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Why Are the Conventionally-Assumed High-Pressure Crystal Structures of Ordinary Semiconductors Unstable?

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Recent high-pressure X-ray experiments show that, contrary to traditional expectations and numerous calculations, the NaCl structure is not present in covalent semiconductors, the diatomic β -Sn structure is absent in all compound semiconductors, and the CsCl structure is not seen in ionic semiconductors. We explain these systematic absences in terms of dynamical phonon instabilities of the NaCl, β -Sn, and CsCl crystal structures. Covalent materials in NaCl structures 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 ξ] branch. The latter lead to predicted new high pressure phases of octet semiconductors. For InSb, we find no phonon instability that could prevent the CsCl phase from forming, but for the more ionic GaP, GaAs, InP, and InAs, we find that the CsCl phase is dynamically unstable at high pressures with respect to TA[$\xi\xi0$] phonons. Analysis of the soft normal modes via "isotropy subgroup" suggests two candidate structures that will replace the CsCl structure at high pressure: the tP4 (B10) InBi-type and the oP4 (B19) AuCd-type. Experimental examination of these predictions is called for.

Introduction: Missing Structures? Our traditional understanding of structure and bonding in $A^N B^{8-N}$ octet semiconductors [1–6] is based on the time-honored notion of competition between "covalent" fourfold coordinated structures (diamond, zincblende (ZB)), "ionic" sixfold coordinated structures (NaCl) and "metallic" structures (diatomic β -Sn). As pressure is raised, one expects [7] that all semiconductors show the sequence of ZB \rightarrow NaCl $\rightarrow \beta$ -Sn structural phase transitions. Indeed, the NaCl high pressure phase was reported in many semiconductors [8] (InP, InAs, CdSe, CdTe, HgSe, and GaN), as was the high pressure diatomic β -Sn structure [8] (AlSb, GaSb, InSb, GaP, InP, InAs, and CdTe). The CsCl structure was seen [9, 10] in antimonides (GaSb and InSb).

As first-principles approaches to the electronic structure of solids became available [11], the total energy vs. volume curves were calculated for ZB, NaCl, β -Sn, and CsCl phases of numerous compounds [12–16]. Having restricted the configuration space to these phases, such calculations showed, via the common tangent construction (Fig. 1), that a ZB \rightarrow NaCl $\rightarrow \beta$ -Sn \rightarrow CsCl transition sequence is a universal feature for most octet compounds. This consistent body of experimental [8] and theoretical [13–16] studies of the ZB \rightarrow NaCl $\rightarrow \beta$ -Sn \rightarrow CsCl 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 highpressure diamond anvil cells [17, 18] has surprisingly revealed that all previous assign-



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

ments of the β -Sn structure to compound semiconductors are incorrect [19] and so are many of the assigned NaCl structures [20]. The CsCl structure has been proposed theoretically [13, 15, 21, 22] for GaP, GaAs, InP, InAs, and InSb but was seen experimentally [9, 10, 23] only for GaSb, InSb, and HgTe. 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 [21] (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

