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Structure of GaSb to 35 GPa

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The structural pressure dependence of GaSb has been determined to 35 GPa. The well-known phase transition at 7 GPa is found to be to a disordered orthorhombic structure with space group *Imma*, rather than to the β-tin structure previously reported. We find the *Imma* phase to be stable to at least 35 GPa, and do not observe the transition to a simple-hexagonal structure previously reported at 28 GPa. Striking similarities with the *Imma* phase of silicon are found in the pressure dependence of the lattice parameters and the variable atomic coordinate.

Since the early work on GaSb under pressure,[1–3] it has attracted special attention among the principal III-V semiconductors as the least ionic of them and thus the one expected to be the closest to silicon and germanium in its high-pressure behavior.[4–6] Previous diffraction studies of GaSb have apparently confirmed this, with a transition from the ambient-pressure zinc-blende phase to a metallic β-tin phase (GaSb-II) at ~ 7 GPa,[1–3,5,7] followed by a transition to a simple hexagonal (SH) phase (GaSb-III) at 27.8 GPa.[7] This corresponds to the diamond $\rightarrow \beta$-tin$\rightarrow$SH sequence reported for silicon and germanium.[8,9] A further transition has been reported in GaSb at 61 GPa,[7] but the structure of this fourth phase (tentatively indexed as orthorhombic[7]) remains as yet unknown. Despite the large difference in scattering between Ga ($Z=31$) and Sb ($Z=51$), previous diffraction work has been unable to determine whether or not the structures of the high-pressure phases are site ordered.

In addition to the important uncertainty about site ordering, there are some other significant questions that have arisen in recent work. The observed transition pressure of 27.8 GPa for the β-tin-to-SH transition is abnormally different from the predictions of total-energy calculations, which give 52.8 GPa.[6] An extended x-ray-absorption fine structure study of GaSb-II indicates that some form of structural distortion or disorder is required to fit the observed absorption spectrum.[10] And the structural sequence in silicon is now known to include an orthorhombic phase (space group *Imma*) between the β-tin and SH phases.[11,12] Calculations of the stability of the *Imma* structure suggest that the same phase exists in germanium.[13]

As part of a systematic study of the structural pressure dependence of the II-VI, III-V, and group-IV semiconductors we have now reexamined GaSb to 35 GPa using angle-dispersive diffraction techniques and an image-plate area detector. We find that the transition at 7 GPa is to a disordered orthorhombic structure, which is the same as the *Imma* phase of silicon, and that this is stable up to at least 35 GPa. Neither the β-tin nor the simple-hexagonal structures are observed in this pressure range.

Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury. The incident wavelength was 0.4654(1) Å, as calibrated from a standard Si sample. Details of our experimental setup and pattern integration software have been reported previously.[14] The sample was a finely ground powder prepared from starting material of 99.99% purity supplied by Johnson Matthey.

Samples were loaded in full conical-aperture diamond-anvil pressure cells with a 4:1 mixture of methanol:ethanol as the pressure-transmitting medium, and the pressure was measured using the ruby-fluorescence technique.[15] All structural parameters, including lattice parameters, were obtained from least-squares (Rietveld) refinement[16] of the full integrated profiles using the program MPROF.[17]

On pressure increase, the high-pressure phase (GaSb-II) was first observed at 7.0 GPa, in good agreement with previously reported values of 6.2, 7.4, and 7 GPa.[5,7,10] On further pressure increase, the fraction of the GaSb-II phase increased and an entirely single-phase pattern was obtained at 9.4 GPa. Some features of the integrated profiles did not accord with the expected (diatomic) β-tin structure, and these features were found to become more apparent as the pressure was increased (in ~ 3 GPa steps) to 18 GPa. The observed profile at 18 GPa is shown (dotted) in Fig. 1. The tick marks under the profile indicate the positions of all the allowed reflections, as given by the best-fitting (diatomic) β-tin cell. It can be seen that the (110) and (310) reflections are absent from the observed profile. Since these arise from the difference in scattering between Ga and Sb in the ordered structure, the fitted profile (solid line) has been obtained by Rietveld refinement of a *disordered* structure with 50:50 occupancy of each site by Ga and Sb. The variables in this refinement were the a and c lattice parameters, a scale factor, an isotropic thermal motion parameter, three peak-shape parameters, and a preferred-orientation parameter.[18] [Inset (i)—which is on the same intensity scale as the main part of the figure—shows the observed and calculated profiles in the region of the (110) reflection for the equivalent ordered structure. Apart from this (large) discrepancy, and a weak (310) reflection of height 10 on the scale of Fig. 1, there are no other discernible differences between the profiles derived from the site-ordered and disordered structures.] The most evident problem is that the tetragonal lattice cannot fit the relative positions of the observed reflections. This is particularly clear for the reflections between 16° and 22° in 2θ. The difference between observed and calculated profiles, plotted below the tick marks, shows that the fit to the low-angle strong reflections is also poor. There are problems with the peak intensities too. For example, the β-tin structure can-

