Calculated equation of state of InAs

N. E. Christensen

*Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80,
Federal Republic of Germany*

Local-density-functional total-energy calculations for InAs are used to derive equilibrium volume and bulk modulus. Further, the zinc blende → rocksalt → β-tin pressure-induced structural phase transitions are determined. Recently published experimental results allow a detailed comparison to the theoretical volume-pressure relations of InAs in all three structures, and excellent agreement is found.

I. INTRODUCTION

In a recent publication[1] Vohra, Weir, and Ruoff report the results of an experimental determination of the crystal structure and the pressure-volume $(P\text{-}V)$ relation of InAs using energy-dispersive x-ray diffraction and the diamond-anvil technique. Their analysis[1] showed that InAs transforms from the zinc-blende $(B3)$ structure to the rock-salt structure $(B1)$ at 70 ± 2 kbar and further to a β-Sn type structure at 170 ± 4 kbar. Since the detailed experimental data for each structure were carefully fitted[1] to analytic equations of state, a unique possibility for comparison to first-principles theoretical calculations over a wide pressure range exists.

Indeed, $P\text{-}V$ relations for compound semiconductors have been reported earlier.[2-12] These all use the local approximation to the density-functional theory.[13-15] One reason, namely, the opportunity for a detailed comparison to experiments, for presenting yet another local-density-approximation (LDA) total-energy calculation has already been given above. Another reason is that the work of Ref. 9 seems to imply that the atomic-sphere approximations inherent in the band-structure scheme,[16] augmented spherical waves (ASW), used by Carlsson and Wilkins[8] are not sufficiently accurate for calculations for crystals with open structures like $B3$ and $B1$. We use the relativistic linear muffin-tin orbital (LMTO) method,[17] of which the ASW can be considered a descendent. Thus, we have in our scheme similar shape approximations (which in some cases must be corrected for[10]), but it was previously shown[18,19] that the introduction of "empty spheres" at the interstitial positions in the diamond lattice produces a structure that is so close packed that the LMTO calculations can reliably predict many ground-state properties. The present calculations improve on those of Ref. 8, which showed that the atomic-sphere approximation implemented with only one sphere per "real" atom results in errors for $B1$ (and $B3$) compounds. Thus, the fact that an underestimate by 16% of the equilibrium volume of BaTe was found[8] should not be taken as a measure of the errors in the ASW and LMTO methods, but rather considered as resulting from the use of a small basis set which can be straightforwardly expanded.

A third objective of the present publication is to comment briefly on the results obtained[5,6] for ZnTe, CdTe, and ZnSe under pressure. Although we found good values for the equilibrium volumes and bulk moduli, the calculated $P\text{-}V$ relations deviated from experiment for P above $\approx 20\text{--}30$ kbar. This was[5,6] tentatively ascribed to a too crude descrip-

tion of the Zn-$3d$ and Cd-$4d$ states in the atomic-sphere approximation (ASA). We also include in the present calculations for InAs the In-$4d$ states (self-consistently) as band states, but since they are more localized than the Zn-$3d$ and Cd-$4d$ states in the compounds mentioned above, their influence on the bonding is less important. Thus, we would expect to obtain $P\text{-}V$ relations of a quality that is similar to that of GaAs (Refs. 4 and 20). As follows from Sec. II, where the results are presented, this is indeed the case.

II. CALCULATED $P\text{-}V$ RELATIONS FOR InAs

The self-consistent LMTO calculations for InAs in the zinc-blende $(B3)$ and rocksalt $(B1)$ structures were calculated by introducing empty spheres. In $B3$, indium occupies the sites (000), As$(111)a/4$, whereas two inequivalent empty spheres are located at E_1:$(111)a/2$ and E_2:$(333)a/4$. The $B1$ structure is obtained by interchanging As and E_1 (and then E_1 and E_2 become equivalent). The β-Sn type structure can be considered as a body-centered tetragonal lattice with two atoms associated to each lattice point. The In atoms are located at the lattice points and As displaced from them by vectors $(1,0,1/2c/a)a/2$, where c/a is the axial ratio. The ideal β-Sn structure, corresponding to the exact coordination number (CN) 6, would have $c/a = \sqrt{(4/15)} \simeq 0.5164$. The β-Sn phase of InAs deviates somewhat from this, having $c/a \simeq 0.503$ at the transition,[1] and a c/a ratio that increases somewhat with further compression.[1] We have decided to keep c/a fixed $(= 0.505)$ in all our calculations for this type of structure. A total-energy minimization with respect to c/a could be performed, but this would require some refinements[10] of our total-energy calculations. The β-Sn structure is so close packed that we did not in that case introduce empty spheres. The energy ranges of the band structures are, in particular for the compressed crystals (β-Sn), so large that two linearization regimes (i.e., two "energy panels"[4,19]) had to be used.[21]

