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Phase transitions in GaSb to 110 GPa (1.1 Mbar)

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The III-V compound GaSb was studied by energy-dispersive x-ray diffraction up to a pressure of 110 GPa with the use of a synchrotron source. The first transformation from the zinc-blende to the β-Sn structure confirmed earlier work. This was followed upon an increase in pressure by a new transformation to a simple hexagonal (SH) structure at 27.8 ± 0.6 GPa. This is the first example of an SH structure in a III-V compound. A transition from the β-Sn to SH structure was predicted recently based on *ab initio* pseudopotential total-energy calculations. Upon a further increase in pressure the simple hexagonal structure transformed to another structure at 61.0 ± 0.7 GPa which persisted to 110 GPa, the highest pressure to which III-V compounds have been studied.

The III-V compound GaSb was chosen for high-pressure x-ray diffraction studies primarily because its relatively low ionicity suggests that its high-pressure sequence of phase transitions should be similar to those of germanium and silicon, two elements whose high-pressure phase transitions have been extensively studied recently.[1,2] With the application of pressure, germanium[1] undergoes the sequence of transitions zinc blende → β-Sn → simple hexagonal → double hexagonal close packed in the range from 0 to 125 GPa, while silicon[2] undergoes the sequence zinc blende → β-Sn → simple hexagonal → intermediate phase → hcp → fcc in the range 0 to 100 GPa. Theoretical predictions of these phases and transition pressures in germanium[1] and silicon[3] were in good agreement with experiment. GaSb is known to transform from the zinc-blende to the β-Sn structure in the vicinity of 6.2 GPa (Refs. 4 and 5) in agreement with theory[6] but no further phase transitions have been discovered in this compound until now.

The ultrahigh-pressure study of GaSb is, furthermore, interesting in its own right. No III-V compound has been pressurized beyond relatively low pressures according to the standards set by modern megabar-range diamond-anvil cells.[7] The search for a more highly coordinated structure for III-V compounds is another motivation for this study. A transition to a simple hexagonal phase has been predicted at 52.8 GPa.[6]

A finely powdered GaSb sample (> 99.999% purity) was loaded into three high-pressure diamond-anvil cells. One of the cells employed beveled diamonds with 300-μm-diameter culets, 100-μm-diameter central flats, 5° bevel angles and a 50-μm-diameter sample region, and was used for taking data up to 110 GPa. The other two cells used 640 and 300 μm flat diamonds, respectively, and were used for pinpointing the pressures of the phase transitions found with the megabar cell.

All the data were taken using the energy-dispersive x-ray diffraction technique at the Cornell High Energy Synchrotron Source (CHESS). Most of the data were collected using a 20-μm collimator and an exposure of 1–2 h. For details of the experimental technique see Refs. 8 and 9. Pressure was measured by ruby fluorescence.[10]

At 6.0 GPa only diffraction peaks from the zinc-blende structure were present, but when the pressure was increased to 7.4 ± 0.4 GPa, peaks of the β-Sn phase were also clearly present. The volume decrease at this transition is 18.6%.

Figure 1 shows an energy dispersive x-ray diffraction (EDXD) spectrum taken of GaSb in the β-Sn structure at a pressure of 23.3 GPa. Table I compares the observed and calculated interplanar spacings and peak intensities based on the β-Sn structure. The data were analyzed as described in Ref. 9.

At 27.8 ± 0.6 GPa upon loading, the sample transformed to a simple-hexagonal-type structure. Figure 2 shows the EDXD spectrum of GaSb in this hexagonal phase at a pressure of 56.6 GPa. Table II lists the observed and calculated interplanar spacings and peak intensities assuming a disordered simple hexagonal structure. Unfortunately, it was not possible to determine the exact