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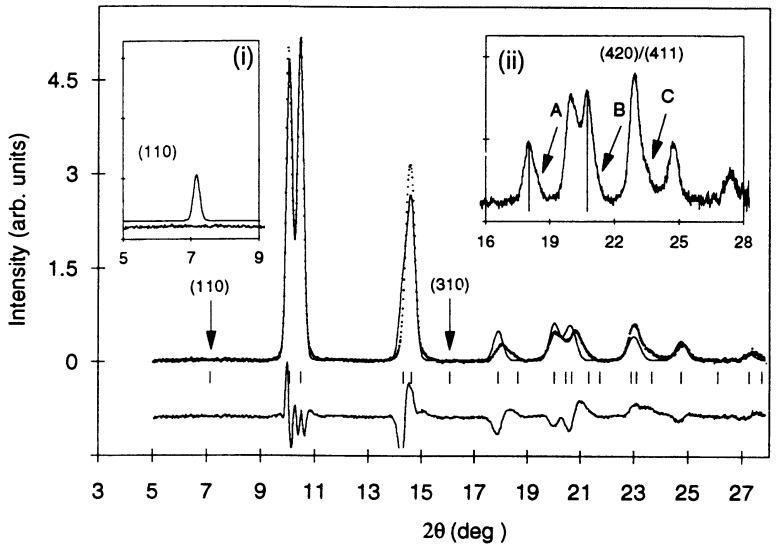

FIG. 1. Rietveld fit of a disordered β-tin structure to the integrated profile collected from GaSb at 18 GPa. The tick marks under the profile indicate the positions of all the reflections allowed for an *ordered* β-tin structure. Inset (i) shows, on the same intensity scale as the main part of the figure, the observed (dotted) and calculated profiles in the region of the (110) reflection for the ordered structure. Inset (ii) shows, arrowed, three shoulders not accounted for by the β-tin structure.

not account for the shoulders marked on part of the observed profile in inset (ii), at A, B, and C. The shoulder at C is distinct, whereas those at A and B show up as asymmetry of the main peaks—as the vertical lines drawn in inset (ii) help to reveal. Though weak, these features have all been reproducibly observed in many different samples. Indeed the shoulder at C appears to be visible in the energy-dispersive spectrum of GaSb at 23.3 GPa obtained by Weir *et al.*,[7] on the (420)/(411) peak shown in their Fig. 1. (A and B are under fluorescence peaks in their spectrum and are more difficult to detect in any case.)

Comparison of the profile shown in Fig. 1 with data we have recently obtained from the orthorhombic *Imma* phase of silicon[11,12] revealed many similarities. We therefore attempted to fit the GaSb-II profiles with an *Imma* structure (Fig. 2) in which each 4(e) site of the *Imma* space group is assigned a 50:50 occupancy of Ga and Sb. The resulting fit to the observed profile is shown in Fig. 2. The orthorhombic structure provides a clearly better fit to the observed peak positions (including the low-angle reflections, as shown by the difference profile) and, as can be seen in the inset, it also accounts for the shoulders identified in Fig. 1. The best-fitting *Imma* structure has $a=5.276(1)$ Å, $b=5.151(4)$ Å, $c=2.886(1)$ Å, and $\Delta=0.340(2)$. In the β-tin structure, $\Delta=0.25$ and the (002), (202)/(022), and (222) reflections responsible for the shoulders (see the Fig. 2 inset) have zero intensity. Their magnitude increases as Δ varies from 0.25 to 0.5, and their presence is thus direct evidence for $\Delta \neq 0.25$. We thus conclude that, at 18 GPa, GaSb does not have the β-tin structure as long supposed, but rather a disordered[19] orthorhombic structure with space group *Imma*.

As noted already, the GaSb-II profiles collected at pressures below 18 GPa contain similar, though weaker, deviations from a true β-tin profile. Figure 3(a) shows part of the observed profile at 9.4 GPa—covering the same 2θ range as the insets of Figs. 1 and 2—and the best fit obtained for a (disordered) β-tin structure. The discrepancies in peak positions at this pressure are small (though still significant), but the shoulders remain quite apparent, as marked by arrows.

