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High-pressure phases of III-V zinc-blende semiconductors

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With the use of the pseudopotential total-energy approach, the stability of two likely high-pressure structures, the *A*5 (β-Sn) and rocksalt structures, for the III-V compounds AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb are investigated. We present the calculated pressures for the phase transformations and compare them with the experimental values. As previously reported for AlP, there are discrepancies in the transition pressures between theory and experiment for Al compounds and these are discussed. A new high-pressure phase of GaSb analogous to the simple hexagonal structure of Si or Ge is predicted to be stable with a transition from the *A*5 phase to the hexagonal phase at a pressure of 528 kbar. Using the measured and calculated results for the high-pressure phases of the zinc-blende compounds, we conclude that the rocksalt phase is stabilized relative to the *A*5 phase by the averaged optical energy gap (both homopolar and heteropolar contributions) of the material.

I. INTRODUCTION

The study of materials at high pressures is experiencing great current activity because of recent refinements of the diamond-anvil technique[1] and the observation that materials often exhibit new crystal phases and novel behavior under pressure. Silicon, for example, becomes metallic and superconducting[2,3] at high pressures. In general, metallic behavior is expected for most semiconductors at high pressures since pressure-induced structural phase transformations occur when the atoms become more closely packed.

The first-principles pseudopotential method for total-energy calculations has been shown to be capable of predicting structural properties for group-IV elements and their high-pressure structures.[4–9] This approach was also applied to III-V zinc-blende compounds. Froyen and Cohen (FC) have calculated the structural properties of AlP, AlAs, GaP, and GaAs,[10] but compounds with heavier elements like In and Sb were not considered because the inclusion of relativistic corrections is necessary. Although the agreement between experiment and theory for group-IV elements is quite impressive, notable discrepancies appear for the four III-V compounds. Some difficulties arise from the fact that there is little experimental knowledge about the structures of the high-pressure phases. Unlike Si or Ge, GaAs is believed to transform to an orthorhombic phase[1,11,12] where the positions of the atoms in the unit cell have not been determined precisely. GaP transforms to a tetragonal phase similar to the β-Sn structure[1,11,12] The available data for AlP and AlAs are even less clear.[11]

The present systematic study which includes compounds containing In and Sb is motivated by the following.

(1) Although the experimental data for AlP, AlAs, GaP, and GaAs are incomplete, information on the structural properties for compounds containing In or Sb are available and more definitive.[11] It is important to show that the first-principles pseudopotential method yields accurate results for these compounds.

(2) The trends found from the previous calculations for AlP, AlAs, GaP and GaAs can be examined within a data base containing more materials. For example, FC have pointed out that the structural properties of zinc-blende compounds under high pressure appear to be closely related to the properties of the cation instead of anion.

It is known that Si will undergo the sequential structural transformations: diamond→β-Sn→simple hexagonal→hcp under pressure.[5,8] A similar sequence is expected for compounds with low ionicities. GaSb, having the smallest ionicity [0.261 (Ref. 13)] within the nine III-V compounds considered, transforms to the polar analog of the β-Sn structure, *A* 5 at 62 kbar.[11] In the present study a new phase of GaSb, which is analogous to the simple hexagonal structure of Si, is found theoretically to be stable at a higher pressure. The rocksalt structure is preferred as the ionicity increases. Hence, most of the ionic compounds transform from the zinc-blende structure to the rocksalt structure. In addition, Vohra *et al.*[14] have reported the observation of a phase transition in InAs from the rocksalt to the *A* 5 structure. However, using only the ionicity of a compound it is still not possible to predict the structural properties at high pressures of all the zinc-blende compounds. For example, although the ionicity of BN (0.256) is smaller than GaSb, the rocksalt structure is clearly more stable than the *A* 5 structure.[15]

Perhaps, the most significant discrepancy between the results of FC and the experimental data is the transition pressure from zinc-blende to rocksalt for AlP which is about 30% lower than the experimental value of 140–170 kbars to a unknown high-pressure phase.[11,16] Since there were no experimental data available for AlAs, it was not clear at the time of the FC calculation whether a similar trend exists. We will show that a similar result does exist for both AlAs and AlSb.

