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

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Recent high pressure x-ray experiments show that, contrary to traditional expectations, the NaCl structure is not present in covalent semiconductors, and the diatomic β-Sn structure is absent in all compound semiconductors. We explain these systematic absences in terms of dynamical phonon instabilities of the NaCl and β-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 β-Sn structure exhibit phonon instabilities in the longitudinal optical LO$[00\xi]$ branch. The latter lead to predicted new high pressure phases of octet semiconductors. [S0031-9007(98)08188-5]

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Our traditional understanding of structure and bonding in $A^N B^{8-N}$ 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 β-Sn). As pressure is raised, one expects [5] that all semiconductors show the sequence of ZB → NaCl → β-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 β-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 β-Sn phases of numerous compounds [8–11]. Having restricted the configuration space to these phases, such calculations showed, via the common tangent construction (Fig. 1), that a ZB → NaCl → β-Sn transition sequence is a universal feature for most octet compounds. This consistent body of experimental [6] and theoretical [8–11] studies of the ZB → NaCl → β-Sn transitions in octet semiconductors revealed interesting chemical regularities and structural systematics that came to occupy a central role in our understanding of structure and bonding [1–4] in this important class of materials.

The recent advent of angle-dispersive x-ray diffraction techniques through the high pressure diamond anvil cells [12,13] has surprisingly revealed that all previous assignments of the β-Sn structure to compound semiconductors are incorrect [14] and so are many of the assigned NaCl structures [15]. In Fig. 2 we have collected and systematized all of the observed data on the sequence of high pressure phases of all $A^N B^{8-N}$ octet compounds in increasing order of pressure (from left to right) and decreasing order of ionicity [16] (from top to bottom). The surprising result is that there is a *systematic absence* of the NaCl phase for all covalent compounds below a critical ionicity value (e.g., GaSb, InSb, AlAs, GaAs, and GaP do not have a stable NaCl phase, but InAs, InP, and ZnO adopt this structure under pressure) and a systematic absence of the β-Sn phase for all compounds, except the most covalent. These "absent structures" are highlighted as the shaded regions in Fig. 2. This realization is very important, since, by invalidating the traditional expectation of a universal structural sequence for the octet family, it also exposes the weakness of the standard theoretical approach ("rounding up the usual suspects") to predicting phase diagrams: these methods work if we know in advance the configuration of the stable (i.e., observed) high pressure phases.

In this work we focus on the *systematic absence of certain phases* (Fig. 2) rather than on the properties of presumed phases. We note that the traditional total energy vs volume $E^{\alpha}(V)$ calculations for preselected phases $\alpha, \beta, \gamma, \dots$, which are thought to be viable candidates on the basis of the empirical tradition of the time, can produce predicted transition pressures $P_t^{\alpha/\beta}, P_t^{\beta/\gamma}, \dots$, delineating the domains of static stability of these phases.

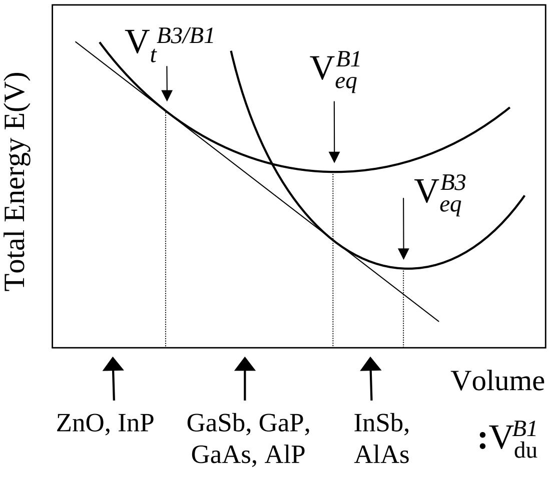

FIG. 1. Equations of state for the zinc blende and NaCl structures, showing the equilibrium volumes of zinc blende (V_{eq}^{B3}), NaCl (V_{eq}^{B1}), and the ZB → NaCl transition volume ($V_t^{B3/B1}$). Arrows show the regions where the TA(X)-phonon mode of NaCl becomes dynamically unstable (du).