Com-	g	ZB	Wurt-	C2221	Cin-	NaCl	Cmcm	β-Sn	Imma,	SH	NiAs	bcc	hcp	fcc
pound			zite		nabar			· · · · ·	Imm2					
HgO	n/a	16 Section			+	+		S						
HgS	n/a	St. 225			+	+		in Calendar Sta						
CdO	n/a	Sec. 1. 2. 10				+		Sec. A.						
ZnO	n/a	3 8 4 8 2	+			+		1. 16						
InN	0.853	24.25	+			+		Statist.						
AIN	0.794	1. 1. 1. 1.	+			+		de falle.						
GaN	0.780	4. 48	+			+		1. 162						
CdS	n/a	+	+			+		+2.4 M						
ZnS	0.673	+	1. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2.			+		Sec.						
CdSe	n/a	+	14.85			+	+	STATE OF CO						
ZnSe	0.597	+	162882			+	+	No Sta						
InP	0.506	+	Constant.			÷	+	1 4 A. 19 6 6						
InAs	0.450	+	a Kanadar			+	+	State 1 the		_		· · · ·		
HgTe	n/a	+	Constant of the	+	+	+	+	Constant of				+		
CdTe	n/a	+	A 16 16 14		+	+	+	の意味な						
HgSe	n/a	+	· · · · · · · · · · · · · · · · · · ·	+	+	+	+	. And the						
ZnTe	n/a		1-6-6-6-6-6-6-		+	Sec.	+	a la Carlos			1			
AIP	0.425	+	a training			t enderte		194. A. J. W.			(+)			(+)
AlAs	0.375	+	Mart and			951261		1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1						
GaP	0.371	+	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1			Strak.	+							
GaAs	0.316	+	1. 24		+	2.4245	+	25.00	(+)	(+)		-		
InSb	0.294	+	180 Sec.			199.684	+	1. A. A. A.	+			+		
AISb	0.230	+	2010			Sec. 24	+	Sector -						
GaSb	0.169	+	San Charles			19 16 2 S		28 Sec. 4	+					
Ge	0	+	A. 6. 6 .			A. *** X & *		+	+	+		(dhcp)	+	+
Si	0	+	12.24			1		+	+	+		mono.	+	+
Sn	0	+	3. C. 186.	100		State of the		+						

Fig. 2. Observed [8, 20] 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. Shaded gray areas show the systematic absence of phases. g is the ionicity scale defined in Ref. [21]. For GaN, the stable structure at zero temperature is wurtzite, although one can force via epitaxial growth a metastable zincblende compound. While the stable structure seen at zero pressure and room temperature for CdSe is wurtzite, the expected ground state structure is zincblende [39, 40]. (Note that Ge, Si, and Sn listed under "ZB" acually refer to the diamond structure, which is the elemental analog of zincblende)

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 two most covalent, i.e., Ge and Si. There are very little experimental data for transitions into the CsCl structure, presumably because the estimated transition pressure into CsCl structure is very high. Nevertheless, at present, this structure seems to exist only for nearly-metallic semiconductors. These "absent structures" are highlighted as the shaded regions in Fig. 2. The realization that the previously assumed simple structures are in fact absent 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 stable structures [13–16]: 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 have first carried out traditional local density approximation (LDA) pseudopotential [11, 24]¹) calculations of $E^{\alpha}(V)$ for structure α of many semiconductors, spanning a broad range of ionicities [21]. We studied the standard zincblende (B3), NaCl (B1), diatomic β -Sn (A5), and CsCl (B2) 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. (The first LDA phonon calculations using the frozen phonon method were done by Ihm et al. [26]; more recently linear response method [27] has been developed.) We find:

(i) NaCl phase: For "covalent" compounds (GaAs, InSb, GaSb, GaP, and AlAs) the transverse acoustic (TA) zone boundary X-point phonon mode $\nu_{TA(X)}$ becomes dynamically unstable $(\nu_{TA(X)}^2 < 0)$ at a volume V_{du}^{B1} that precedes the ZB \rightarrow NaCl transition \mittheta volume $V_{t}^{B3/B1}$, so the NaCl structure cannot materialize in these compounds. Yet, for "ionic" compounds (AlP, InP, and ZnO) the instability sets in only 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_{du}^{B1} 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 [20] in the III–V compounds is caused by this universal instability of the TA(X) mode in the NaCl structure.

(*ii*) β -Sn phase: Similarly, the diatomic β -Sn structure of the ionic compound semiconductors 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.

¹) The nonlinear core correction has been used for As, Ga, In, and Sb to account for the extended core d states [25]. Zn d states were treated as valence. Our calculations are converged to within a few mRy/atom with respect to the plane wave cutoffs. Extra attention was paid to Brillouin zone integrations: 145 (309) special points and Fermi-Dirac broadening with T = 300 K were used for the NaCl (β -Sn) structure, and the existence of instabilities was checked in each case by doubling the density of the k point mesh.