The rest of this paper is organized as follows: in Sec. II, we describe the calculational procedure. Results related to the static structural properties and structural properties under pressure are presented in Sec. III. Section IV contains some discussion of the results.

II. CALCULATIONAL METHOD

A. Pseudopotential approach

Ab initio (Refs. 17 and 18) pseudopotentials are generated using the method of Hamann, Schlüter, and Chiang[19] with the modification introduced by Kleinman[20] for relativistic corrections. There is no experimental input for the pseudopotentials but they are required to reproduce the all-electron results in the atomic limit. The atomic calculations are performed using the density-functional formalism[21–23] with the Wigner interpolation formula for the exchange and correlation energies.[24] Later, the same functional is used for the crystal calculations. Separate potentials are generated from given atomic configurations (see Table I) for electronic orbitals of *s*, *p*, and *d* symmetries. A good choice of atomic configurations ensures that the pseudopotentials accurately simulate the core-valence interactions. The potentials are then tested to give the correct atomic wave functions, energy levels, and excitation energies for a number of electronic configurations For Al, P, As, and Sb, the errors are less than 1 mRy in both the energy levels and the excitation energies for atomic excitations up to +1.0 Ry. It would be preferable if negatively charged excitations were also tested, but unfortunately for most of these cases the numerical results diverge. The *d* core states in gallium and indium atoms are not completely frozen. This leads to errors of around 3 mRy for atomic excitations near 1.0 Ry. Pseudopotentials for Al and P have been used previously for structural calculations of single crystals of these elements and yield reasonably good results.[25,26]

TABLE I. Atomic configurations used in generating *ab initio* pseudopotentials.

	Atomic configurations
Al	$3s^{1.0}3p^{1.0}3d^{1.0}$
Ga	$4s^{1.5}4p^{0.5}4d^{0.5}$
In	$5s^{1.9}5p^{0.8}5d^{0.2}$
P	$3s^{2.0}3p^{1.7}3d^{0.5}$
As	$4s^{2.0}4p^{2.5}4d^{0.3}$
Sb	$5s^{2.0}5p^{2.1}5d^{0.5}$

In order to see whether Al pseudopotentials cause any of the discrepancies mentioned in Sec. I, different atomic configurations were tested. As long as the potentials reproduce the atomic limit the calculated change in the structural properties of the Al compounds is negligibly small. We also considered the core size effect of Al. Results for AlSb indicate the inclusion of partial core corrections[27] has little effect on transition pressures. Since the Al potentials have been proven able to predict both static and dynamic properties of the Al crystal and also the electron-phonon coupling constant λ (Refs. 25 and 28) the pseudopotential used should be capable of giving accurate results for the Al compounds. The disagreement between the theory and experiment could arise from the fact that the ideal structural model assumed in our calculation is not appropriate for the samples studied.

B. Formalism for total-energy calculations

The total energy per unit cell is calculated in the momentum representation and is given by (in Rydberg atomic units)

$$\begin{aligned} E_{\mathrm{tot}} = \Omega_c \Bigg[& \sum_{i,\mathbf{k},\mathbf{G}} |\psi_i(\mathbf{k}+\mathbf{G})|^2(\mathbf{k}+\mathbf{G})^2 + \sum_{\mathbf{G}(\neq 0)} S(\mathbf{G})V_{\mathrm{ion}}^{L}(\mathbf{G})\rho(\mathbf{G}) \\ & + \sum_{i,\mathbf{k},l,\mathbf{G},\mathbf{G}'} S(\mathbf{G}'-\mathbf{G})\psi_i^*(\mathbf{k}+\mathbf{G})\psi_i(\mathbf{k}+\mathbf{G}')V_l^{NL}(\mathbf{k}+\mathbf{G};\mathbf{k}+\mathbf{G}') \\ & + \tfrac{1}{2}\sum_{\mathbf{G}(\neq 0)} V_H(\mathbf{G})\rho(\mathbf{G}) + \sum_{\mathbf{G}} E_{\mathrm{xc}}(\mathbf{G})\rho(\mathbf{G}) + \gamma_{\mathrm{Ewald}} \Bigg] + E_0 \ , \end{aligned} \tag{1}$$