All our band calculations, which are relativistic, include the so-called combined correction term[17] which corrects for the deviation between the actual cell shape and spheres in the calculation of the LMTO overlap integrals. In addition,[22] this term compensates for the truncation of the angular-momentum expansions at a finite l (we include here s, p, and d partial waves).

The total energy (E) was calculated from the ASA version of the total-energy functional in the local-density ap-

proximation (LDA). However, a small correction, the ASA approximation to the muffin-tin Coulomb cell-cell interaction was included (see ΔU_{MT}^{ASA} in Ref. 10). This term has little importance in the present calculations for the $B1$ and $B3$ structures, but is somewhat more significant for the comparison of the $B1$ and β-Sn total energies.

The stable structure, at a given pressure, is determined as the one for which Gibbs free energy is lowest. At $T = 0$ K this is simply the enthalpy $H = E + PV$. We calculated, for a large number of volumes, the total energy, the pressure, and derived H as a function of (the theoretical) pressure. The results of these calculations for InAs are shown in Fig. 1. It follows that the zinc-blende structure is stable up to $P_t^{(1)} = 78$ kbar, $B1$ from this pressure and up to $P_t^{(2)} \cong 195$ kbar above which the β-Sn-type structure has the lowest enthalpy. These transition pressures (and the sequence) agree well with the experimental data; ($P_t^{(1)} = 70 \pm 2$ kbar, $P_t^{(2)} = 170 \pm 4$ kbar). $P_t^{(2)}$, however, is a little overestimated in the calculation.

The theoretical P-V relation is shown in Fig. 2. The lower scale gives the lattice dimensions in terms of an atomic-sphere radius S. This is defined in such a way that the crystal volume is filled by associating four spheres of equal radius, S to each lattice point. This scale also refers to the β-Sn structure, although in reality only two spheres per point are used in the calculation. The upper horizontal axis gives the volume relative to the experimental equilibrium volume.

The theoretical equilibrium volume agrees with the observed. Also the bulk modulus as calculated ($B_0 = 581$ kbar) agrees extremely well with the result (580 kbar) obtained[23] from ultrasonic data, and with the value (592 ± 5 kbar) deduced by Vohra et al.[1] It follows from Fig. 2 that,

FIG. 2. The curves show the calculated P-V relations for InAs in the zinc-blende ($B3$), rocksalt ($B1$), and β-Sn-type structures. The parts of the curves drawn from full lines represent the stable phases. The lower scale gives the radius (S) of space-filling atomic spheres assuming four spheres per lattice point (see text). The upper scale gives the volume relative to the observed equilibrium volume, $V_0(B3)$. Experimental data (circles, triangles, and crosses) are calculated from the Birch equations given in Ref. 1.

according to the present theory, both structural phase transitions are associated with volume reductions. The $B3 \rightarrow B1$ transition occurs with a volume change of 17.3%, whereas the $B1 \rightarrow \beta$-Sn transition is accompanied by a volume reduction of only $\cong 0.5\%$. These two numbers also agree with the observations. Vohra et al.[1] found that the first transition had a (17.0 ± 0.2)% volume reduction, whereas within the experimental accuracy, no volume change could be observed for the second transition.

