High-pressure phase transitions in diamond and zinc-blende semiconductors

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With the advent of accurate total-energy methods for solids, it has become feasible to determine the relative structural energies of simple solids as a function of pressure. We use such a method coupled with an empirical ionicity scale to predict phase transitions as a function of pressure for all diamond and zinc-blende semiconductors of the form $A^N B^{8-N}$ where A and B are simple metals or metalloids and N is the number of valence electrons for species A. We find satisfactory agreement between the predicted transition from zinc-blende structure to rocksalt or β -Sn structures and highpressure experiments. In addition, we find that changes in ionicity to a large extent control whether the diamond or zinc-blende structure will transform preferentially to rocksalt or to β -Sn; whereas, for changes in the equilibrium crystal volume, we find the magnitude of the transition pressure changes, but not the structural preference.

I. INTRODUCTION

Perhaps the greatest success of total-energy methods¹⁻¹⁰ has been their ability to predict the relative stability of semiconductor phases and determine the pressure at which these transitions occur.^{1,2,11,12} Within the last several years, phase diagrams of a number of solid-state systems have been predicted. For example, pseudo-potential solid-state stability studies for silicon correctly predicted the pressure for the transition from diamond structure silicon to white tin (β -Sn) structure silicon.¹ Other calculations have been performed which predict the phase behavior for solids beyond the current pressure capabilities.

While these calculations are very accurate and powerful in their descriptions of solid-state systems, they are sufficiently complex to restrict their applicability to specific materials such as simple ordered solids. Thus, it is difficult to obtain a global picture for an entire family of structures. Conversely, empirical approaches have yielded a limited overview of high-pressure transitions, but these methods are based on experimental scaling rules which have yet to be justified from any microscopic theory. Here, we demonstrate how the results of total-energy calculations can be used as input to derive scaling rules which can then be used to predict high-pressure transitions for an entire crystal family.

The family of crystals we examine is made up of simple, binary octets: $A^N B^{8-N}$, where A and B are simple metals or metalloids (no transition metals or rare earths) and N is the number of valence electrons on species A. This family includes all the tetravalent semiconductors; we will concentrate on the diamond and zinc-blende structural members of this family. Our goal is to present an overview of the high-pressure forms of this family. We limit our discussion to transitions involving highpressure structures of white tin (β -Sn) and rocksalt as these are the most common structures at high pressure. The β -Sn structure is a prototypical metallic structure for octet binaries and the rocksalt structure is a prototypical ionic structure. While we concentrate on these archetypical structures, in a number of cases our calculated transition pressures will be appropriate for other structures.

II. FIRST-PRINCIPLES COMPUTATIONAL METHODS FOR HIGH-PRESSURE PHASE TRANSITIONS AND STABILITY

In this section we review the essential features of our computational approaches; details of our method have been presented elsewhere. $^{9,13-15}$

We evaluate the total energy of a crystal by solving a single-particle Schrödinger equation within a local-density approximation for exchange and correlation. Our crystalline potential is determined by constructing *ab initio* ionic pseudopotentials¹⁶ which are screened in an approximate self-consistent fashion.¹³ As a basis we take Gaussian orbitals; thirty orbitals are used per atom. The basis is assumed to be structurally independent. The accuracy obtained from this approach is rather good. Typically, one has confidence in the calculated cohesive energies to within 10%, the lattice parameters to within 2-3%, and the bulk modulus to within 5%.

In order to determine how such trends as ionicity affect the structural properties of tetrahedral semiconductors, we modify the total crystalline potential in a systematic fashion. For a given modification of the crystalline potential, we can calculate how the relative stability of a given structure is altered and extract the essential features which control phase stability. To be more specific, we consider a prototypical zinc-blende crystal. If the crystalline potential is modified to replicate a more ionic material, we can directly calculate the effect of increasing ionicity on the stability of the zinc-blende structure versus a high-pressure structural form such as rocksalt or white tin.