where Ω_c is the cell volume, **G**'s are reciprocal-lattice vectors and $S(\mathbf{G})$ is the structure factor. The quantities $\psi_i(\mathbf{k}+\mathbf{G})$, $V_H(\mathbf{G})$, $\rho(\mathbf{G})$, $E_{\mathrm{xc}}(\mathbf{G})$, $V_{\mathrm{ion}}^{L}(\mathbf{G})$, and $V_l^{NL}(\mathbf{k}+\mathbf{G};\mathbf{k}+\mathbf{G}')$ are the Fourier transforms of the wave function, the Hartree potential, the charge density, the exchange-correlation energy, the local part of the pseudopotential, and the nonlocal part of the pseudopotential, respectively. The symbol **k** is the crystal momentum vector in the first Brillouin zone; *i* is the band index which is summed over all occupied bands. γ_{Ewald} is the electrostatic energy of positive point ions in a uniform negative background (the Ewald energy).[7,29] In Eq. (1), terms with nonzero *G* components are obtained from the expression for homopolar materials.[30] The $\mathbf{G}=0$ component, E_0, contains the compensating divergent terms and thus requires more careful examination because the static dipole contribution of polar materials has been omitted in Ref. 30. We have not included in E_0 the $\mathbf{G}=0$ component from the exchange-correlation energy since this term does not diverge.

Following the discussion of Ihm *et al.*,[30] E_0 for III-V compounds can be written as

$$E_0 = \frac{4\pi}{\Omega_c}\left[\frac{\mathbf{G}\cdot(\mathbf{P}_e + Z_d\tau)}{G}\right]^2_{G\to 0} + (\alpha_c + \alpha_a)Z_t \ , \tag{2}$$

where the Z's are the valences with $Z_c=3$ for the cation, $Z_a=5$ for the anion; $Z_t=Z_c+Z_a$ and $Z_d=Z_c-Z_a$. The quantity $\mathbf{P}_e=\int \mathbf{r}\rho(\mathbf{r})d^3r$ is the dipole moment due to the electronic charge distribution. $\rho(\mathbf{r})$ does not contain the electron charge $-e$. We have chosen the origin at the center of the cation and anion and τ is the position vector of the anion. The α's are given by

$$\alpha_\gamma=\frac{1}{\Omega_c}\int\left[V^L_{\text{ion},\gamma}(\mathbf{r})+\frac{2Z_\gamma}{r}\right]d^3r \tag{3}$$

for $\gamma=c$ or a.

For a homogeneous system the total static dipole moment $\mathbf{P}_{\text{tot}}=\mathbf{P}_e+Z_d\tau$ is zero, the first two terms in Eq. (2) vanish and

$$E_0=(\alpha_c+\alpha_a)Z_t\ . \tag{4}$$

If the system is not homogeneous a total static dipole contribution to the energy might exist. It is positive and inversely proportional to the lattice constant which causes an increase in transition pressure. However, we will not estimate this correction here since detailed information about the inhomogeneity is required.

