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Theoretical predictions of expanded-volume phases of GaAs

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By reducing the (4;2)-connected regular three-dimensional nets of $AlPO_4$ zeolites to simply four-connected nets of III-V semiconductors such as GaAs, we introduce a variety of expanded structures for compound semiconductors. An *ab initio* local-orbital quantum molecular-dynamics method is used to determine the optimized geometries, energetics, and electronic properties of the proposed structures. We specifically treat GaAs, and find that even with the 90° bond angles required for these expanded structures, most of these phases remain semiconducting with band gaps ranging from slightly above that of the zinc-blende structure, to about 0.6 eV smaller than it. Two compounds with the same volume as the room pressure phase are predicted to be metallic. The total energies of the expanded phases are in the range of 0.2 eV/atom higher than the zinc-blende structure, less than or comparable to the energies of known or predicted high-pressure phases, and are energetically less favorable than analogous expanded phases of elemental semiconductors such as Si. [S0163-1829(97)03608-4]

I. INTRODUCTION

Open framework structures such as the aluminosilicate zeolites or $AlPO_4$ molecular sieves are of great technological importance, and many form beautiful structures in nature. The tetrahedral SiO_2 polymorphs are (4;2)-connected nets where the basic building block is the SiO_4 tetrahedron. Each silicon atom (four-connected) is bonded *via* sp^3-like hybrids to four oxygen corners of a SiO_4 tetrahedron. The oxygen bridge atom (two-connected) bonds to two Si atoms, which topologically can be described as a sharing of a vertex by two tetrahedra. The lowest energy polymorph is α quartz which has a fairly compact structure. However, by altering the framework topology a whole host of expanded volume phases can be synthesized, to form the high-silica zeolites and clathrasils, as well as microporous materials. Replacing Si by Al in the framework (in addition to adding a charge balancing cation) is common, and the tetrahedral atom is generally referred to as simply the ‘‘*T*’’ atom. In the $AlPO_4$ molecular sieves, two Si atoms are replaced by Al and P. The expanded phases of SiO_2 can easily have two to three times the volume per SiO_2 unit as the ground state α-quartz structure.

A related family of expanded volume phases is found for crystalline H_2O, which forms ‘‘hydrate I’’ and ‘‘hydrate II’’ structures.[1,2] Here each oxygen is at the center of an irregular tetrahedron, with two short legs along intramolecular hydrogen donor atoms, and two long legs toward acceptor hydrogen atoms. These expanded phases or ‘‘clathrates’’ often form in the presence of impurities (which are incorporated as guests into polyhedral cages within the structure). In water hydrates, the prototypic example of a guest is a Cl_2 molecule. Analogous compounds based on silica frameworks are the ‘‘clathrasils.’’

Recently it was suggested that a new class of materials (the silisils) may exist, based on silicon atoms joined in a network topology similar to that of the zeolites, but without oxygen.[3] Two such structures have been described experimentally, as the silicon frameworks of the Na_xSi_{46} or Na_xSi_{136} ‘‘silicon clathrates.’’[4] In these structures, the (4;2)-connected network of a SiO_2 zeolite is simply replaced by Si in the same zeolite framework, which is now four-connected. The suggestion of their existence was motivated by the fact that both silica zeolites and H_2O hydrates are based on a tetrahedral configuration. Since elemental Si is a prototype tetrahedral material, by analogy it is natural to expect silicon under the right conditions to form such structures. The two silisils already synthesized experimentally are entirely analogous to the structures of water hydrate I and II—in terms of zeolites, they are melanophlogite and dodecasil 3C, which in standardized zeolite nomenclature[5] are MEP and MTN, respectively.

