered in NaCl-like planes alternately displaced along y by $\alpha/2 \sim 0.2$ (referred to the larger cell) to give a structure in which each atom has six unlike nearest neighbors [3]. The true structure is evidently quite similar to this in its general arrangement, but even more complex. In particular, the puckering of four of the six xy planes, and the six-layer (rather than two-layer) repeat of the In and Sb site ordering, gives rise to some significant distortions of the coordination. The In and Sb atoms in the flat planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ both have six nearest unlike neighbors at ~3 Å—four in the same yz plane and two at $\pm\frac{1}{2}$ in x—and two like neighbors at ~3.3 Å in the same yz plane. The atoms in the puckered planes both have *five* nearest unlike neighbors at ~3 Å, with a sixth one considerably further away at ~3.5 Å. In these planes, the In atom has two like neighbors at

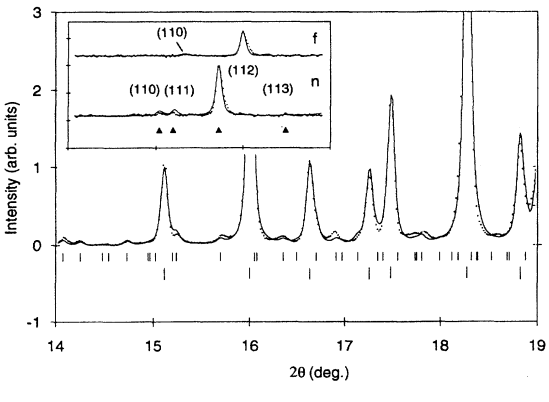

FIG. 2. Rietveld fit to the superlattice reflections shown in inset (ii) of Fig. 1. The upper tick marks show the positions of all the superlattice reflections; the lower tick marks show those of the *Pmm*2 subcell. The inset shows the fit, both near to (n) and far from (f) the In K edge, to the low-angle reflections shown in inset (i) of Fig. 1. The two profiles in the inset are on a common intensity scale.

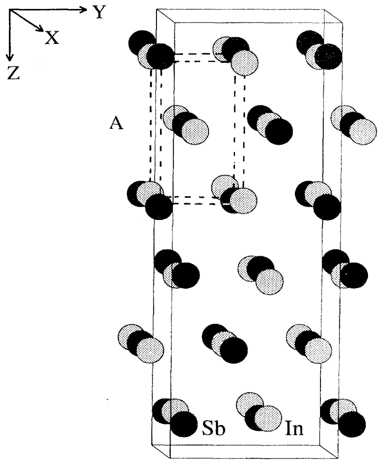

FIG. 3. The *Cmcm* structure of InSb-IV. For clarity, the difference between z(In) and z(Sb) in the puckered layers and the difference between the flat and puckered layers in their positions along y have been slightly exaggerated—by a factor of 1.5. The *Pmm*2-like subcell is outlined at A.

~3.2 Å (closer than the sixth unlike neighbor), and the Sb atom has one like neighbor at 3.4 Å and one at 2.9 Å (slightly closer than *any* of the unlike neighbors). All atoms thus have eight neighbors between 2.9 and 3.5 Å in a very approximately simple-hexagonal (SH) array—though the ordering means the symmetry could not be hexagonal even if the atomic positions corresponded to SH.

There is an interesting relationship between the InSb-IV structure and another new structure recently found in ZnTe and other II-VI semiconductors and possibly in some III-V systems. We have solved the structure of ZnTe-III [16] and found it to have the same *Cmcm* spacegroup symmetry. In that case the unit cell contains only two NaCl-like planes along z. In this smaller cell, all the atoms lie on the mirror planes in 4(c) positions, so there can be no puckering by relative displacement along z. Although the slight In-Sb-In zigzag along x and y introduced into the InSb-IV structure by the z displacements is thus absent in ZnTe-III, there is a similar magnitude of zigzag along x in the latter due to the Zn and Te y coordinates not differing by exactly 0.5. Also, adjacent NaCl-like planes in ZnTe-III are separated by a relative displacement of the order of $0.2b$, as in the InSb-IV, and the coordination of closest near neighbors in ZnTe-III is fivefold as around some sites in InSb-IV. These are remarkable similarities, and evidence of the same structure as ZnTe-III has been found in CdTe [17] and HgTe [18] and possibly InAs and InP [19].

It is very surprising that a simple system like InSb should form such a relatively complex structure as its equilibrium stable phase over a pressure range that may be as large as 7 GPa [8]. As far as we have found so far, it is unique in this behavior among the core II-VI and III-V systems—although the other III-V's we have studied (GaSb, GaAs, InP, InAs) have such relatively broad diffraction peaks as to make superlattice reflections difficult to detect. In any case, the InSb-IV structure raises fundamental new questions about the stabilizing effect of ordered superstructures and should also throw particular light on the growing evidence that a zigzag stacking of slightly distorted NaCl-like planes is a structural arrangement common to most of the more ionic II-VI and III-V semiconductor systems [20].

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[6] In previous work we have denoted InSb-II and InSb-IV as $P3$ and $P4$, respectively [4,5]. A distinction is thereby made between the observed phases and the (now evidently incorrect) P-T fields of stability identified with InSb-II and InSb-IV in the literature [1,2]. However, that distinction is not necessary here, and the familiar nomenclature can be used without ambiguity.

[7] The possibility of a very small orthorhombic distortion is discussed (briefly) in Ref. [20].

[8] The fact that the transformation from InSb-II to InSb-IV is inhibited at pressures above ~3 GPa [4,5] may indicate that the upper limit of true thermodynamic stability for InSb-IV is somewhat below 9 GPa. As yet, this remains uncertain.

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