The wave functions in the solid are obtained by solving the Schrödinger equation using a plane-wave basis. Plane waves with kinetic energy $(\mathbf{k}+\mathbf{G})^2$ up to 13 Ry are included in the basis set for AlP and GaP. A smaller energy cutoff of 12 Ry is used for AlAs, AlSb, GaAs, GaSb, and InP. For InAs and InSb, the cutoffs used are 11 and 9 Ry, respectively. The matrices are larger than 200×200 at equilibrium volumes for all nine compounds. In order to obtain a relative convergence of about 2 mRy between the various structures of InSb, we found it necessary to include plane waves up to a kinetic energy of 9 Ry. Tests for AlSb, GaAs were also done. The choice of energy cutoff for the other compounds was made assuming the convergence scales as the inverse of the atomic volume.

For the insulating zinc-blende structure, 10 k points in the irreducible Brillouin zone are sufficient to obtain an accuracy of better than 2 mRy. However, the Fermi surfaces of the metallic structures may create convergence problems. In these calculations, 55 and 110 k points are used for the $A5$ and rocksalt structures, respectively. The two sets of k points were tested for GaAs and they give an accuracy of better than 2 mRy compared to a test with 300 k points. They were then used for other compounds without further testing. The calculations were iterated until E_{tot} is self-consistent to about 0.01 mRy.

III. RESULTS

A. Static properties

To obtain the static properties, we calculated the total energies at ten or more different volumes and fitted them with an equation of state. As discussed by FC, the choice of the equation of state, in particular the Murnaghan[31] or Birch[32] equations, does not change the calculated structural properties within the desired accuracy.[10] Therefore, only Murnaghan's equation of state is used and it fits the data to better than 0.2 mRy. The calculated lattice constants, bulk moduli, and the derivatives of the bulk moduli are shown in Table II. For comparison, this table also contains the experimental values.[33,34] The bulk modulus is defined as the derivative of pressure P with respect to volume V

$$B=-V\frac{\partial P}{\partial V}=V\frac{\partial^2 E}{\partial^2 V}=B_0+B_0'P\ , \tag{5}$$

where E, B_0, and B_0' are the calculated total energy, the equilibrium bulk modulus, and the derivative of the bulk modulus with pressure, respectively.

In general, our results are in good agreement with the experimental values to within a few percent. Singh and Varshni[35] have also calculated the static properties of InSb using the pseudopotential method; their results for the lattice constant ($a_0=6.34$ Å) and bulk modulus ($B_0=50.7$ GPa) are similar to those presented here but with a slightly larger deviation from experiment. To be consistent, we have calculated the static properties for all nine compounds using the same correlation energy functional. Therefore, the results for AlP, AlAs, GaP, and GaAs are slightly different from FC.[10] The lattice constants for GaAs and AlAs are close to the previous results of Ihm and Joannopoulos[36] although the bulk moduli differ somewhat. We believe the higher cutoffs used in our calculation are responsible for the differences since

TABLE II. Lattice constants, equilibrium bulk moduli, and the derivatives of the bulk moduli with pressure. The lattice constants are measured at room temperature. The experimental data are taken from Ref. 33 and 34. In parentheses, the bulk moduli calculated using an empirical method (Ref. 37) are also shown.

		a_0 (Å)			B_0 (GPa)		B'
	Calculated	Expt.	Difference (%)	Calculated	Expt.	Difference (%)	Calculated
AlP	5.471	5.451	0.4	84.5	86.0(87.0)	−1.7	4.18
AlAs	5.678	5.662	0.3	71.0	77.0(79.0)	−7.8	3.26
AlSb	6.153	6.135	0.3	54.3	58.0(57.0)	−6.4	4.01
GaP	5.386	5.451	−1.2	86.8	88.7(87.0)	−2.1	4.00
GaAs	5.601	5.653	−0.9	70.8	74.8(77.0)	−5.3	3.36
GaSb	6.032	6.118	−1.4	55.7	57.0(58.0)	−2.3	3.83
InP	5.688	5.869	−3.1	70.0	71.0(67.0)	−1.4	4.93
InAs	5.906	6.036	−2.1	58.1	60.0(61.0)	−3.2	3.60
InSb	6.359	6.49	−2.0	47.0	48.3(47.0)	−2.7	5.21

the bulk modulus is more sensitive to the cutoffs than is the lattice constant.