Much effort is placed in making new phases of materials by applying pressure, since pressure allows researchers to explore higher energy structures. It is remarkable that the theoretical predictions of Ref. 3 find that many of the silisil structures are lower in energy than any previously studied *high*-pressure silicon phase. The calculations for pure Si expanded phases, coupled with experimental data of the excess enthalpy for expanded phases of SiO_2 (Ref. 6) indicate that compressing a structure has a large energy cost, while expanding the structure and maintaining the four-connected net generally costs very little energy. However, successful synthesis of the expanded volume phases requires design of metastable formation routes from appropriate precursors, or

TABLE I. The four-coordinated networks are considered. Lattice parameters are given in angströms. The space group is for a compound semiconductor, thus the symmetry is lowered from that for the net of identical T atoms. The number of atoms/cell is for the conventional cell.

Polymorph	Lattice type. parameters (Å)	Atoms/cell	Space group (No.)	Rings	Coordinates	x	y	z
ZB	cubic	8	$F\overline{4}3m$		atom type I:			
	$a=5.658$		(No. 216)	$6_2 6_2 6_2 6_2 6_2 6_2$	$4a$ (0,0,0;etc.)			
					atom type II			
					$4c$ $(\frac{1}{4},\frac{1}{4},\frac{1}{4}$;etc.)			
SOD	cubic	12	$Pm\overline{3}n$		atom type I:			
	$a=6.930$		(No. 223)	446666	$6c(\frac{1}{4},0,\frac{1}{2}$;etc.)			
					atom type II:			
					$6d$ $(\frac{1}{4},\frac{1}{2},0$;etc.)			
LTA	cubic	192	$Fm\overline{3}c$		atom type I:			
	$a=18.757$		(No. 226)	464648	$96i(0,y,z$;etc.)		0.0924	0.1848
					atom type II:			
					$96i(0,y,z$;etc.)		0.1848	0.0924
ATV	orthorhombic	24	$Abm2$		atom type I:			
($AlPO_4$-25)	$a=7.715$		(No. 39)	$4c;66_2 66_2 6_2 6_2$	$4c(x,\frac{1}{4},z$;etc.)	0.849		0.692
	$b=11.760$			$8d;46_2 66_3 6_2 6_3$	$8d$ $(x,y,z$;etc.)	0.651	0.099	0.192
	$c=6.377$				atom type II:			
					$4c(x,\frac{1}{4},z$; etc.)	0.849		0.308
					$8d(x,y,z$;etc.)	0.651	0.099	0.808
AFI	hexagonal	24	$P6cc$		atom type I:			
($AlPO_4$-5)	$a=11.062$		(No. 184)	$46_2 66_3 6_2 6_3$	$12d(x,y,z$;etc.)	0.455	0.122	0.192
	$c=6.368$				atom type II:			
					$12d(x,y,z$;etc.)	0.545	0.878	0.808
VFI	hexagonal	36	$P6_3cm$		atom type I:			
(VPI-5)	$a=14.911$		(No. 185)	$6c;46_3 46_3 66_4$	$6c(x,0,z$;etc.)	0.4227		0.063
	$c=6.551$			$12d;46_2 66_3 6_2 6_2$	$12d(x,y,z$;etc.)	0.1786	0.5120	0.563
					atom type II:			
					$6c(x,0,z$;etc.)	0.5773		0.937
					$2d(x,y,z$;etc.)	0.8214	0.488	0.437
ATO	hexagonal	36	$R\overline{3}$		atom type I:			
($AlPO_4$-31)	$a=16.660$		(No. 148)	$46_2 66_2 66_3$	$18f(x,y,z$;etc.)	0.1992	0.251	0.250
	$c=3.866$				atom type II:			
					$18f(x,y,z$;etc.)	0.0518	0.251	0.250
CrB_4	tetragonal	8	$P4_2/mnm$		atom type I:			
	$a=7.350$		(No. 136)	$46_2 6666$	$4f(x,x,0$;etc.)	$\frac{1}{6}$		
	$c=3.465$				atom type II:			
					$4f(x,\overline{x},0$;etc.)	$\frac{1}{6}$		
Net 109	tetragonal	32	$I4_1/a$		atom type I:			
	$a=14.347$		(No. 88)	$46_2 6666$	$16f(x,y,z$;etc.)	0.585	0.080	0.125
	$c=3.486$				atom type II:			
					$16f(x,y,z$;etc.)	0.415	0.080	0.125

synthesis about a structure-directing guest or template. This is a problem in synthetic chemistry.