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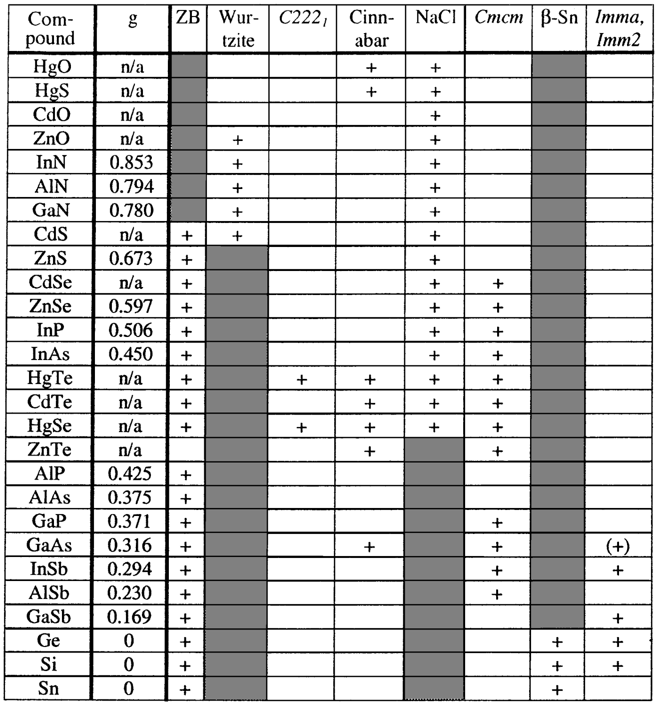

Compound	g	ZB	Wurtzite	*C222₁*	Cinnabar	NaCl	*Cmcm*	β-Sn	*Imma, Imm2*
HgO	n/a	▨			+	+		▨	
HgS	n/a	▨			+	+		▨	
CdO	n/a	▨				+		▨	
ZnO	n/a	▨	+			+		▨	
InN	0.853	▨	+			+		▨	
AlN	0.794	▨	+			+		▨	
GaN	0.780	▨	+			+		▨	
CdS	n/a	+	+			+		▨	
ZnS	0.673	+	▨			+		▨	
CdSe	n/a	+	▨			+	+	▨	
ZnSe	0.597	+	▨			+	+	▨	
InP	0.506	+	▨			+	+	▨	
InAs	0.450	+	▨			+	+	▨	
HgTe	n/a	+	▨	+	+	+	+	▨	
CdTe	n/a	+	▨		+	+	+	▨	
HgSe	n/a	+	▨	+	+	+	+	▨	
ZnTe	n/a		▨		+	▨	+	▨	
AlP	0.425	+	▨			▨		▨	
AlAs	0.375	+	▨			▨		▨	
GaP	0.371	+	▨			▨	+	▨	
GaAs	0.316	+	▨		+	▨	+	▨	(+)
InSb	0.294	+	▨			▨	+	▨	+
AlSb	0.230	+	▨			▨	+	▨	
GaSb	0.169	+	▨			▨		▨	+
Ge	0	+	▨			▨		+	+
Si	0	+	▨			▨		+	+
Sn	0	+	▨			▨		+	

FIG. 2. Observed [6,15] high pressure structures of semiconductor compounds. Increasing pressure corresponds to going from left to right. "+" indicates that the corresponding phase has been observed, and "(+)" 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 $E^{\alpha}(V)$ 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 $E^{\alpha}(V)$ for many semiconductors, spanning a broad range of ionicities [16]. We studied the standard zinc blende ($B3$), NaCl ($B1$), and diatomic β-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 $\nu_{\mathrm{TA}(X)}$ of the NaCl structure becomes dynamically unstable ($\nu^2_{\mathrm{TA}(X)} < 0$) at a volume V^{B1}_{du} that precedes the ZB → NaCl transition volume $V_t^{B3/B1}$, 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 arrows the volume V^{B1}_{du} at which the high pressure $B1$ phase becomes dynamically unstable (du). Thus, *a specific dynamic instability provides a natural demarcation line for the systematic absence of the NaCl phase.* We identify from the unstable phonon eigenvectors the "structural motif" that is dynamically stabilized and obtain the identity of the dynamically stable high pressure phase. We suggest that the ubiquitous presence of the recently discovered *Cmcm* phase [15] in the III-V compounds is caused by this universal instability of the TA(X) mode in the NaCl structure. Similarly, the diatomic β-Sn structure of the ionic compound semicondutors has phonon instabilities in the longitudinal optical (LO) branch along the $[00\xi]$ direction, which lead to distorted structures with considerably lower energies than the diatomic β-Sn structure. This family of structures is offered as a prediction and is yet to be identified experimentally.