The differences in lattice constants and bulk moduli between experiment and our calculation show a systematic dependence on cation. For Al compounds, the lattice constants are larger than the experimental values by 0.3%. Gallium compounds, however, exhibit an opposite trend with lattice constants which are about 1% smaller than the experimental values. The differences for indium compounds are slightly larger and the calculated lattice constants are about 2% smaller.

From Table II, one observes similarities between the results for the Al and Ga compounds. The lattice constants and bulk moduli of the two compounds are nearly identical for a given anion. In contrast, there is no such coincidence between the Ga and In compounds. Since Al, Ga, and In belong to the second, third, and fourth rows of the Periodic Table in the same column, respectively, it would be expected that the lattice constants of Al, Ga and In compounds increase as the row number increases. The fact that the lattice constants and bulk moduli do not increase from Al compounds to Ga compounds can be understood because of the absence of *d*-core states of Al. The valence electrons of Ga compounds (or In compounds) are affected in part by the extra attractiveness of the nuclear charge of the cation. Their lattice constants are contracted with respect to Al compounds. Hence, incomplete screening in Ga compounds causes the lattice constants and bulk moduli of Al compounds and Ga compounds to be very close.

The bulk moduli obtained from the empirical formula[37] $B_0 = 1761d^{-3.5}$, where d is the nearest-neighbor distance given by experiment, are also shown in Table II. The agreement between the results of the two theories and experiment are quite good. Bulk moduli obtained from *ab initio* calculations for all the nine compounds are systematically lower than the experimental values.

B. High-pressure phases

To determine the most stable structure at finite pressure and temperature, the Gibbs free energy, $G = E + PV - TS$, should be considered; the structure with lowest free energy is the most stable. It is however difficult to minimize the free energy from randomly generated structures even with modern supercomputers. We therefore only compare the stability of candidate structures. Hence we cannot exclude the possible existence of other structures that are even more stable. To further simplify our calculations, the temperature has been set to zero. The entropy of the crystal is therefore ignored. However the contribution of temperature to the free energy is small for the experimental data considered.

In this paper, three structures, zinc-blende, $A5$, and rocksalt structures are considered. Previously two different structures, NiAs and CsCl were also studied by FC.[10] They showed the total energy of the NiAs structure is very close to the rocksalt structure and that the CsCl structural energy is much higher than for the structures discussed here. The zinc-blende structure is the most stable structure at atmospheric pressures. The $A5$ structure can be obtained from the zinc-blende structure by compressing the crystal along one of the cubic axes. More details about this structure can be found in FC.

The results are summarized in Fig. 1 which displays the total energy as a function of volume for five III-V compounds. Similar curves for the other four compounds are given in FC. The zero of energy has been taken at the minimum for each curve and the volume is normalized to the calculated equilibrium volume. Table III lists the