Since some of the zeolite structures are formed from stacked fullerenelike cages, Nesper *et al.*[7] and Adams *et al.*[8] have investigated elemental carbon in these structures. It was found that these structures are very low in energy, in fact much lower than fullerene themselves. Recently Teter[9] has investigated elemental carbon in silica structures, including α quartz and found exciting results for compressed phases.

To extend our previous work on elemental Si and C, we investigate the energetics and electronic states of compound semiconductors in expanded phases. The specific material chosen is GaAs. Our aim is to examine the energetics and potentially interesting material properties for such expanded phases to help guide experimental synthesis programs. The calculations are used to assess the feasibility of synthesizing these phases, and to establish which classes of structures would form the best synthesis targets.

Just as silisils are four-connected networks derived from SiO_2 (4;2) networks, the compound semiconductor four-connected nets are derived from the (4;2) nets of materials such as $AlPO_4$. To our knowledge, there is no experimental evidence yet concerning the existence of such expanded phases of pure GaAs or other III-V compound semiconductors. The main questions we desire to answer in the present work are (i) what is the energy scale for the formation of an expanded compound semiconductor (GaAs) phase, and (ii) if these materials could be synthesized, what would be their electronic properties. For the silisils studied previously, it was found that they had surprisingly low energies (compared with diamond structure), and some had wide band gaps (wider by $+0.7$ eV compared to diamond Si), as well as a possible Mott transition upon doping with alkali metals.[10]

There is, however, a fundamental difference between compound (GaAs) and elemental (Si) expanded phases—Si will easily allow structures with 5-rings. In GaAs structures, 5-rings formation is energetically very costly since Ga-Ga or As-As bonds must be formed [these are the equivalent of ‘‘antisite’’ defects in zinc-blende (ZB) GaAs]. In expanded Si phases, it was found that the lowest energy structure contained the largest number of five rings. This is because the bond angle in a planar pentagon is 108°, which is very close to the ideal tetrahedral bond angle, $\theta_{\mathrm{Tet}}=109.5°$. For GaAs, we have limited our search to structures with even rings—4, 6, 8, or larger rings. Four rings are associated with 90° bond angles, which deviate considerably from θ_{Tet}. We anticipate that energetically favorable structures will have a low number of four rings.

The determination of the total energy, optimized geometry, and electronic structure is achieved through a local orbital quantum molecular dynamics (QMD) method.[11] In this method, the local density approximation (LDA) to density functional theory is used in a minimal basis of sp^3 orbitals on the atoms. A pseudopotential is used,[12] so that only the valence electrons are explicitly included in the electronic structure. The orbitals of the atoms are slightly excited from their ground states, and these orbitals are referred to as ‘‘fireballs.’’[11,13] A fireball orbital satisfies the boundary condition that its wave function vanishes at a finite distance R_c, and remains zero outside this radius. The values of R_c chosen are 5.4 and 5.0 bohr for Ga and As, respectively. The Harris functional[15] is used where the input density is taken as a sum of neutral atoms. We have checked the effects of charge transfer by computing the energetics of some GaAs polytypes using a self-consistent procedure[13] and find that charge transfer effects do not affect in a significant way the trends discussed here. In all cases, we use a Brillouin zone sampling that is dense enough to ensure the convergence of the force and total energy. A standard Monkhorst-Pack[14] special k-point sampling was used and energies were converged to better than 5 meV per atom. Typically this led to 64 k points in the first Brillouin zone. This leads to a high density of k points since the Brillouin zone is quite small in the expanded phases due to the large number of atoms per cell. A local form of the exchange/correlation potential without gradient corrections is used.