(i) Dynamical instability of the NaCl structure and the emergence of Cmcm.—We determine (Table I) the respective equilibrium volumes of each phase V^{α}_{eq}, as well as the transition volumes $V_t^{\alpha/\beta}$ and pressures $P_t^{\alpha/\beta}$ (see their definitions in Fig. 1). From the phonon dispersion curves of GaP in the NaCl structure (shown in Fig. 3), we see that at the equilibrium volume of the NaCl structure, V^{B1}_{eq}, all phonon modes are stable ($\nu_i^2 > 0$). With increasing pressure (decreasing V) the frequencies of the optical modes increase sharply, while the frequencies of the TA branch along $[\xi 00]$ decrease. This decrease implies negative Grüneisen parameters $\gamma_i = \frac{\partial \ln \nu_i}{\partial \ln V} < 0$ of the TA$[\xi 00]$ modes in the NaCl structure at all pressures. At the transition volume $V_t^{B3/B1}$ from the zinc blende to the NaCl phase (Table I), the frequency of this branch has become imaginary at the zone boundary X point [see Fig. 3(b)], signaling a structural instability of the NaCl phase. Inspection of the phonon eigenvectors shows that this mode involves alternate shuffles of (100) planes in the direction perpendicular to [100], as shown in the inset of

TABLE I. Normalized equilibrium volumes of the NaCl ($B1$) and β-Sn ($A5$) structures, along with the transition pressures $P_t^{\alpha/\beta}$ (kbar) and normalized transition volumes $V_t^{\alpha/\beta}$ between phases α and β. "n/a" denotes that the corresponding transition does not occur for the investigated range of positive $P_t^{\alpha/\beta}$. All volumes are given as fractions of the equilibrium volumes of the respective zinc blende phases.

	V^{α}_{eq}		$P_t^{\alpha/\beta}$			$V_t^{\alpha/\beta}$		
Compound	$B1$	$A5$	$B3/B1$	$B3/A5$	$B1/A5$	$B3/B1$	$B3/A5$	$B1/A5$
ZnO	0.826	n/a	7.3	43.7	n/a	0.795	0.659	n/a
InP	0.799	0.785	5.4	9.7	45.0	0.759	0.714	0.592
AlP	0.783	n/a	9.2	18.1	157	0.729	0.684	0.451
AlAs	0.788	0.790	7.9	14.2	82	0.736	0.701	0.498
GaP	0.820	0.792	16.8	16.9	17.1	0.725	0.698	0.697
GaAs	0.821	0.800	12.4	11.7	6.5	0.739	0.720	0.772
InSb	0.796	0.776	2.1	1.6	n/a	0.771	0.756	n/a
GaSb	0.815	0.806	5.2	4.7	n/a	0.764	0.759	n/a
Si	0.796	0.755	12.6	7.7	n/a	0.723	0.713	n/a

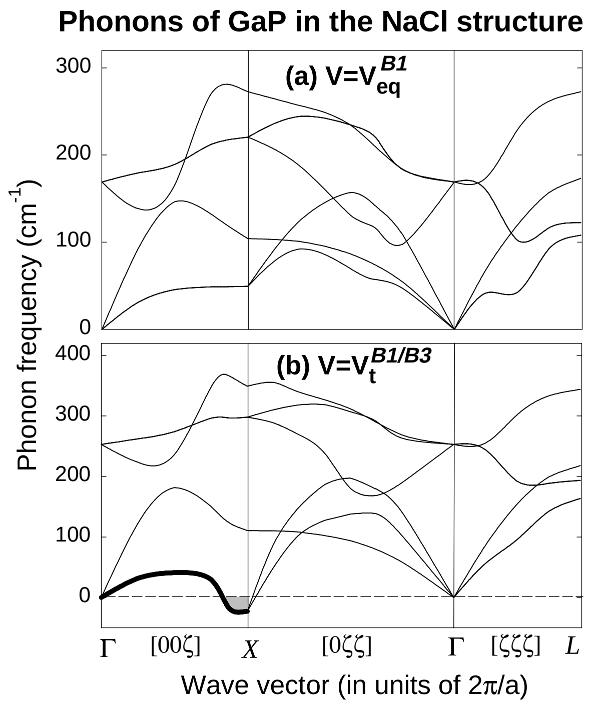

FIG. 3. Phonon dispersion of GaP in the NaCl structure (a) at the equilibrium volume $V = V_{\text{eq}}^{B3}$, and (b) at the ZB → NaCl transition volume $V = V_t^{B3/B1}$. Since GaP in the NaCl structure is metallic, there is no LO/TO splitting at the zone center. The unstable TA[ξ00] phonon branch is marked by a bold line.