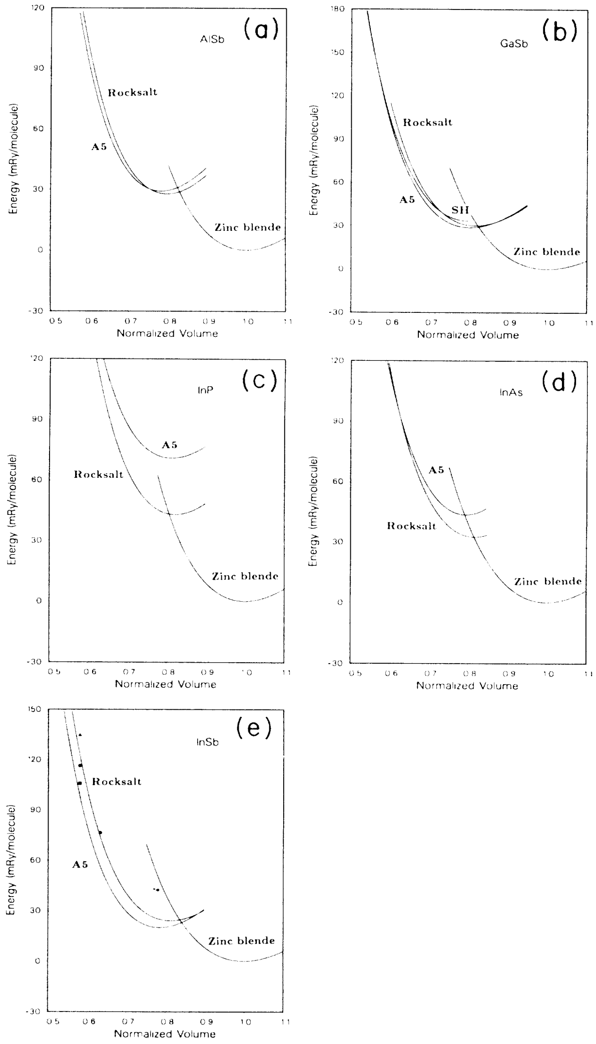

FIG. 1. Calculated total energies per molecule for (a) AlSb, (b) GaSb, (c) InP, (d) InAs, and (e) InSb in the structures indicated as a function of volume. In panel (e), the diamond and the triangle give the energies for the orthorhombic and hexagonal orthorhombic structures suggested in Ref. 50, respectively. The cross is the energy of the orthorhombic structure given in Ref. 47. The square and the circle indicate the energies for the two hexagonal structures discussed in the text.

TABLE III. Comparison of experimental and calculated high-pressure phase structures, transition pressures (P_t), and relative volume changes [$\Delta V^{\alpha\beta}(P_t)/V^{\alpha}(P_t)$] for zinc-blende III-V compounds without first row elements. The calculated results for AlP, AlAs, GaP, and GaAs and most of the experimental data are taken from Refs. 10 and 42, respectively. Other references are given explicitly. The short notations, RS, orth. and "*A* 5" stand for the rocksalt, orthorhombic, and *A* 5-like structures. For AlSb and InSb, more than one structure have been reported experimentally; the alternative structures are given in the parentheses.

	Structure		P_t (kbar)		$\Delta V^{\alpha\beta}(P_t)/V^{\alpha}(P_t)$	
Substance	Expt.	Calculated	Expt.	Calculated	Expt.	Calculated
AlP		RS	140[a], 170[b]	93		0.189
AlAs		RS	120[c]	76		0.207
AlSb	RS[b]	RS	83[b]	56	0.20[b]	0.191
	(*A* 5)	(*A* 5)	96–105[d]	54	0.165	0.206
GaP	"*A* 5"[e]	RS	200–240[b,c]	217	0.175[e]	0.155
GaAs	orth.[b]	RS(*A* 5)	160–190[b,c,e]	160	0.15[b], 0.173[e]	0.174
GaSb	*A* 5	*A* 5	62[b],67–84[d]	63	0.171	0.186
InP	RS	RS	105–110[d]	128	0.196	0.166
InAs	RS	RS	70–84[c,f,g]	84	0.15[f],0.188	0.165
InSb	orth.[b]		23[h]		0.193[b]	
	("*A* 5")	*A* 5	23[h]	33	0.185–0.197[i]	0.207

[a] Reference 16.
[b] Reference 11.
[c] Reference 38.
[d] Reference 39.
[e] Reference 12.
[f] Reference 14.
[g] Reference 40.
[h] Reference 41.
[i] Reference 45.

high-pressure phases, relative volume changes, and transition pressures for all nine III-V compounds. Both experimental and calculated results are included for comparison. Our results for the five III-V compounds not studied by FC are generally in good agreement with experiment.