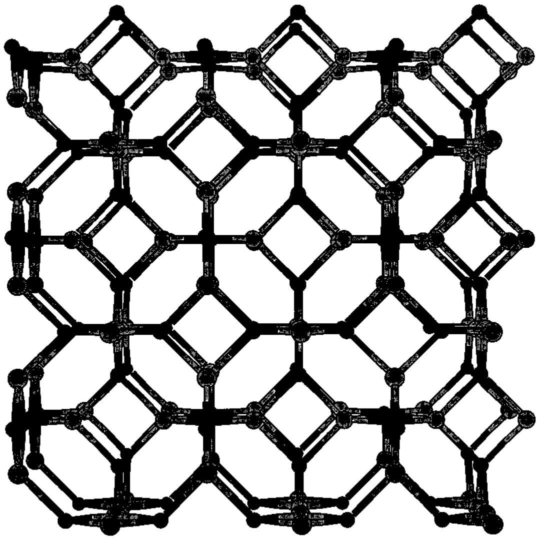
Structural optimization is done in two steps. We begin with an ideal structure (with uniform bond lengths), and vary the lattice parameters until the minimum volume is found. Once the external parameters are optimized, we perform a molecular-dynamics ‘‘dynamical quenching’’ simulation of the internal coordinates of the cell, within that structure. This means that we allow the atoms to move according to Newton’s laws, but quench the system (set all velocities to zero) whenever the average kinetic energy (‘‘temperature’’) reaches a maximum. The process is repeated until the system finds a zero force minimum energy configuration.

II. GaAs EXPANDED STRUCTURES

Our selection of GaAs expanded phases is aided by the inspection of $AlPO_4$ molecular sieve materials. In $AlPO_4$, the T atoms consist of alternating Al and P, presumably governed by similar bonding constraints to these which will be encountered in a compound semiconductor expanded phase. There are very many $AlPO_4$ structures to choose from, and we have focused our search to those containing a minimal number of four rings. All T atoms are tetrahedral (the tetrahedra are actually distorted) with four bonds, and therefore six (6) bond angles. Each of these six bond angles forms two legs of one (or more) of the primitive rings. We indicate the ring structure of each network with the long Schläfli symbol—an example is $46_2 66_3 6_2 6_3$ to indicate that the six bond angles give one 4 ring and five 6 rings. The subscript (e.g., the 3 in 6_3) indicated the number of ways of completing the circuit for that ring. The Schläfli symbols are useful since they give an indication of the expected number of 90° angles, and can help eliminate unlikely structures. For example, the aluminophosphate $AlPO_4$-C (APC) has a ring structure $4448_2 88_2$, which because of the high number of 4-rings (50%) was not studied here. Also the silica MEP with a 555 556 structure was not chosen, because of the 5-rings which would require high energy antisites.

The expanded-volume networks chosen for study are sodalite (SOD), Linde type A (LTA), $AlPO_4$-25 (ATV), $AlPO_4$-5 (AFI), VPI-5 (VFI), $AlPO_4$-31 (ATO), and two networks based on CrB_4 and net-109. Zinc blende is the ground state structure of GaAs and is included for comparative purposes. The structures SOD, LTA, ATV, AFI, VFI, and ATO

(a) Sodalite



(b) Linde A

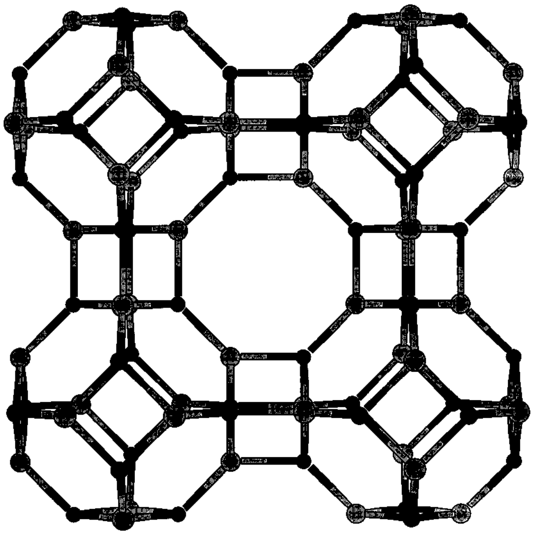


FIG. 1. (a) A projection of the cubic sodalite (SOD) structure of GaAs onto (001). The stacking of cubo-octahedral β cages along x, y, and z produces an interstitial cage from shared atoms centered at $a/2(1,1,1)$; (b) A projection along (001) of the cubic Linde type A (LTA) structure. The β cages are connected through bonds, which produces the large supercage (α-cage) in the center. Because there are two type of atoms, the lattice changes from simple cubic to fcc.