For our prototypical crystal, we modified the crystalline potential for GaAs by adding a single Gaussian well to the ionic components of the cation and the anion. We constrain the size of the well to be that of the ion cores and the same for both the cation and anion. As for the depth of the well, we choose the wells to have equal depths, but of opposite sign. This leaves the average ionic potential unchanged and allows us to modify the potential through a single parameter. Of course, there are other modifications which one might consider, but this one will allow us in a simple fashion to obtain general changes in structural transitions with pressure as a function of crystal ionicity.

In order to categorize our results for different potentials, we perform a charge-density population¹⁷ analysis for each modified potential. This anaysis will allow one to examine in a semiquantitative fashion the nature of the potential construction. For example, if one finds two electrons associated with the cation and six with the anion, then the semiconductor is labeled as a II-VI compound. As our basis is structurally independent, we expect the relative charge transfer to be physically meaningful.

Given that we can determine ground-state properties as a function of charge transfer, we can define a global picture of crystal structure stability. We can determine the free energy from¹⁸

$$G(p) = B_0 V_0 [(1 + pB'_0 / B_0)^{\gamma} - 1] + E_0 , \qquad (1)$$

where $\gamma = (B'_0 - 1)/B_0$. B_0 is the equilibrium bulk modulus, B'_0 is the derivative of the bulk modulus with pressure, V_0 is the equilibrium volume, E_0 is the equilibrium energy, and p is the external pressure. By calculating the crystalline total energy as a function of volume, we can fit an equation of state, such as the Murnaghan equation of state,¹⁸ and determine the values of B_0 , B'_0 , V_0 , and E_0 . By considering a sequence of different charge configurations, we can determine how these ground-state quantities change with charge transfer and find the free energy as a function of both pressure and charge transfer, or ionicity.

We can do this for a variety of structures. Here we concentrate on the diamond, zinc-blende, rocksalt, and β -Sn structures. For each structure we considered six different charge configurations and at least four different volumes. Hence, over 70 independent band-structure calculations were undertaken.

In Fig. 1, we present the overview from our free-energy calculation for the structures considered here. This global picture is consistent with the known facts concerning this family of structures. However, it is restricted in its appli-



FIG. 1. Phase diagram for a prototypical zinc-blende semiconductor. The diagram is appropriate for only those zincblende (or diamond) semiconductors with an atomic volume corresponding to GaAs.

cability to zinc-blende semiconductors which preserve the bond length of the reference crystal, in this case GaAs. Consider the case of the diamond semiconductors: silicon, germanium, and α -Sn. These structures all transform to β -Sn, but at very different pressures. Figure 1 would be appropriate only for the diamond structure which has the same crystal volume as the GaAs reference structure, in this case germanium. In order to include other structures in our study we will have to examine how the pressure transitions are altered by volume changes and include proper scaling arguments to extract accurate transition pressures.

III. EMPIRICAL SCALES FOR TRANSITION PRESSURES AS A FUNCTION OF IONICITY AND BOND LENGTH

One possible way of predicing the phase behavior of zinc-blende materials under pressure is to use experimental data to extract quantitative trends. At least two such approaches have been used for these materials. One of the earliest approaches¹⁹ involved correlating the transition pressures with the optical band gap, e.g., the band gap for α -Sn is zero and the pressure for a transition to β -Sn is vanishingly small, whereas for Si with a band gap of 1 eV, the pressure for the analogous transition is approximately 120 kbar. This procedure gives at best a rough correlation and fails badly for some materials such as AlSb which have larger band gaps than Si, but have a lower transition pressure. The more recent effort is from Van Vechten²⁰ in which he used the dielectric theory of Phillips²¹ to scale the zinc-blende to β -Sn transition with the ionic and covalent components of the chemical bond. His theory is a considerable improvement over the earlier efforts; however, it is limited to the zinc-blende to β -Sn transition. As Van Vechten noted at the time, his empirical approach was prompted by a lack of theoretical calculations for the various phases present. While Van Vechten's assessment of the theoretical "state of the art" remains somewhat valid, it is now possible to gain a semiquantitative overview as indicated in our previous discussion. However, it is still not feasible to produce a detailed overview without further empirical input. Moreover, theoretical calculations are still somewhat limited in the overview they produce. At present, it is beyond our means to consider phases other than zinc-blende, rocksalt, and white tin for all AB compounds which number about 70 species.