The results for GaSb are especially interesting. Not only is the theoretical result for the high-pressure phase consistent with the experiment, but also the transition pressure is within the range of the recent[11] experimental value, 62±3 kbar. Among the nine compounds, GaSb has the smallest ionicity. It is the best candidate for testing the analog of the simple hexagonal phase of Si (or Ge). Figure 2 shows the hexagonal structure which can be obtained from the *A* 5 structure by displacing one type of atoms in the direction of the *c* axis by $c/4$, followed by a slight change of the c/a ratio. In this geometry, there are eight nearest-neighbor atoms with two atoms alike and six atoms unlike. We have calculated the total energy for this structure using 144 *k* points and found it energetically favorable. The transition from the *A* 5 phase to the new phase occurs at a pressure of 528 kbar which is higher than the pressure found for the transition from the β-Sn phase to the simple hexagonal phase of Si, 120 kbar (Ref. 8) but lower than the transition pressure for Ge, 840 kbar.[9]

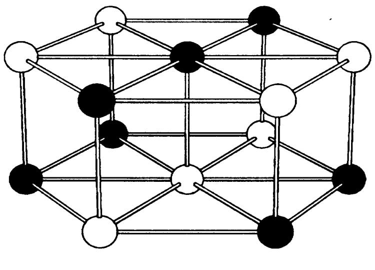

FIG. 2. The conventional unit cell of the hexagonal structure of GaSb.

Both the rocksalt and *A* 5 phases were reported for AlSb.[11,42] Our results show that the energies of the two structures are very close. The energy minimum of *A* 5 phase has a volume smaller than the rocksalt phase. Therefore, the transition pressure to the *A* 5 phase is slightly lower. The calculated transition pressures for AlSb, 54 kbar (*A* 5) or 56 kbar (rocksalt) are considerably lower than the experimental value of 83–105 kbar. This is similar to the situation found previously for AlP (Ref. 10) in which the calculated transition pressure is about 30% lower than the measured transition pressure. It has been found that the rocksalt phase is much more stable than the *A* 5 phase[10] for AlP and AlAs. This trend does not hold for AlSb. From the ionicity changes of Al compounds it is difficult to explain why the trend breaks down. Later, this will be explained in terms of the increased metallicity of AlSb using an empirical method.

A few high-pressure phases have been found[41–50] for InSb. The first of these has orthorhombic structure[41] but the atomic positions are unknown. Yu *et al.*[50] suggested a structure for the orthorhombic phase in which the unit cell contains two sets of sublattices with one type of atom at the origin and the other at $(0,\frac{1}{2},\frac{1}{4})$. In this arrangement atoms are octahedrally coordinated with six neighbors. Our calculation shows that this geometry is unstable compared with the $A5$ structure. The Ewald energy is increased by the fourfold coordination with the same type of atoms. The total energy is about 18 mRy/molecule higher than the $A5$ structure at the given volume. Another structure suggested by Kasper and Brandhorst[47] with one atom at the origin and the other at $(0,\frac{1}{2},\frac{1}{2})$ is also unstable relative to the $A5$ phase. Furthermore, the $A5$ phase is stable against the stretch along the [010] direction accompanied by a compression along the [001] direction of the tetragonal unit cell and followed by subsequent relaxation of the atoms to form an orthorhombic unit cell. A transition to the $A5$ phase has been found with a transition pressure of 22 kbar around 100 °C. Since the transition pressure is small, temperature effects could make a significant difference (see Ref. 50, for example). A linear extrapolation of the data at finite temperatures in Ref. 50 shows the transition pressure to the $A5$ phase at 0 K is around 29 kbar and is quite close to our result. An orthorhomic hexagonal phase also exists above 90 kbar at room temperature for InSb.[48] We have calculated the energies for two different hexagonal structures. One of the structures has been discussed and found stable for GaSb. In the other structure, the nearest neighbors include six like and two unlike atoms. None of these structures has energies lower than the $A5$ phase up to a compression in which the volume is reduced by 50%. The structure suggested by Yu *et al.* for the hexagonal phase[50] was also tested but the energy is quite high [see Fig. 1(e)].