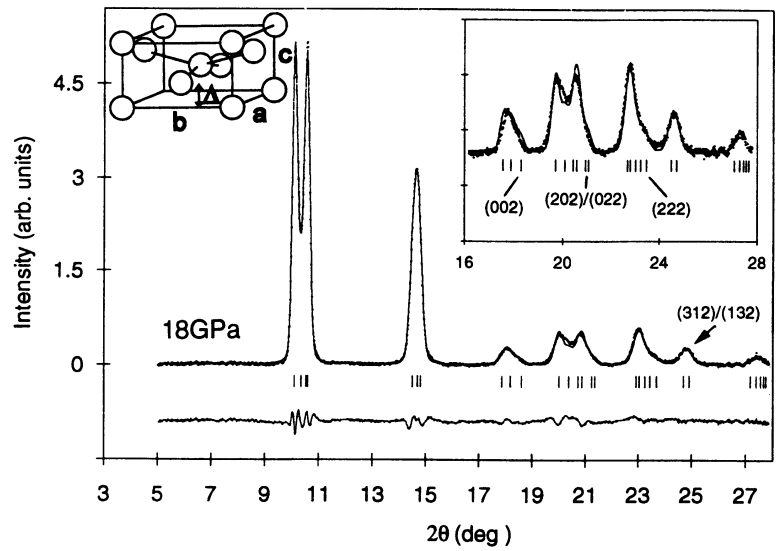

FIG. 2. The *Imma* structure and a Rietveld fit to the integrated profile collected from GaSb at 18 GPa. The inset shows an enlargement of the high-angle part of the pattern. Those *Imma* reflections responsible for the shoulders highlighted in inset (ii) of Fig. 1 are labeled in the inset. The *Imma* structure is shown, with its origin moved by $(0,-1/4,-\Delta/2)$ from its standard position to facilitate comparison with the β-tin and simple-hexagonal structures: when $a=b$ and $\Delta=0.25$, the *Imma* structure is equivalent to the β-tin structure, while if $b/c=\sqrt{3}$ and $\Delta=0.50$, it is equivalent to the SH structure.

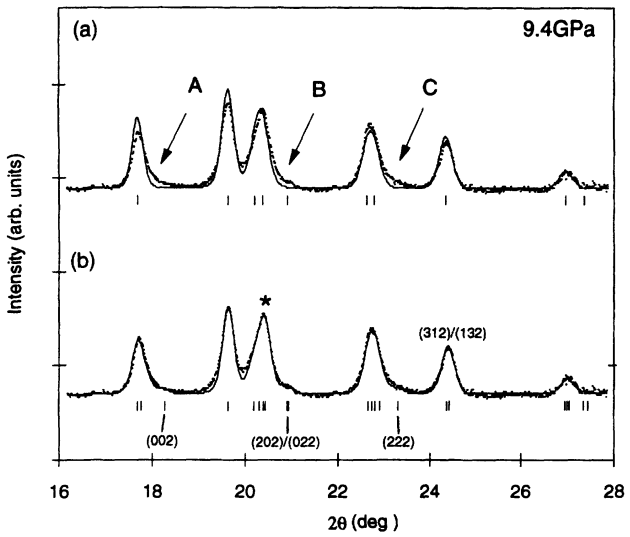

FIG. 3. Part of the observed profile obtained from GaSb at 9.4 GPa with the best fit obtained using (a) a (disordered) β-tin structure, and (b) the *Imma* structure. The arrows in (a) mark the same features as in inset (ii) of Fig. 1. The peak marked with an asterisk in (b) is discussed in the text.

The *Imma* fit [Fig. 3(b)] accounts for these and for some other significant features. For example, the peak marked with an asterisk is clearly asymmetric and is fitted poorly by the β-tin structure. Also, though the misfits of β-tin to the low-angle strong reflections (not shown) are less pronounced than at 18 GPa, the same *kinds* of improvement are obtained with the *Imma* fit. The fact that the (002), (202)/(022), and (222) shoulders are weaker than at 18 GPa shows directly that Δ is closer to 0.25. This is also evident from the (312)/(132) peak, which is clearly stronger than it is at 18 GPa (Fig. 2): its intensity is zero for $\Delta=0.5$ and increases as $\Delta\rightarrow0.25$. The refined value of Δ is 0.302(2), with lattice parameters $a=5.306(1)$ Å, $b=5.275(2)$ Å, and $c=2.928(1)$ Å. Although it is not possible to observe the (002), etc., shoulders in the mixed-phase GaSb-I/GaSb-II profile obtained at 7.6 GPa, due to overlapping GaSb-I peaks, the misfit to the low-angle strong reflections is still clearly evident at this pressure. GaSb thus transforms directly from an ordered zinc-blende structure to a *disordered*[19] *Imma* structure at ~7 GPa. No true β-tin phase is observed.