Unlike Van Vechten's approach²⁰ which assumes a specific power-law scaling of the covalent contributions to the chemical bond, we have assumed a more general form. From a knowledge of the form of the phase diagram in Fig. 1, we can assume a simple functional form for the pressure transitions. The form we take is given by

$$P_t^{\alpha}(f_i, V) = P_r^{\alpha}(f_i, V_r) S^{\alpha}(V - V_r) , \qquad (2)$$

where P_t^{α} is the transition pressure for a zinc-blende or diamond structure to the structure α where α is taken to be either rocksalt or β -Sn. f_i is the crystal ionicity from the dielectric theory of Phillips²¹ and V is the volume. We assume that if we know the pressure transition for either the zinc-blende to rocksalt or white tin structure at some reference volume, i.e., $P_r^{\alpha}(f_i, V_r)$ from Fig. 1, then we can rescale the transition pressure by a factor independent of the ionicity, i.e., $S^{\alpha}(V - V_r)$. We proceed by expanding both P_r^{α} and S^{α} :

$$P_{r}^{a}(f_{i}, V_{r}) = P_{0}^{a}(V_{r})(1 + a_{1}f_{i} + a_{2}f_{i}^{2}) ,$$

$$S^{a}(V - V_{r}) = 1 + b_{1}(V - V_{r}) + b_{2}(V - V_{r})^{2} + b_{3}(V - V_{r})^{3} .$$
(3)

We fix P_0^{α} and the parameters a_i and b_i by comparisons to our calculations or by experiment. The expansions yield an accurate fit, but do not have an unmanageable number of parameters. However, we do not expect our interpolation to be valid for atomic volumes which have large departures from V_r . For example, we would not expect our expressions to be valid for compounds containing only first-row elements, i.e., we expect volume differences to become large enough that our simple expansion becomes invalid.

With respect to fixing the various parameters, for P_0^{α} in the case of the zinc-blende to β -Sn transition, we can use data for germanium which has the nearly the same atomic volume as GaAs, i.e., our V_r , to fix this parameter. For the value of P_0^{α} for the case of zinc blende to rocksalt, we use our calculated phase diagram. For the parameters a_i , we use our calculated diagram. In this case we must convert our population analysis to an ionicity scale. For this purpose we use a scale suggested by Coulson *et al.*:²²

$$f_i^c = (4 - N)/4 + \alpha \,\delta Q \quad (4)$$

where N is the number of valence electrons on the cation atom and δQ is the charge transfer accompanying the formation of the solid-state system. To bring this scale, f_i^c , in registry with Phillips's scale,²¹ f_i , we fix α so that for GaAs we have $f_i^c(GaAs) = f_i(GaAs)$.¹⁴ For a given material and f_i , we can then read off our phase diagram in Fig. 1, the predicted transition pressure. For the parameters b_i , we use experimental data, e.g., the diamond structure to β -Sn structure transition can incorporate data from Si, Ge, and α -Sn. Values for P_0^{α} and the parameters $(a_i \text{ and } b_i)$ are given in Table I. In Table II we present our predictions for the transition pressure from the zincblende structure to both the β -Sn structure and for the rocksalt structure. In Fig. 2, we display an overview with various semiconductors categorized by ionicity and by bond length, and the corresponding predictions as to whether the preferred high-pressure phase is white tin or rocksalt. In Fig. 3, we give a contour plot of the transition pressures predicted for each phase regime.