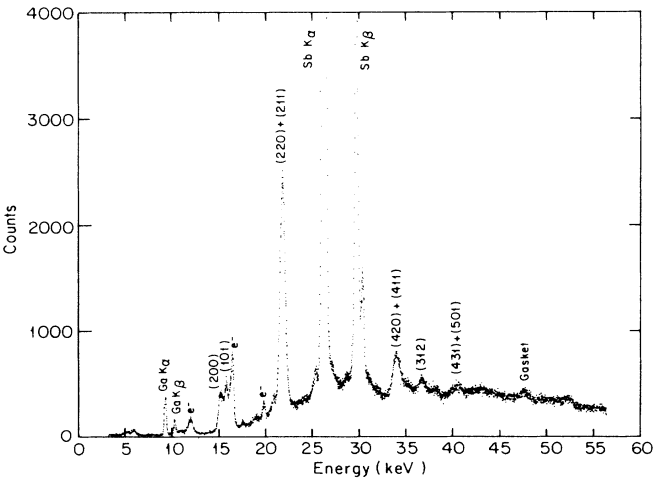

FIG. 1. EDXD spectrum of GaSb at a pressure of 23.3 GPa. The diffraction angle is 9.0350°. The sample is in the β-Sn structure at this pressure. Escape peaks from the detector are labeled e^-. The electron energy at CHESS was 5.3 GeV and average beam current was 30 mA.

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TABLE I. Comparison of calculated and experimental interplanar spacings and intensities of GaSb in the β-Sn structure at 23.3 GPa. The lattice parameters used are $a=5.1785$ Å and $c=2.8494$ Å. The calculated relative intensities were obtained using the procedure described in Ref. 9. A sample thickness of 20 μm was assumed.

hkl	d_{obs} (Å)	d_{calc} (Å)	Obs. int.	Calc. int.
200	2.610	2.589	20.0	43.7
101	2.482	2.496	44.8	47.0
220+211	1.811	1.831, 1.797	100.0%	100.0%
411+420	1.162	1.149, 1.158	49.0	14.5
312	1.076	1.075	14.0	9.2
431+501	0.974	0.973, 0.973	12.7	3.8

TABLE II. Comparison of calculated and experimental interplanar spacings and intensities of GaSb in the (disordered) simple-hexagonal-type structure at 56.6 GPa. The lattice parameters used are $a=2.6981$ Å and $c=2.4790$ Å. The calculated relative intensities were obtained using the procedure described in Ref. 9. A sample thickness of 20 μm was assumed.

hkl	d_{obs} (Å)	d_{calc} (Å)	Obs. int.	Calc. int.
001	2.468	2.479	33.2	18.0
100	2.336	2.336	64.7	57.9
101	1.702	1.700	100.0%	100.0%
110	1.348	1.349	30.5	27.9
002	1.240	1.240	4.9	6.8
111+200	1.185	1.185, 1.168	61.5	47.2

ordering of the gallium and antimony atoms in the lattice due to the fact that certain important peaks were obscured by other peaks. In particular, we were unable to confirm or deny the hexagonal ordering suggested by Zhang and Cohen,[6] which is quasieightfold with six nearest-neighbor atoms at a distance of 2.698 Å and two at 2.479 Å.

Finally, at 61.0 ± 0.7 GPa upon loading, a phase transition occurred from the simple-hexagonal-type structure to another structure. The phase transition is quite distinct and is marked by the disappearance of the (001) reflection of the simple hexagonal (SH) phase and the appearance of additional strong diffraction peaks. The sample remains in this structure up to the maximum pressure of 110 GPa reached in this experiment. The ruby-fluorescence spectrum at this pressure is shown in Fig. 3. It still shows distinct R_1 and R_2 peaks. In expectation of a high-pressure phase-transition sequence for GaSb similar to that of germanium[1] or silicon,[2] we tried indexing the observed peaks to various close-packed hexagonal structures including the hcp, dhcp, and fcc structures, but none of these structures agreed well with the observed peaks. We did find, though, that the observed interplanar spacings and intensities can be satisfactorily described by an orthorhombic unit cell with atoms at 000 and $\frac{1}{2}\frac{1}{2}0$. This structure can be obtained by an orthorhombic distortion of the simple hexagonal lattice. We list the calculated and experimental interplanar spacings and intensities assuming this structure in Table III. Again, the scattering factors of gallium and antimony atoms are not sufficiently different to determine their ordering in the tentative structure. We also emphasize that due to the limitations of the EDXD method such as the poor resolution of closely spaced diffraction lines, we choose to not make a definite claim for this structure. It is worth noting, though, that Kasper and Brandhorst[11] proposed this same structure for the orthorhombic phase of InSb (InSb IV). A plot of the reduced-volume-versus-pressure equation of state of GaSb is shown in Fig. 4, including the tentative orthorhombic structure as a dashed line.