The experimental P-V relations for the three phases of InAs are indicated in Fig. 2 by circles, triangles, and crosses. These were calculated from the first-order Birch equation with the parameters given in Ref. 1. For all three structures excellent agreement is found. The only noteworthy deviations are maybe the slightly larger equilibrium volumes extrapolated to $P = 0$ from the experimental data for the compound in the β-Sn and $B1$ structures.
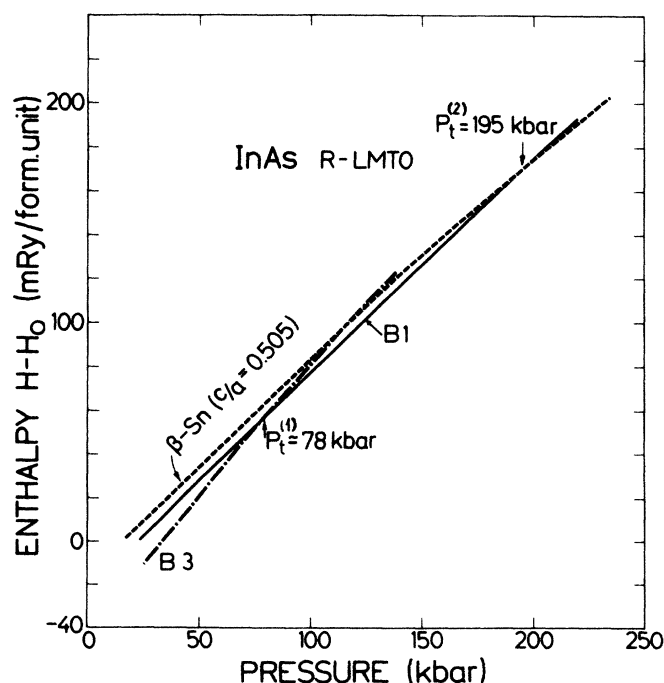

FIG. 1. Calculated enthalpies for InAs in the zinc-blende ($B3$), rocksalt ($B1$), and β-Sn-type structures. $P_t^{(1)}$ and $P_t^{(2)}$ are the theoretical transition pressures.
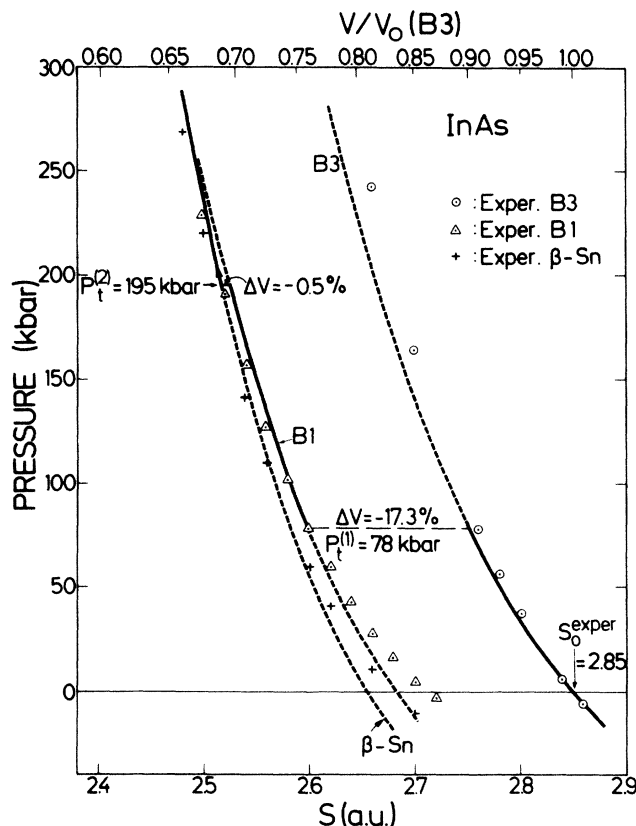
III. CONCLUDING REMARKS

The equation of state calculated from first principles within the local-density approximation for InAs, considering the three observed crystal structures, agree extremely well

with experiment.[1] This applies to the calculated characteristic pressures, as well as the volume change accompanying the transitions. InAs in the $B3$ structure is semiconducting,[24] whereas we find the two other phases to be metallic. Some insight in the mechanism of the $B3 \rightarrow B1$ transition is obtained by a "frozen potential" analysis as presented in Ref. 5. The covalent energy stabilizes the $B3$ structure at low pressures, but when the volume is reduced, the Madelung term drives the structure into $B1$ in which it can overcome the bonding contribution due to the larger coordination number. We have not yet performed a similar analysis of the $B1 \rightarrow \beta$-Sn transition. It is, however, not surprising that the β-Sn structure is favorable for compressed compounds of the type considered here. The