IV. DISCUSSION

While the calculated results for some of the III-V compounds are in excellent agreement with experiment, some of them disagree considerably. In the case of AlP, a correction as large as 20 mRy/molecule is required to obtain the measured transition pressure.[10] Possible corrections arising from zero-point motion have been estimated assuming the phonon frequencies scale with the elastic constants.[51] The zero-point energy is then proportional to the square root of the bulk modulus. Within the model, the correction raises the calculated transition pressure, especially for AlP, but only by a small amount (a few kbars).

Although the III-V compounds are similar in their structural properties at atmospheric pressure, their high-pressure structures differ. FC argued previously that the rocksalt structure is stabilized by the ionic energy gap. The band structure of GaAs shows that for the rocksalt structure there is a relatively large energy gap over most of the Brillouin zone. Only around the X point, does the conduction band come down to close the energy gap which makes the high-pressure rocksalt phase metallic. In contrast, the conduction and valence bands for the $A5$ structure overlap considerably and near the Fermi level, the density of states resembles that of a free electron gas (see Figs. 8 and 9 in Ref. 10).

Recently, Chelikowsky *et al.*[52,53] also examined the high-pressure $A5$ and rocksalt phases for zinc-blende compounds. By altering the ionic components of the potentials of the cation and anion relatively and then converting the associated charge transfer to the ionicity change, the relative stabilities of the two phases are studied. While the role of ionicity in phase transformation is elucidated by this approach the model assumes fixed volume and first row elements are not considered.

Since several diamond and zinc-blende compound semiconductors have been studied at high pressures, it is possible to examine proposals for explaining the observed trends. Figure 3 shows a diagram containing most of the compounds with the zinc-blende (or diamond) structure at atmospheric pressure. The homopolar energy gap E_h and ionic energy gap C are plotted as the horizontal and vertical axes, respectively. Except for a few compounds where neither experimental data nor pseudopotential calculations on their high-pressure phases is available, all the zinc-blende compounds can be considered as separating into two groups having small or large average energy gaps ($E_g^2=E_h^2+C^2$). Compounds with small E_g prefer the $A5$ structure while the rocksalt structure is stabilized when the gap becomes larger. There is a critical region containing most of the III-V compounds in which the two phases have been found stable at different pressures. It is therefore likely that not only the ionic energy gap, as previously discussed by FC, but also the homopolar energy gap contribute to the stability of the rocksalt phase. From the atomic point of view, the homopolar energy gap scales with the separation between the bonding and antibonding orbitals at each atom. Smaller energy separation makes it easier to form a metallic phase.

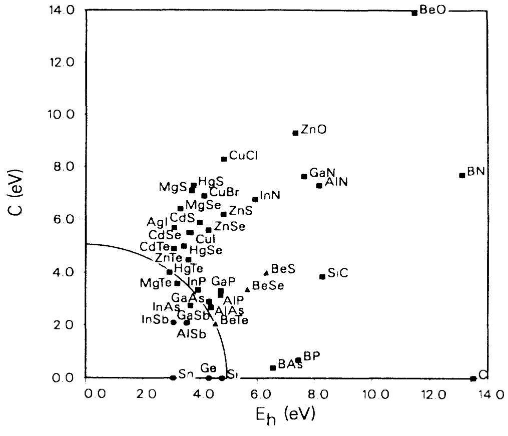

FIG. 3. Phase diagram for zinc-blende compounds under pressure. The horizontal and vertical axes are the Phillips (Ref. 13) homopolar and ionic energy gaps, respectively. A circle centered at the origin is drawn to separate the two high-pressure phases. It is possible that the contributions from the homopolar and ionic energy gaps to the relative stability of the two phases are not exactly equal therefore a small ellipticity exists for the separating line (if accurately determined). The solid circles and squares correspond to the $A5$ and rocksalt phases, respectively. For points marked with triangles, there are no available data.

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