Instability of the high-pressure CsCl structure in most III-V semiconductors

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Using the density-functional linear response method, we study dynamical instabilities of the high-pressure CsCl phase in III-V semiconductors. For InSb, we find no phonon instability that could prevent the CsCl phase from forming, consistent with the experimental observation. In contrast, for the more ionic GaP, GaAs, InP, and InAs, we find that, while statically stable, the CsCl phase is dynamically unstable at high pressures with respect to transverse-acoustic $[\xi\xi 0]$ phonons. Analysis of the soft normal modes via ''isotropy subgroup'' suggests two candidate structures that will replace CsCl structure at high pressure: the tP4 (B10) InBi type and the oP4 (B19) AuCd type. Experimental examination of these predictions is called for.

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The classic thinking on the phase stability of covalent zinc-blende semiconductors suggests[1–3] that as pressure is applied these phases transform into crystal structures that exist at zero pressure in more ionic $A^{(n)}B^{(8-n)}$ octet com-

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$[1\bar{1}0]$. We see that such distortions result in a lower energy phase when the volume V/V_0 (where V_0 is the theoretical equilibrium volume in zinc-blende phase,) is smaller than about 0.42. This is still in the volume regime where static calculations of the type shown in Fig. 1 predict a stable CsCl phase. Figure 2(b) shows the total-energy changes due to tetragonal c/a distortions, carrying the B2 (CsCl) structure (cubic symmetry) to the $\mathrm{L1}_0$ (CuAu) structure (tetragonal symmetry). We see that here too the B2 structure is unstable in the volume range $V/V_0 = 0.40 - 0.55$. As the volume is decreased below $V/V_0 = 0.45$, a second minimum around $c/a = 1.7$ appears. The shear modulus $C_s = (C_{11} - C_{12})/2$ of the CsCl structure, given by the curvature of the total energy around $c/a = 1$ in Fig.2(b), becomes soft when V/V_0 is below 0.45. The velocity of a $[\bar{1}10]$-polarized shear wave propagating along the $[110]$ direction is given[15] by $V_{s[\bar{1}10]} = [(C_{11} - C_{12})/2\rho]^{1/2}$, where ρ is the mass density. Thus, the softening of the shear modulus indicates a corresponding softening of acoustic phonon mode along the $[110]$ direction with atomic displacements polarized in the $[\bar{1}10]$ direction. Results similar to those shown in Fig. 2 for InP were obtained for InAs showing its instability in the B2 structure. However, for InSb, the B2 structure was stable with respect to both distortions.

We thus see that even though static total-energy calculations of hydrostatic compression suggest the stability of the assumed B2 structure of InP and InAs in some volume range, nonhydrostatic strain (Fig. 2) clearly demonstrates that this phase is unstable in these volume ranges. While calculations

pha Fig. 2

eter irreducible representations are compiled by Stokes and Hatch.[19] There are 6 isotropy subgroups for M_2^- and 26 subgroups for M

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meV between B10 and B2 and -92 meV between B19 and B2.

In conclusion, we found that the CsCl structure is dynamically unstable for InP as well as for GaP, GaAs, and InAs. For InP, it could be replaced by the B10 and the B19 structures while other structural modifications are possible[18] (Table I), the general method we have outlined is capable of finding the stablest. For InSb, our calculations show no instability, which is consistent with experimental observation of the B2 (or disordered bcc) phase.[13] Experimental searches for the proposed B10 and B19 crystal structures are called for.

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