

Theory of Systematic Absence of NaCl-Type (β -Sn-Type) High Pressure Phases in Covalent (Ionic) Semiconductors

V. Ozoliņš and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 23 July 1998)

Recent high pressure x-ray experiments show that, contrary to traditional expectations, the NaCl structure is not present in covalent semiconductors, and the diatomic b-Sn structure is absent in all compound semiconductors. We explain these systematic absences in terms of dynamical phonon instabilities of the NaCl and b-Sn crystal structures. Covalent materials in the NaCl structure become dynamically unstable with respect to the transverse acoustic TA[001] phonon, while ionic compounds in the b-Sn structure exhibit phonon instabilities in the longitudinal optical LO Γ g branch. The latter lead to predicted new high pressure phases of octet semiconductors. [S0031-9007(98)08188-5]

PACS numbers: 61.50.Ah, 63.20.Dj, 64.60.-i

Our traditional understanding of structure and bonding in $A^N B^{8-2N}$ octet semiconductors [1–4] is based on the time-honored notion of competition between “covalent” fourfold coordinated structures [diamond, zinc blende (ZB)], “ionic” sixfold coordinated structures (NaCl), and “metallic” structures (diatomic b-Sn). As pressure is raised, one expects [5] that all semiconductors show the sequence of ZB \rightarrow NaCl \rightarrow b-Sn structural phase transitions. Indeed, the NaCl high pressure phase was reported in many semiconductors [6] (InP, InAs, CdSe, CdTe, HgSe, and GaN), as was the high pressure diatomic b-Sn structure [6] (AlSb, GaSb, InSb, GaP, InP, InAs, and CdTe). As first-principles approaches to the electronic structure of solids became available [7], total energy vs volume curves were calculated for ZB, NaCl, and b-

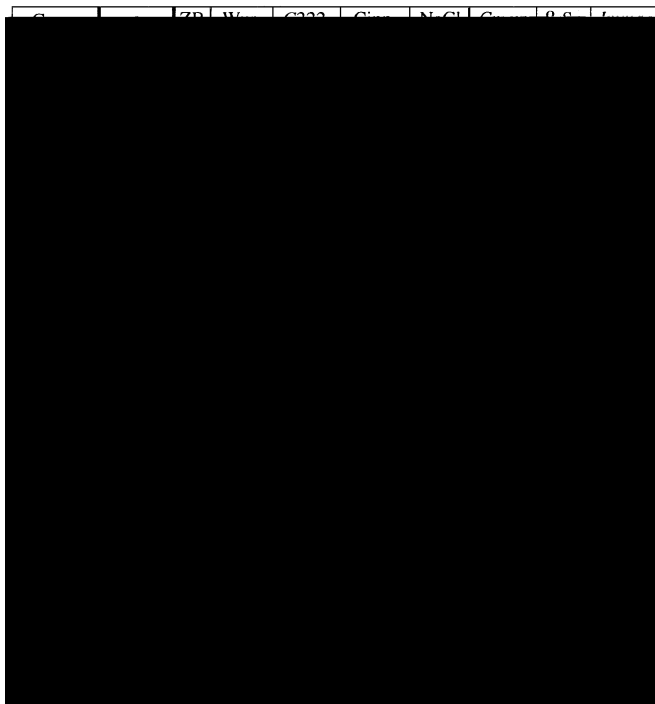


FIG. 2. Observed [6,15] high pressure structures of semiconductor compounds. Increasing pressure corresponds to going from left to right. “1” indicates that the corresponding phase has been observed, and “(1)” mark the cases where some doubt exists about the identity of the phase. The dots indicate the systematic absence of phases. g is the ionicity scale defined in Ref. [16].

However, this approach may have some shortcomings: (i) It may miss unsuspected, yet more stable structures and/or (ii) result in theoretically predicted transitions that are unphysical because the predicted phases could be dynamically unstable. In either case, static $E^{\text{as}}V_d$ calculations do not contain any “feedback information” telling us whether case (i) or (ii) has occurred and how to search for the physical phase.

We have first carried out traditional local density approximation (LDA) pseudopotential [7] calculations of $E^{\text{as}}V_d$ for many semiconductors, spanning a broad range of ionicities [16]. We studied the standard zinc blende ($B3$), NaCl ($B1$), and diatomic b-Sn ($A5$) structures; in our approach, this initial set of structures need not contain the most stable high pressure forms. We then perform phonon dispersion calculations for the high pressure phases using the first-principles LDA linear response approach [17,18]. We find that for covalent compounds (GaAs, InSb, GaSb, GaP, and AlAs) the transverse acoustic (TA) zone boundary X -point phonon mode n_{TA,X_d} of the NaCl structure becomes dynamically unstable ($n_{\text{TA},X_d}^2 < 0$) at a volume V_{du}^{B1} that precedes the $ZB \rightarrow \text{NaCl}$ transition volume $V_t^{B3 \rightarrow B1}$, so the NaCl structure cannot materialize at $T = 0$ K in these compounds. Yet, for “ionic” compounds (AlP, InP, and ZnO) the instability sets in after the $B3 \rightarrow B1$ transition pressure, so the NaCl structure can be stable over some pressure range. The bottom part of Fig. 1 shows via ar-