IV. RESULTS AND DISCUSSIONS

In Table III and Fig. 4, we compare our calculated transition pressures with experiment. First, we should note the limitations of our theoretical predictions. As mentioned previously, we have only examined two highpressure phases of zinc-blende structures: the white tin structure and the rocksalt structure. It is quite probable that a number of phases may exist at high pressure with nearly equal free energies for some species. For example, in our calculation for GaAs we find that the β -Sn and rocksalt phases are nearly equal in free energy, and other calculations have suggested that the NiAs structure has nearly the same free energy.¹¹ Given this situation, we believe that our calculated transition pressure may be reasonable, but not our predicted structure. In the case of GaAs, we predict a transition pressure of 168 kbar as compared to the experimental value of 172 kbar.²³ However, the GaAs high-pressure phase is known not to be a simple β -Sn structure, although the present form has not been well characterized.²³ In our comparisons, we incident the experiment-versus-theory predictions for the transition pressures of all zinc blendes, regardless of whether the high-pressure phase is white tin or rocksalt. Overall, the agreement is quite good for even those highpressure phases which are observed to occur in structures other than white tin or rocksalt.

In making a comparison between experiment and theory, we have not listed our predictions for zinc blende, or diamond, materials which have a very small lattice constant, e.g., carbon or BN. We feel that our expansion is not adequate for this purpose. For the case of carbon in the diamond structure, we would predict a diamond to white tin transition at about 1 Mbar, in agreement with the prediction of Van Vechten. However, we know this value to be incorrect, both in terms of experiment and theory.^{24,25} We have confidence in our predictions only for bond lengths which exceed about 2.25 Å. For very large bond lengths, e.g., over 2.8 Å, octet crystals are not stable in the ground state in the zinc-blende structure.

The domains present in Fig. 3 are physically reasonable in terms of the overall shape. For example, covalent zinc blendes, i.e., those with f_i under 0.3 and predominantly III-V compounds, transform to the β -Sn structure under pressure, while more ionic zinc blendes, i.e., those with f_i over 0.6, transform to rocksalt. In terms of the bondlength change, we expect weaker bonds, i.e., those with long bond lengths, to be more metallic and thus favor the white tin structure. At shorter bond lengths, we have less confidence in our results, not only because the simple scal-

TABLE I. Expansion parameters for Eq. (3). P_0 is in kbar and V is the equilibrium atomic volume in Å³ with V_r equal to 22.5932 Å³. Units for a_n are dimensionless, for b_n are Å⁻³ⁿ.

α	P_0	<i>a</i> ₁	<i>a</i> ₂	<i>b</i> ₁	<i>b</i> ₂	<i>b</i> ₃
3-Sn	80	3.7933	- 1.0706	-0.140 600	0.015 271	-0.000 862
Rocksalt	380	-0.8385	-0.5144	-0.229936	0.024 469	-0.000679

two high-pressure structures are considered: white tin (β -Sn) and rocksalt.

	Lattice		Transition pressure		
Semiconductor	constant	Ionicity	β-Sn	Rocksalt	
Si	5.431	0.000	119.5	680.4	
Ge	5.650	0.000	81.4	390.6	
α-Sn	6.491	0.000	7.1	212.9	
AgI	6.473	0.770	32.8	10.2	
AlAs	5.620	0.274	167.8	310.1	
AlP	5.451	0.307	238.0	450.8	
AlSb	6.135	0.250	76.7	101.7	
ВеТе	5.540	0.169	158.6	440.8	
CdS	5.818	0.685	192.5	44.8	
CdSe	6.050	0.699	142.7	23.3	
CdTe	6.480	0.717	28.2	28.0	
CuBr	5.691	0.735	243.8	36.9	
CuCl	5.406	0.746	403.9	63.5	
CuI	6.043	0.692	143.2	25.1	
GaAs	5.654	0.310	167.5	266.8	
GaP	5.451	0.327	245.2	435.6	
GaSb	6.118	0.261	80.1	100.6	
HgS	5.853	0.790	196.7	3.6	
HgSe	6.084	0.680	134.7	26.5	
HgTe	6.429	0.650	49.1	45.2	
InAs	6.036	0.357	103.0	92.7	
InP	5.869	0.421	139.1	117.2	
InSb	6.478	0.321	19.4	140.9	
ZnS	5.409	0.623	366.2	198.9	
ZnSe	5.668	0.630	234.0	99.5	
ZnTe	6.089	0.600	125.4	42.8	

ing may break down, but also because other forms may become more dominant at high pressure. For example, in the case of diamond, a modified body-centered cubic structure is known to be the preferred structure.²⁴ While the gross features of Fig. 3 can be understood from this perspective, we note how subtle some of these effects can be. For example, in the series InP, InAs, and InSb, our theory reproduces the pressure transitions quite well and predicts that the lowest-energy high-pressure phase should be rocksalt for InP and InAs, but β -Sn for InSb. While InSb is known to "prefer" an orthorhombic form at high pressure, the other two indium III-V compounds are known to favor the rocksalt structure. The subtleties which dictate the differences between these III-V compounds are difficult to state in terms of simple classical arguments.