Above 18 GPa, the pressure on both GaSb samples was increased in approximately 4 GPa steps to a maximum pressure of 35 GPa in one sample, and 29.7 GPa in the other. In contrast to the previous diffraction study of Weir *et al.*,[7] no transition to the simple-hexagonal structure was observed at 27.8 GPa. The SH structure requires $b=\sqrt{3}c$ and $\Delta=0.5$ (Fig. 2). Figure 4 shows the profile collected at 35 GPa, and it is clear that the (312)/(132) peak is present, showing $\Delta\neq0.5$. From the (reduced) intensity of the reflection compared with 18 GPa (Fig. 2), Δ is closer to 0.5 but the structure is clearly not SH. The inset shows the best SH fit to the higher-angle part of the profile (with 50:50 occupancy of each site by Ga and Sb), and there are other evidently substantial discrepancies besides the absence of (312)/(132) from the calculated profile. The *Imma* structure provides a much better fit to the observed peak positions and intensities, as illustrated in the main figure, with $a=5.100(1)$ Å, $b=4.933(4)$ Å, $c=2.774(1)$ Å, and $\Delta=0.375(3)$. Preliminary work on other samples shows that the (312)/(132) peak is present to at least 50 GPa. If there is a transition to a true SH phase, it occurs at a much higher pressure than previously reported. [It is to be noted that Weir *et al.*[7] do not specify how they identified a transition at 27.8 GPa, and the spectrum they show is from a sample at the much higher pressure of 56.6 GPa. In this spectrum, there is a gasket line at the position where the (312)/(132) peak would be.]

Figure 5 shows the pressure dependence of the volume, (V/V_0), for GaSb to 35 GPa. The relative volume change at the zinc-blende-to-*Imma* transition, expressed as a proportion of the zinc-blende volume at the transition $[\Delta V^{\alpha\beta}(P_t)/V^{\alpha}(P_t)]$, is 18.3(1)%—the same within error as earlier measurements.[5] [The orthorhombic distortion is too small near the transition to affect the value of $\Delta V^{\alpha\beta}(P_t)$ significantly.] Above this transition, no discontinuities are observed in either the lattice parameters or unit-cell volume to at least 35 GPa. The c lattice parameter is less compress-

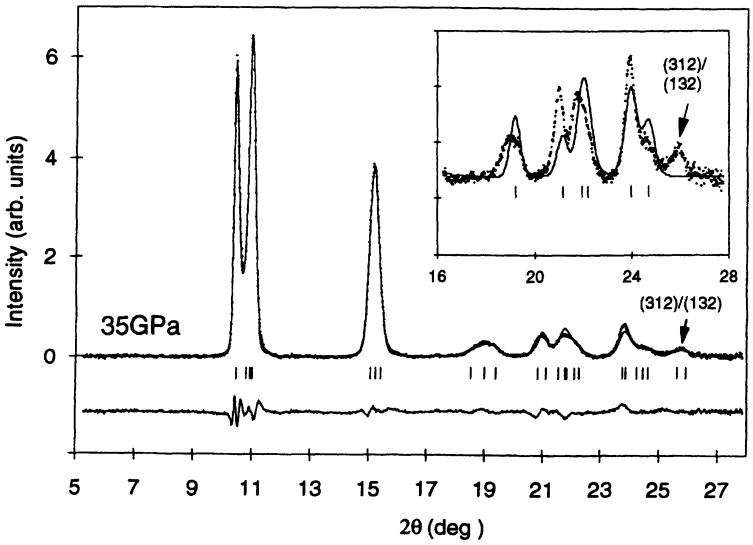

FIG. 4. Rietveld fit of the *Imma* structure to the integrated profile collected from GaSb at 35 GPa. The inset shows the best simple-hexagonal fit to the higher-angle part of the profile (with 50:50 occupancy of each site by Ga and Sb). The (312)/(132) reflection, which has zero intensity in the SH structure, is labeled in both the inset and the main figure.