Fig. 4(a). The stable high pressure phase can be identified by searching for the global energy minimum in the subspace spanned by the eigenvectors of the unstable mode and the additional degrees of freedom (e.g., the strain tensor) induced by the symmetry lowering due to the unstable mode [19]. The total energy curve in Fig. 4(a) shows that the lowest energy is achieved for a finite shuffle of (100) planes along the ⟨001⟩ direction. This distortion, coupled with an orthorombic strain, transforms the NaCl structure into the lower symmetry *Cmcm* structure [20,21]. Although the energy lowering in Fig. 4 is only a few meV/atom, it clearly demonstrates that NaCl and β-Sn are not $T = 0$ K ground states. Further optimization with respect to the remaining degrees of freedom (as done in Refs. [20,21]) increases this energy gain to a few tens of meV/atom.

The existence of a negative TA(X) mode Grüneisen parameter is a generic feature of the NaCl structure. This can be seen qualitatively by noting that the phonon properties are dominated by the competition between the attractive electrostatic Madelung energy $-Z^2/R$ (where Z is the excess charge within the atomic sphere) and the repulsive short-range energy $\propto A/R^n$ ($n \gg 1$), acting between the nearest neighbors separated by distance $\mathbf{R}$. For this generic potential, the force constant is

$$\Phi_{\alpha\beta} = \frac{nA}{R^{n+2}}\,\delta_{\alpha\beta} - \frac{Z^2}{R^3}\,\delta_{\alpha\beta} - \lambda\,\frac{R_\alpha R_\beta}{R^5}\,.$$

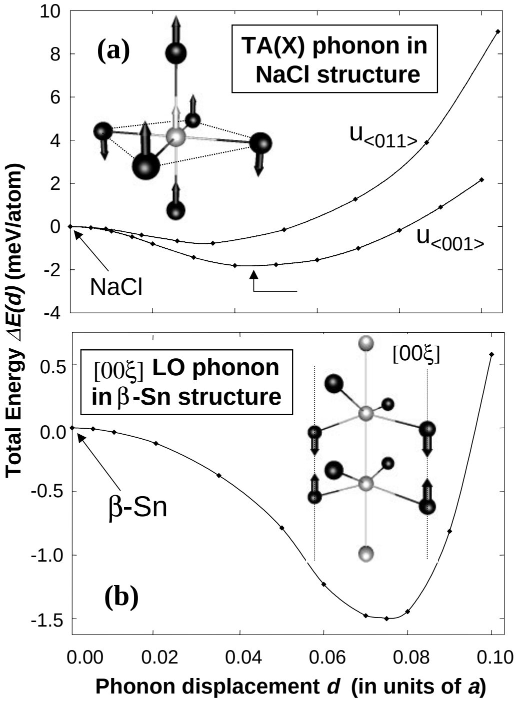

FIG. 4. Total energy of GaP as a function of the atomic displacements of the unstable phonon modes in (a) NaCl and (b) diatomic β-Sn structures. Insets show the structural motifs involved in these modes.

For a shear-type TA(X) mode [Fig. 4(a)], the third term vanishes. Thus, the TA(X) mode *lowers* the repulsive energy (the first term, contributing to $\gamma_{\text{TA}(X)} < 0$) and *raises* the Madelung energy (the second term, contributing to $\gamma_{\text{TA}(X)} > 0$). Since the repulsive term increases upon decreasing R much faster than the Madelung term, it leads to $\gamma_{\text{TA}(X)} < 0$, which, for sufficient compression, causes an instability $\nu^2_{\text{TA}(X)} < 0$. The more ionic the material is (larger Z^2), the larger the volume compression needed to achieve a dominance of the repulsive potential and, thus, an unstable mode.

(ii) Instabilities in the β-Sn structure.—The Γ-point LO phonon of β-Sn has often been studied [22,23] in connection with the structural transition to the simple hexagonal phase in Si and Ge. Figure 5 shows our calculated phonon dispersion curves along the tetragonal c-axis [00ξ] direction for compounds in the β-Sn structure. We find no evidence that the Γ-point LO-phonon mode ever becomes unstable in the compound semiconductors. Instead, we find a pronounced anomaly in the LO[00ξ] branch around $\xi \approx 0.5$, which rapidly softens with increasing ionicity (going from Si to InP) and reaches imaginary frequencies for GaAs, GaP, and InP. Figure 5 shows that this anomaly is present even in metallic white tin (in excellent agreement with the neutron scattering data of Rowe [24], shown as solid symbols, and with the calculations of Ref. [25]). Therefore, in analogy with the TA(X) mode in the NaCl structure, we characterize the LO[00ξ]-phonon anomaly as an incipient instability intrinsic to the β-Sn structure.