(iii) CsCl phase: The CsCl structure of the more ionic compound semiconductors (GaP, GaAs, InP, and InAs) has phonon instabilities in the TA modes along the $k = [\xi\xi 0]$ direction. From symmetry analysis of the soft phonon modes we propose two high-pressure structures that replace the CsCl phase in the high-pressure phase diagrams of III-V semiconductors: the oP4 (AuCd structure-type) with space group Pmma, and the tP4 (InBi structure-type) with space group P4/nmm.

Results

Dynamical instability of the NaCl structure and the emergence of Cmcm We determine (Table 1) the respective equilibrium volumes of each phase V_{eq}^{α} , 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_{eq}^{B1} , all phonon modes are stable $(v_i^2 > 0)$. 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 $\gamma_i = \partial \ln \nu_i / \partial \ln V < 0$ of the TA[$\xi 00$] modes in the NaCl structure at all pressures. At the transition volume $V_t^{B3/B1}$ from the zincblende to the NaCl phase (Table 1), the frequency of this branch has become imaginary at the zone boundary X-point (see Fig. 3b), 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 Fig. 4a. 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 [28]. The total energy curve in Fig. 4a shows that the lowest energy is achieved for a finite shuffle of (100) planes along the (001) direction. This distortion, coupled with an orthorhombic strain, transforms the NaCl structure into the lower symmetry Cmcm structure [22, 29]. Although the energy lowering in Fig. 4 is only a few meV/atom, it clearly demonstrates that NaCl and β -Sn

Table 1

Normalized equilibrium volumes of the NaCl (B1) and β -Sn (A5) structures, along with the transition pressures $P_t^{\alpha/\beta}$ (kbar) between phases α and β , and the normalized transition volumes $V_t^{\alpha/\beta}$. "n/a" denotes that the corresponding transition does not occur for the investigated range of positive $P_t^{\alpha/\beta}$. All volumes are normalized with respect to the respective volumes of the zincblende phase at zero pressure

compound	$V^{lpha}_{ m eq}$		$P_{\mathrm{t}}^{lpha/eta}$			$V_{ m t}^{lpha/eta}$			
	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	



Phonons of GaP in the NaCl structure

Fig. 3. Phonon dispersion of GaP in the NaCl structure a) at the equilibrium volume $V = V_{eq}^{B1}$, and b) at the ZB \rightarrow 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[ξ 00] phonon branch is marked by a bold line

are not T = 0 K ground states. Further optimization with respect to the remaining degrees of freedom (as done in Refs. [22, 29]) dramatically enhances this energy gain, increasing it to a few tens of meV/atom.

Therefore, the NaCl structure cannot exist in GaP at ambient temperatures since it becomes dynamically unstable before the $ZB \rightarrow$ NaCl transition. The situation is similar in the other partially cova-

lent compounds GaSb, InSb, AlAs, which all exhibit the TA(X) instability already at the equilibrium volume of the NaCl structure (Fig. 1). In contrast, the more ionic compounds AlP, InP and ZnO all have a region of stability for the NaCl phase, since the TA(X) instability sets in only *after* the ZB \rightarrow NaCl transition pressure (Fig. 1). Therefore, the "systematic absence" illustrated in Fig. 2 is naturally explained by the TA(X) phonon instability.



Instabilities in the β -Sn structure The Γ point LO-phonon of β -Sn has often been studied [30–32] 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 [00 ξ] 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

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



Phonon dispersion in the β -Sn structure

Fig. 5. Phonon dispersion of compounds in the diatomic β -Sn structure. As in Fig. 3, the LO/TO splitting at the zone center is absent due to the metallic character of these compounds

a pronounced anomaly in the LO[00 ξ] branch around $\xi \approx 0.5$ that rapidly softens with increasing ionicity (going from Si to InP) and eventually 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 [33], shown as solid symbols, and with the calculations of Ref. [34]). Therefore, in analogy with the TA(X) mode in the NaCl structure,