With respect to the experimental values, we have some confidence in the measured values, although the uncertainties in the transition pressures can be as large as 10% or more. It is well known that the experimental highpressure measurements can suffer from several problems including calibration, inhomogeneous pressures, and metastability. Van Vechten²⁰ has briefly discussed these aspects, e.g., the role of metastability in pressure experiments. Following his discussion, we have adjusted the older data to agree with the modern pressure scale. We expect the errors in the experimental measurements to be

comparable to theoretical uncertainties.

We note that for the zinc-blende to white tin transition our predictions are quite similar to Van Vechten's. A detailed comparison is made in Table IV. This is to be expected since the essential ingredients are similar. For a specific example, we predict a phase transition for AIP of zinc blende to white tin at about 240 kbar; Van Vechten predicts the transition at 270 kbar. Experimentally a transition is observed at about 150-170 kbar to a phase which has not been characterized. AlP is a very difficult material to work with as it is reactive and exhibits considerable hysteresis in the pressure measurements.^{30,31} One can rationalize Van Vechten's and our estimates with experiment by noting that the observed phase may have lower free energy than the assumed structure of white tin.

AlP presents another challenge in the sense of our Fig. 3. We have implicitly assumed that the chemical coordinates of volume, or bond length, and crystal ionicity play the dominant role in determining the structural properties of these materials. On the basis of Fig. 3, AlP and GaP must have similar properties as the lattice constants are nearly identical and the ionicities are very similar. Therefore, any differences between the two materials can give insights into the parameters responsible for dictating structural energies. At present, the experimental situation with AlP is suggestive that other parameters may play a role in determining the structural trends, but a clearer pic-



FIG. 2. High-pressure domains for diamond and zinc-blende semiconductors. The zinc-blende to white tin transition $(Zb-\beta-Sn)$ and zinc-blende to rocksalt (Zb-Rs) regimes are indicated in an "ionicity-bond length" space. Above the critical ionicity of 0.79 (see Ref. 21), zinc-blende structures are not stable at normal pressure. Also, for bond lengths greater than about 2.8 Å no zinc-blende structures exist. The theory is not applicable to compounds with bond length less than ~2.3 Å.

ture must await further experimental data.

One notable discrepancy occurs in our predictions versus the measured transition pressures. In the case of ZnTe we predict a transition pressure of approximately 50 kbar, whereas the measured pressure is approximately 100 kbar. Given the fact that our calculations do not include



FIG. 3. Transition pressures as predicted from a rescaling of Fig. 1 with bond length, or volume changes. The regimes shown are as in Fig. 2. The contours mark pressures in kbar for the zinc-blende (or diamond) transition to the high-pressure phases of white tin or rocksalt.

explicit treatment of *d*-orbital effects, one might question our predictions for the Zn, Cd, and Hg chalcogenides. In fact, it is known that such materials are difficult to discuss in terms of their structural properties with pseudopotentials which do not properly describe the outermost cation *d* shells.¹⁵ However, our predictions for all the II-VI compounds are fairly good except for ZnTe. Another possibility is that the Phillips ionicity value for ZnTe is

TABLE III. Comparison between predicted high-pressure forms and transition pressures for zincblende and diamond semiconductors and experiment. The transition pressures are in kbar. The highpressure phases predicted are restricted to white tin (β -Sn) and rocksalt (NaCl). Other observed highpressure forms are orthorhombic (orth), tetragonal (tetr), and cinnibar (cinn).