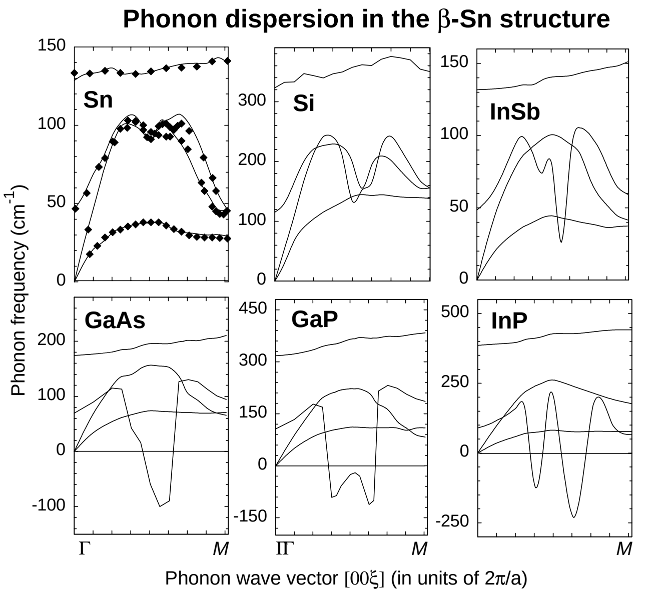

FIG. 5. Phonon dispersion of compounds in the diatomic β-Sn structure. LO/TO splitting at Γ is due to tetragonal symmetry.

In white tin, it is caused by the complicated shape of the Fermi surface [24]. The unstable LO$[00\xi]$ modes have positive Grüneisen parameters and should eventually stabilize with increasing pressure. The inset of Fig. 4(b) depicts the structural motif involved in this eigenmode at $\xi = \frac{1}{2}$, showing the dimerization of cation chains along the tetragonal axis. Figure 4(b) shows that the total energy of GaP supercell vs the amplitude of the LO$[00\frac{1}{2}]$-phonon mode reaches minimum at a finite displacement. Further optimization of the cell vectors and three internal degrees of freedom (u_1, u_2, and u_3) lowers the total energy to 10 meV/atom below the β-Sn structure. The resulting tetragonal superstructure, described by lattice vectors $\{\mathbf{a} = \mathbf{b}, \mathbf{c}\}$, has eight atoms in the unit cell: Ga$_1$ at $(0, 0, u_1)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4} - u_1)$, Ga$_2$ at $(0, 0, 1 + u_2)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4} - u_2)$, P$_1$ at $(0, \frac{1}{2}, \frac{1}{8} + u_3)$ and $(0, \frac{1}{2}, \frac{5}{8} - u_3)$, and P$_2$ at $(\frac{1}{2}, 1, \frac{3}{8})$ and $(\frac{1}{2}, 1, \frac{7}{8})$. It is distinct from the *Imma* and *Imm*2 phases found in Si, Ge, InSb, and GaSb (see Fig. 2) and is offered as a prediction to be examined experimentally [26,27].

In conclusion, we have explained the universal absence of the NaCl (β-Sn) structure in the covalent (ionic) semiconductors as arising from specific dynamical phonon instabilities in TA$[00\xi]$ and LO$[00\xi]$ branches, respectively. Since these instabilities are found in all compounds studied, it is conjectured that they are intrinsic features of the NaCl and β-Sn structures. We also demonstrate how linear response phonon calculations [18] can be used to identify new high pressure phases, thus supplementing the traditional method of static total energy calculations [8–11,21].

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[26] In fact, it is apparent from Fig. 5 that there is a family of low energy structures derived from *A*5 via *incommensurate* LO$[00\xi]$ instabilities. It is possible that they are masked in the phase diagram by competing phases which cannot be derived from the β-Sn or NaCl structures via phonon instabilities (such as the *Imma* phase, which requires an orthorombic strain of the β-Sn structure; see Ref. [21]).
[27] We have checked that the elastic constants and phonons at the Γ point are stable for GaP in this structure.