we characterize the LO[00 ξ]-phonon anomaly in the β -Sn structure as an incipient instability intrinsic to the β -Sn structure. In contrast to the real space explanation given for the NaCl TA(X) anomaly, the β -Sn instability is explained by reciprocal space arguments: It is caused by the shape of the Fermi surface, which has nesting wave vectors along the $[00\xi]$ direction [33]. The unstable LO $[00\xi]$ modes have positive Grüneisen parameters, and should eventually stabilize with increasing pressure. To illustrate the type of stable superstructures that are derived from β -Sn via this instability, the inset of Fig. 4b depicts the structural motif involved in this eigenmode at $\xi = \frac{1}{2}$, showing the dimerization of cation chains along the tetragonal axis. As Fig. 4b shows, 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 the lattice vectors $\{\mathbf{a} = \mathbf{b}, \mathbf{c}\}\$, has eight atoms in the unit cell: Ga₁ at $(0, 0, u_1)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4} - u_1)$, Ga₂ at $(0, 0, 1 + u_2)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4} - u_2)$, P₁ at $(0, \frac{1}{2}, \frac{1}{8} + u_3)$ and $(0, \frac{1}{2}, \frac{5}{8} - u_3)$, and P₂ at $(\frac{1}{2}, 1, \frac{3}{8})$ and $(\frac{1}{2}, 1, \frac{7}{8})$. It is distinct from the Imma and Imm2 phases found in Si, Ge, InSb, and GaSb (see Fig. 2) and it is offered as a theoretical prediction to be examined experimentally²).

²) In fact, it is apparent from Fig. 5 that there is a family of low energy structures derived from A5 via incommensurate LO[00 ξ] instabilities. It is possible that it is masked in the phase diagram by a competing phase which cannot be derived from the β -Sn or NaCl structures via a phonon instabilities (such as the Imma phase, which requires an orthorhombic strain of the β -Sn structure; see Ref. [22]). We have checked that the elastic constants and phonons at the Γ -point are stable for GaP in this structure.



Fig. 6. Phonon dispersion curves in the B2 structure of a) InP and b) InSb at a few normalized volumes V/V_0 . Imaginary phonon frequencies are shown as negative

Instabilities in the CsCl structure Figure 6 shows the phonon dispersion curves for InP and InSb in the B2 structure at volumes where, according to the static total energy calculation, this structure is statically stable. We find that in InP two transverse acoustic (TA) modes along the $k = [\xi\xi 0]$ direction are unstable ($\nu^2 < 0$). The degree of instability (as measured by the magnitude of $-\nu^2(k)$) is most severe at the zone boundary M-point corresponding to $k = (\frac{1}{2} \frac{1}{2} 0)$. Symmetry group of this wavevector is 4/mmm, and the allowed irreducible representations are M_2^- , M_3^- , and $2M_5^-$. These include two degenerate acoustic modes (M_5^-) and two degenerate optic modes (M_5^-), in addition to a non-degenerate acoustic mode (M_2^-) and an optic mode (M_3^-) [35]. From inspection of the eigenvectors of the unstable mode, we find that they belong to the TA₁(M_2^-) and TA₂(M_5^-) representations.

We next describe how "isotropy subgroup" analysis can be used to find the structure that replaces the phonon-unstable B2 structure. The eigenfuctions for the soft modes $TA_1(M_2^-)$ and $TA_2(M_5^-)$ are depicted in Fig. 7a and 8a, respectively. We see that the $TA_1(M_2^-)$ mode is polarized along the [001] direction, while the $TA_2(M_5^-)$ mode displacements are in the [110] direction. Having identified the symmetries $TA_1(M_2)$ and $TA_2(M_5^-)$ of soft modes, we consider the corresponding modes as order parameters in a pressure-induced phase transition that can be described by Landau expansion of the enthalpy function. During a second order phase transition where the original symmetry is lowered by a continuous structural distortion, the new symmetry must leave the distortion invariant. Thus, there is a group/subgroup relation between the undeformed/ deformed phases. Such a subgroup is called an "isotropy subgroup" [36]. The allowed isotropy subgroups for each space group and for given order parameter irreducible representations are compiled by Stokes and Hatch [36]. There are six isotropy subgroups for M_2^- and 26 subgroups for M_5^- . Using the isotropy subgroup table [36], it is easy to identify the structure type for each case (Table 2). For the sake of simplicity, we now confine ourselves to those subgroups for which all nonzero components of the order parameters are equal (except possibly sign differences). These are called "maximal isotropy subgroups". For M_2^- , there are three (first three rows (1-3) in