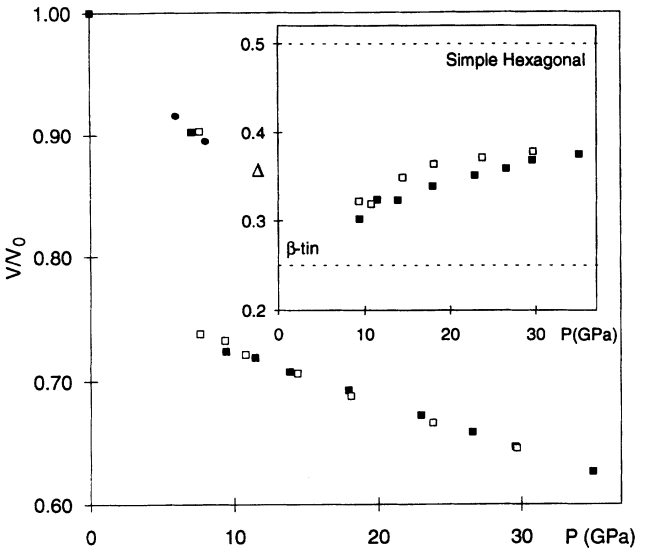

FIG. 5. V/V_0 as a function of pressure for two samples of the *Imma* phase of GaSb on pressure increase (■ and □). The pressure dependence of the atomic coordinate Δ in the *Imma* phase of GaSb is shown in the inset. In the β-tin phase, Δ is fixed by symmetry at 0.25, while in the simple hexagonal phase it is fixed at 0.5.

ible than b, with the consequence that the b/c ratio decreases with pressure, falling from 1.802(2) at 9.4 GPa to 1.778(3) at 35 GPa. The latter is still far from the ratio of 1.732 ($\sqrt{3}$) required for a SH structure. The pressure dependence of Δ in GaSb to 35 GPa is shown in the inset of Fig. 5. The results for the two different samples give an indication of the true accuracy with which Δ can be determined in this case. Δ clearly increases from ~0.31 to 0.37 over the range up to 35 GPa where—as for the b/c ratio—it remains far from the value (0.50) required for a SH structure.

Comparison of the behavior of b/c and Δ with the same variables in the *Imma* phase of silicon is intriguing. In silicon, this phase is stable over only ~2.5 GPa.[12] In GaSb, there is no reported transition above 35 GPa until 61 GPa,[7] and our preliminary work at higher pressures shows *Imma*-type profiles to above 50 GPa. The probable range of stability is thus ~50 GPa, twenty times that of silicon. However, despite this difference, b/c has almost the same values and change (1.80 to ~1.76) over the full stability range of both materials. [A simple linear extrapolation has been used for GaSb.] The accompanying change in Δ also appears to be very similar—from just over 0.3 to approaching 0.4. This is remarkable, and suggests an underlying relationship between the distortion of the quasi-SH planes (the bc planes in Fig. 2) and the range of structural stability. The difference in the latter is also reflected in the pressure dependence of the orthorhombic distortion $(a-b)/(a+b)$, which increases much more rapidly in silicon than in GaSb. The form of the pressure dependence of Δ (Fig. 5 inset) suggests that it may not rise above 0.375, which is the midpoint between the β-tin and SH values. In silicon, there is a discontinuous transition to SH from Δ ~ 0.375 in the *Imma* phase,[12] and so the trend in GaSb raises the interesting possibility that stable structures may not be found with Δ between ~0.375 and 0.5.

We thus conclude that GaSb transforms under pressure from an ordered zinc-blende phase to a disordered[19] orthorhombic phase which is stable to at least 35 GPa. This behavior is considerably different from what has been reported previously. Yet the results fulfill the expectation that GaSb—the least ionic of the principal III-V materials—will behave similarly to Si (and Ge). The absence of long-range order may be important in this, in that GaSb is then a quasi-monatomic system.

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[18] Separate measurement showed that preferred orientation (PO) effects were moderately strong, mainly reducing the (020) reflection. The same PO model was found to give a good fit to all three different samples used in this work.
[19] Some degree of short-range order is probable, but we cannot distinguish that from random site disorder. However, the apparently complete absence of the (110) reflection, which would have almost the same positions and (easily detectable) intensity in a long-range ordered *Imma* structure as is shown for β-tin in Fig. 1, indicate that the length scale of any ordering can be no more than a few unit cells.