- A starting of the starting o	Theory		Experir		
Semiconductor	P_t	Phase	P_t	Phase	References
Si	119.5	β-Sn	125	β-Sn	19,26
Ge	81.4	β -Sn	80	β-Sn	19,23,26
α-Sn	7.1	β-Sn	0	β-Sn	19
AgI	10.2	NaCl	3	tetr	27,28,29
AIP	238.0	β-Sn	150-170		30,31
AlSb	76.7	β-Sn	77-83	orth	19,23,30,32
CdS	44.8	NaCl	40	NaCl	33,34
CdSe	23.3	NaCl	23	NaCl	33,34
CdTe	28.0	NaCl	30	NaCl	34,35
CuBr	36.9	NaCl	50	tetr	29
CuCl	63.5	NaCl	44-50	tetr	29,36
CuI	25.1	NaCl	18		29
GaAs	167.5	β-Sn	172 - 188	orth	19,23,30,32,37
GaP	245.2	β-Sn	215-253	β-Sn	23,26,32,37
GaSb	80.1	β-Sn	62	β-Sn	19,30
HgS	3.6	NaCl	~0	cinn	33,34
HgSe	26.5	NaCl	7	cinn	33,34
HgTe	45.2	NaCl	14	cinn	33,34
InAs	92.7	NaCl	72-84	NaCl	19,38
InP	117.2	NaCl	95-110	NaCl	19,38
InSb	19.4	β-Sn	23	orth	19,30,39
ZnS	198.9	NaCl	150-155	NaCl	26,37
ZnSe	99.5	NaCl	137	NaCl	26
ZnTe	47.8	NaCl	100-129	NaCl	35,37



FIG. 4. A comparison between the predicted transition pressures and the measured transitions pressures. The theoretical results correspond to transitions from the zinc-blende, or diamond, structure to the high-pressure structures of rocksalt and white tin. The solid points corresponds to experimental determined structures which are either rocksalt or white tin. The open points correspond to structures other than those examined theoretically.

not correct; however, in our calculations it would take an adjustment of nearly 30% in terms of reducing the ionicity of ZnTe to bring it into registry with experiment. We do not believe this is reasonable in terms of the accuracy of the ionicity parameter with other data and other structural trends.

V. CONCLUSIONS

By combining *ab initio* pseudopotential total-energy methods with empirical formulations, we have obtained a global picture of high-pressure transitions for the zincblende semiconductors. We assumed a simple rescaling of transition pressures with crystal volume of the calculated total-energy phase diagrams. Two parameters entered our discussion: the crystal ionicity from the dielectric theory²¹ and the equilibrium crystal volume. By fixing our scaling parameters by experiment and theory, we were able to determine the transition pressures for the zinc-

TABLE IV. Comparison between present theoretical work and the transition pressures predicted by Van Vechten (Ref. 20). The transition pressures are in kbar. The predictions are for zinc-blende or diamond semiconductors transforming into the white tin structure. Experimentally the high-pressure form is known not to be white tin for InAs, InP, InSb, and GaAs as indicated. The experimental data are from the same references as in Table III

Theory					
Semiconductor	Present	Quantum dielectric	Experiment		
Si	119.5	148	125		
Ge	81.4	92	80		
α-Sn	7.1	0	0		
AlAs	167.8	220			
AlP	238.0	269	150-170		
AlSb	76.7	122	77-83		
GaAs ^a	167.5	153	172-188		
GaP	245.2	216	215-253		
GaSb	80.1	73	62		
InAs ^a	92.7	92	72-84		
InP ^a	117.2	141	95-110		
InSb ^a	19.4	43	23		

^aHigh-pressure phase is experimentally observed to be a structure which does not correspond to the white tin structure.

blende to white tin structure and for the zinc-blende to rocksalt transition.

Qualitatively, we find that ionicity, or charge transfer, dictates to a large extent the structural form of the highpressure phase. For the more covalent materials, i.e., the III-V semiconductors, we find that the zinc-blende structure transforms predominantly to the white tin structure under pressure and for the more ionic materials, i.e., the II-VI semiconductors, the transition is to the rocksalt structure. For a given ionicity we find that the transition pressure to either high-pressure form increases with decreasing lattice constant.

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