Fig. 7. $TA_1(M_2^-)$ derived structure from the B2 (CsCl) starting point: (a) the phonon eigen mode; (b) the undistorted B2 structure. Arrows denote displacements of anions leading to (c) the B10 structure

Table 2), while for M_5^- , there are seven such sets (the seventh to thirteenth rows (1–7) in Table 2).

 M_2^- mode and the B10 crystal structure: Figure 7c gives the crystal structure that will result from one of the highest symmetry members of the unstable M_2^- mode. The new structure has P4/nmm symmetry. This is the tP4, InBi-type [38] structure (B10) derived by a soft M₂⁻ mode. In this structure two In atoms are in one (100) plane, and two P atoms are at two different (100) planes, separated by (1-2z) c/a, where z is a dimensionless cell-internal parameter. In the undistorted B2 structure (Fig. 7b) each anion has four nearest neighbor cations on each side of the shaded (001) plane. In the distorted tP4 structure (Fig. 7c) the anions are displaced in the [001] direction (see arrows) so that now each anion has four nearest neighbor cations at distance $R_{\text{In-X}}^{(1)} = a[((c/a) z)^2 + \frac{1}{4}]^{1/2}$ forming a square to one side of the (001) plane, and four additional next nearest neigh-bors at a distance $R_{\text{In-X}}^{(2)} = a[(c/a(1-z))^2 + \frac{1}{4}]^{1/2}$. When $z \to 1/2$ and $c/a \to 1/\sqrt{2}$ then $R_{\text{In-X}}^{(1)} = R_{\text{In-X}}^{(2)}$, thus restoring the eightfold coordinated B2 structure. M_5^- mode and the B19 crystal structure: Figure 8c gives the B19 crystal structure derived from the M⁻ mode. This orthorhomic structure has Parme summation and some has con-

from the M₅⁻ mode. This orthorhombic structure has Pmma symmetry and can be con-



Fig. 8. $TA_1(M_5^-)$ derived structure from the B2 (CsCl) starting point: (a) the phonon eigen mode; (b) the undistorted B2 structure. Arrows denote the displacement of atoms on alternating (110) planes leading to (c) the B19 structure

Table 2

Isotropy subgroups of the parent CsCl structure $(Pm\bar{3}m;O_h^1)$ that correspond to the $M_2^$ and M_5^- order parameters. Atomic positions are given in terms of Wyckoff notation. In parentheses we give the pages in Ref. [37] where the positions are given. The maximal symmetry isotropy subgroups are the first three rows (1–3) for M_2^- , and the first seven rows (1–7) for M_5^-