The P-V data for the various phases were fitted with a Birch[12] first-order equation of state

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

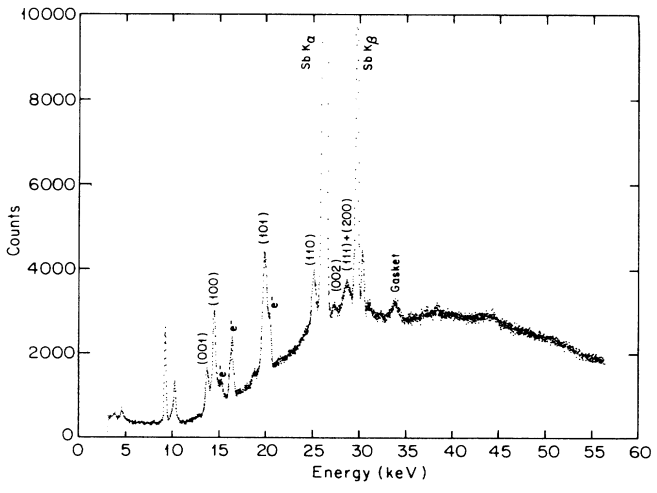

FIG. 2. EDXD spectrum of GaSb at a pressure of 56.6 GPa. The diffraction angle is 10.5235°. The sample is in the simple hexagonal structure at this pressure. Escape peaks from the detector are labeled e^-. The electron energy at CHESS was 5.3 GeV and average beam current was 30 mA.

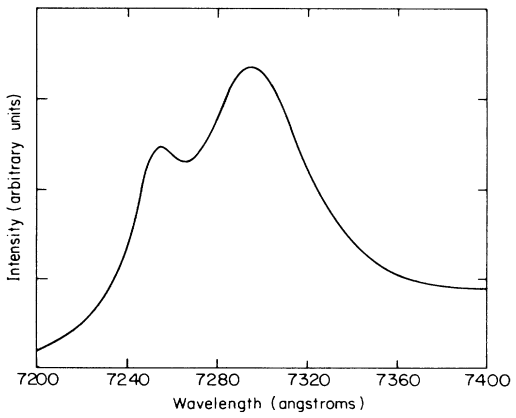

FIG. 3. The ruby fluorescence spectrum taken at the maximum pressure of 110 GPa. Note that the R_1 and R_2 fluorescence lines can still be resolved at this pressure.

TABLE III. Comparison of calculated and experimental interplanar spacings and intensities of GaSb in the tentative (disordered) orthorhombic structure at 92.4 GPa. The lattice parameters used are $a=2.6122$ Å, $b=4.2727$ Å, and $c=2.2479$ Å. The calculated relative intensities were obtained using the procedure described in Ref. 9. A sample thickness of 20 μm was assumed.

hkl	d_{obs} (Å)	d_{calc} (Å)	Obs. int.	Calc. int.
001	2.262	2.248	11.2	33.0
110+020	2.169	2.229, 2.136	100.0	100.0%
021	1.549	1.549	21.3	47.3
200	1.305	1.306	16.3	14.5
130	1.255	1.250	38.0	25.0
201+002	1.130	1.129, 1.124	2.6	21.6
131	1.100	1.093	4.0	23.8

where

$$x=V_N/V \tag{2}$$

and V is the volume per GaSb pair, V_N is a fitting parameter which corresponds to the extrapolated volume per GaSb pair of the Nth phase at zero pressure, B_0 is the isothermal bulk modulus at zero pressure, and B_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure. These results are shown in Table IV. Here V_0 is the volume of the GaSb pair in the zinc-blende phase at zero pressure (57.01 Å^3).