coordination number is approximately the same as in $B1$ [for $c/a = \sqrt{(4/15)}$ is the same, CN6]. In addition, it allows the formation of bonds which have some reminiscence of the covalent bonds in the sp^3 bonded semiconductors. It will be interesting to examine whether such bonds increase in strength when the pressure is increased beyond the range considered here. It might be expected to be the case, and simultaneously the c/a ratio should increase with P. Such an increase was indeed observed, and in our tentative picture the actual c/a ratio at a given pressure is simply determined by the competition between the covalent bonding, trying to increase c/a to the theoretical limit,[25] $\sqrt{2}$, and the point-ion Coulomb interaction favoring the structure with larger "effective" coordination number.

[1]Y. K. Vohra, S. T. Weir, and A. L. Ruoff, Phys. Rev. B **31**, 7344 (1985).

[2]S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

[3]K. J. Chang, S. Froyen, and M. L. Cohen, Phys. Rev. B **28**, 4736 (1983).

[4]N. E. Christensen, Phys. Rev. B **32**, 207 (1985).

[5]N. E. Christensen and O. B. Christensen, Phys. Rev. B (to be published).

[6]S. Ves, K. Strössner, N. E. Christensen, C. K. Kim, and M. Cardona, Solid State Commun. **56**, 479 (1985).

[7]N. E. Christensen, Phys. Status Solidi B **123**, 281 (1984).

[8]A. E. Carlsson and J. W. Wilkins, Phys. Rev. B **29**, 5836 (1984).

[9]S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).

[10]N. E. Christensen and S. Satpathy, Phys. Rev. Lett. **55**, 600 (1985).

[11]S. Satpathy, N. E. Christensen, and O. Jepsen, Phys. Rev. B **32**, 6793 (1985).

[12]References 2–11 given above are not a complete list of works presenting total-energy calculations for semiconductors under pressure. They have been chosen in order to represent a wide selection of group-IV elemental and III-V, II-VI, and I-VII compound semiconductors. Further theoretical studies are referred to in the publications listed (2–11).

[13]P. Hohenberg and W. Kohn, Phys. Rev. **13**, B864 (1964).

[14]W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1113 (1985).

[15]L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[16]A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B **19**, 6094 (1979).

[17]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[18]See, for example, the equation of state of GaAs given in Fig. 4 of Ref. 4 and the comparison between the first-principles pseudopotential calculation and the LMTO bands in Ref. 19.

[19]G. B. Bachelet and N. E. Christensen, Phys. Rev. B **31**, 879 (1985).

[20]M. Hanfland, K. Syassen, and N. E. Christensen, J. Phys. (Paris) Colloq. **45**, C8-57 (1984).

[21]The use of two energy panels is, in fact, also necessary in the case of BaTe under pressure [N. E. Christensen (unpublished)]. This is probably also relevant in a discussion of the calculation of Ref. 8. The same is the case for compressed CsI (Refs. 10 and 11).

[22]In Ref. 8 it is stated that ASW has the same accuracy as LMTO with the combined correction term. It should be noted, however, that the ASW only includes the first part of the correction, i.e., the finite-l summation is not corrected for. It might be assumed that this is the reason why the inclusion of f states appeared to be important to some of the calculated quantities in Ref. 8. Nevertheless, we also need to include f partial waves to obtain reliable calculations of the gaps in compressed BaTe [N. E. Christensen (unpublished)].

[23]K. Kunc, Ann. Phys. (N.Y.) **8**, 319 (1973).

[24]The LDA underestimates the gaps in semiconductors. In the case of InAs we find that the direct gap at Γ, in fact, is closed at equilibrium. The Γ_6 conduction state lies slightly below the p-band top. The overlap and the error in occupation numbers, however, are so small that the total energies are not affected by this. Increasing the (theoretical) pressure to $\sim$ 10 kbar produces a gap.

[25]For $c/a = \sqrt{2}$ the β-Sn structure is equivalent to $B3$, i.e., the tetrahedral bond angle is restored.