	subgroup	basis vectors	atomic positions (page no.)	structure type	example						
(1)	$P4/nmm(D_{4h}^7)$	Irrep $(1,1,0), (\bar{1},1,0), (0,0,1)$	$= TA_1(M_2^-) 2a; 2c (439)$	tP4 (B10)	InBi, BaO, PbO, FeS						
(2)	$I4/mcm(D_{4h}^{18})$	(0, 0, 2), (2, 0, 0), (0, 2, 0)	8g; 8h (471)	tI16							
(3)	$I\bar{4}3m(T_d^3)$	(2,0,0), (0,2,0), (0,0,2)	2a; 6b; 8c (653)	cI16	S_4Tl_3V						
(4)	$Ibam(D_{2h}^{26})$	(0, 0, 2), (2, 0, 0), (0, 2, 0)	4a; 4b; 8j (317)	oI16							
(5)	$I\bar{4}2m(D_{2d}^{11})$	(0, 0, 2), (2, 0, 0), (0, 2, 0)	2a; 2b; 4c; 8i (417)	tI16							
(6)	$I222(D_2^8)$	(2, 0, 0), (0, 2, 0), (0, 0, 2)	2a; 2b; 2c; 2d; 8k (205)	oI16							
	Irrep – $T\Delta_{a}(M^{-})$										
(1)	$Pmma(D_{2h}^5)$	$(1,0,\bar{1}), (0,1,0), (1,0,1)$	2e; 2f (265)	oP4 (B19)	AuCd, CdMg, IrW, NbPt						
(2)	$Cmmm(D_{2h}^{19})$	(0, 0, 2), (2, 0, 0), (0, 1, 0)	4h; 4i (295)	oC8							
(3)	$R3m(C_{3v}^5)^{2m}$	$(\bar{2}, 2, 0), (0, \bar{2}, 2), (1, 1, 1)$	3a; 9b; 3a; 9b (519)	hR8							
(4)	$R32(D_3^7)$	$(\bar{2}, 2, 0), (0, \bar{2}, 2), (1, 1, 1)$	3a; 9d; 3b; 9e (507)	hR8							
(5)	$I4/mmm(D_{4h}^{17})$	(0,2,0), (0,0,2), (2,0,0)	4d; 4e; 8h (469)	tI16	Ag ₃ InLa ₄						
(6)	$I4/mmm(D_{4h}^{17})$	(2,0,0), (0,2,0), (0,0,2)	4d; 4e; 8h (469)	tI16	Ag ₃ InLa ₄						
(7)	I213(T ⁵)	(2, 0, 0), (0, 2, 0), (0, 0, 2)	8a; 8a (603)	cI16	CoU						
(8–26)) $P2/m(C_{2h}^1)$, $Imma(D_{2h}^{28})$, $Immm(D_{2h}^{25})$, $Immm(D_{2h}^{25})$, $C2/m(C_{2h}^3)$, $Fmm2(C_{2v}^{18})$, $Fmm2(C_{2v}^{18})$, $R3(C_3^4)$, $C2/m(C_{2h}^3)$, $C2/m(C_{2h}^3)$, $Cm(C_s^3)$, $C2(C_2^3)$, $I2_12_12_1(D_2^9)$, $Imm2(C_{2v}^{20})$, $P\overline{1}(C_1^1)$, $C2(C_2^3)$, $Cm(C_s^3)$, $Cm(C_s^3)$, $P1(C_1^1)$										

sidered as a distorted diatomic hcp structure. The B2 structure transforms into this structure when (i) the hexagonal B2 faces (the (110) plane shown as top view at the bottom of Fig. 8) become regular hexagons and (ii) the second (110) layers of atoms are placed at the center of the triangles. That is, the b/a ratio becomes $1/\sqrt{3}$ rather than $1/\sqrt{2}$ in the B2 structure and the atoms in alternate (110) planes shift by $\sqrt{3}/6a_{bcc}$ in $[1\overline{10}]$ direction as shown with arrows, making it an ideal hcp stacking as shown in Fig. 8c. In practice, due to orthorhombic symmetry, in general $b/a \neq 1/\sqrt{3}$ and the shift $\delta \neq \sqrt{3}/6a_{bcc}$.

Having identified, via a symmetry analysis of the B2 soft modes, B10 and B19 as candidate structures that can replace the B2 structure (Figs. 7c and 8c), we now compute the static total energies of InP in these structures, relaxing the cell-internal and cell-external structural parameters allowed by symmetry. We find that both the B10 and the B19 phases are lower in energy than the B2 phase at the volumes where the B2 is expected to be stable according to hydrostatic calculations alone (Fig. 1). Near the transition pressure into the B2 phase, B10 is the lowest energy phase. At $V/V_0 = 0.50$, the total energy of the B10 phase is lower than that of the B2 phase by 29 meV and B19 is lower by 1 meV. As the pressure is raised further, B19 becomes the lowest energy structure. At $V/V_0 = 0.42$, the total energy differences are -73 meV between B10 and B2 and -92 meV between B19 and B2.

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