Upon decreasing the pressure of the diamond-anvil cell from 110 GPa, we found a large degree of hysteresis at the hexagonal-to-tentative-orthorhombic transition. Whereas the sample started to transform from the hexagonal to the tentative orthorhombic phase at 61 GPa with increasing pressure, no transition back to the hexagonal

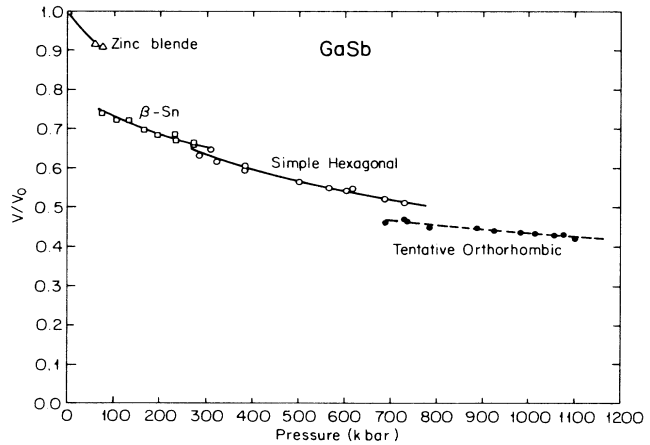

FIG. 4. Plot of reduced volume vs pressure to 1100 kbar (110 GPa). The solid and dashed lines result from fits of the data to the first-order Birch (Ref. 12) equation. The parameters obtained by these fits are listed in Table IV. Although peaks began to appear for the structure tentatively indexed as orthorhombic at 61 GPa, insufficient data were present to get an accurate volume until higher pressures were reached.

TABLE IV. Parameters obtained by fit of the Birch first-order equation of state.

Structure	V_N/V_0	B_0 (GPa)	B_0'
Zinc blende	1.000	56.1[a]	4.78[a]
β-Sn	0.817 ± 0.005	58.8 ± 1.7	7.7 ± 0.04
Simple hexagonal	0.918 ± 0.006	37.1 ± 0.5	4.2 ± 0.01
Tentative orthorhombic	0.722 ± 0.005	44.7 ± 0.5	5.9 ± 0.01

[a]These values for B_0 and B_0' of the zinc-blende structure were obtained from Ref. 13.

phase was found upon decreasing the pressure (from a maximum pressure of 110 GPa) through this region. Only when the pressure was decreased to 38.0 GPa were the lines corresponding to the hexagonal phase seen. The hysteresis associated with the β-Sn to hexagonal transition was much less, the transition occurring at 25 GPa with decreasing pressure while the transition occurred at 27.8 GPa with increasing pressure. Taking the average of these two pressures, we obtain a value of 26.4 ± 2.6 GPa for the β-Sn to simple-hexagonal transition pressure. Using the fitted curves the volume per GaSb pair of the β-Sn phase at this pressure is 37.78 Å^3 and the volume decreases by 2.0% at the transition.

It is interesting to note that the β-Sn to simple hexagonal transition pressure of 26.4 ± 2.6 GPa found in this experiment is much lower than that of 52.8 GPa predicted by the recent *ab initio* pseudopotential energy calculations of Zhang and Cohen[6] for a hexagonal phase with six unlike neighbors and two like nearest neighbors. However, we note that these calculations did predict correctly a transition to the simple hexagonal phase. As mentioned earlier, we were unable to determine the atomic ordering of the gallium and antimony atoms. No theoretical predictions have been made for the phase appearing at 61 GPa which we have tentatively indexed as an orthorhombic structure.

In summary, we report two new phase transitions in GaSb to 110 GPa as well as confirming the zinc-blende to β-Sn transition. (1) The transition from β-Sn to the simple hexagonal structure occurs at 27.8 GPa on loading and 25.0 GPa on unloading. (2) We were unable to confirm or refute that this was an ordered structure. (3) The pressure at which this transition occurs (26.4 GPa) is substantially lower than the recent theoretical calculation[6] of 52.8 GPa. (4) A further transition occurs on loading at 61.0 GPa to a structure which is tentatively indexed as a disordered orthorhombic structure with a basis 000 and $\frac{1}{2}\frac{1}{2}0$. There is a large hysteresis associated with this transition.

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