are described in Ref. 5 and Ref. 16. The CrB_4 and net-109 structures were obtained from Ref. 16. A review of some fourfold nets can also be found in Ref. 17.

All the relevant structural information concerning these structures is given in Table I. The optimized bond length d in all structures is near 2.45 Å, as in ZB GaAs. The number of atoms per cell shown in Table I refers to the Ga plus As atoms in the conventional cell. In calculations, we reduced this number to the primitive cell if appropriate. The space groups beginning with F reduce this number by 4, while groups beginning with I or C reduce this number by 2. The fractional coordinates are our starting coordinates (before optimization) and are those of the ideal structure (where all the bond lengths are equal) from Ref. 16. The nomenclature used is the standard crystallographic nomenclature of Ref. 18. We now give a brief description of the structures.

SOD and LTA are a related pair of structures with 446 666 and 464 648 ring structures, respectively. The percent of 4 rings in this fundamental zeolite structures is fairly high (33% and 50%, respectively), which permits us to examine the effects of the 4-ring population on the energetics. The building unit is the so called β cage (a truncated cubo-octahedron, also known as the Kelvin polyhedron) of 24 atoms composed of six squares and eight hexagons. Stacking the polyhedra on top of one another yields the SOD network [Fig. 1(a)], while connecting them with bonds across the square faces yields the LTA network [Fig. 1(b)]. The faujasite (FAU) network is similar to LTA, but is connected across hexagonal faces. We did not consider faujasite which has three sets of 4 rings (4 446 612), and is expected to be energetically similar to LTA. As can be seen for LTA [Fig. 1(b)], two adjacent cages have their arrangement of Ga and As atoms inverted to ensure no antisite defects. This causes the unit cell to be doubled to 48 atoms per cell compared to 24 atoms/cell when all the T-site atoms are considered equivalent.

The three nets ATV,[19] AFI,[20] and VFI (Ref. 21) can each be thought of as a stacking of a pseudo-two-dimensional three-coordinated networks to form a four-connected net with a short c axis. A view of these three structures down the c axis for VFI, ATF, and AFI is shown in Figs. 2(a), 2(b), and 2(c), respectively. The layers are only pseudo-two-dimensional, since each layer is not flat. The four rings within the plane form an up-down-up-down pattern of atoms around the ring. In the AFI structure, all atoms are related to one another by symmetry if all the T atoms are considered identical.

The molecular sieve $AlPO_4$-31 (Ref. 22) forms the ATO (Ref. 19) structure (Fig. 3) which is hexagonal. In projection, it looks similar to AFI, with a puckered 12-ring pore opening down the c axis. The six rings are composed of three sides from zigzag chains parallel to c, and three sides from 4 rings. The 6-rings are nonplanar and so appear to be irregular in projection. The 4-rings are planar, but tilted with respect to the c axis.

The nets corresponding to CrB_4 and net-109 (Ref. 16) are very similar. They are included here because of their low fraction of four rings ($46_{2}6666$ or 17% four rings). Both structures are body-centered tetragonal and the (001) projection of both structures is shown in Fig. 4. The CrB_4 net is so named because it is the framework formed of B atoms in CrB_4. The four atoms forming a square in Fig. 4 are at the same z height for the CrB_4 net, but the two nearest neighbor squares are at different heights with the difference being $\frac{1}{2}c$. Thus the octagon consists of edges which zigzag. In projection, net-109 looks identical to CrB_4 but pairs of atoms on a projected square differ in z height by $\frac{1}{8}c$. This net has

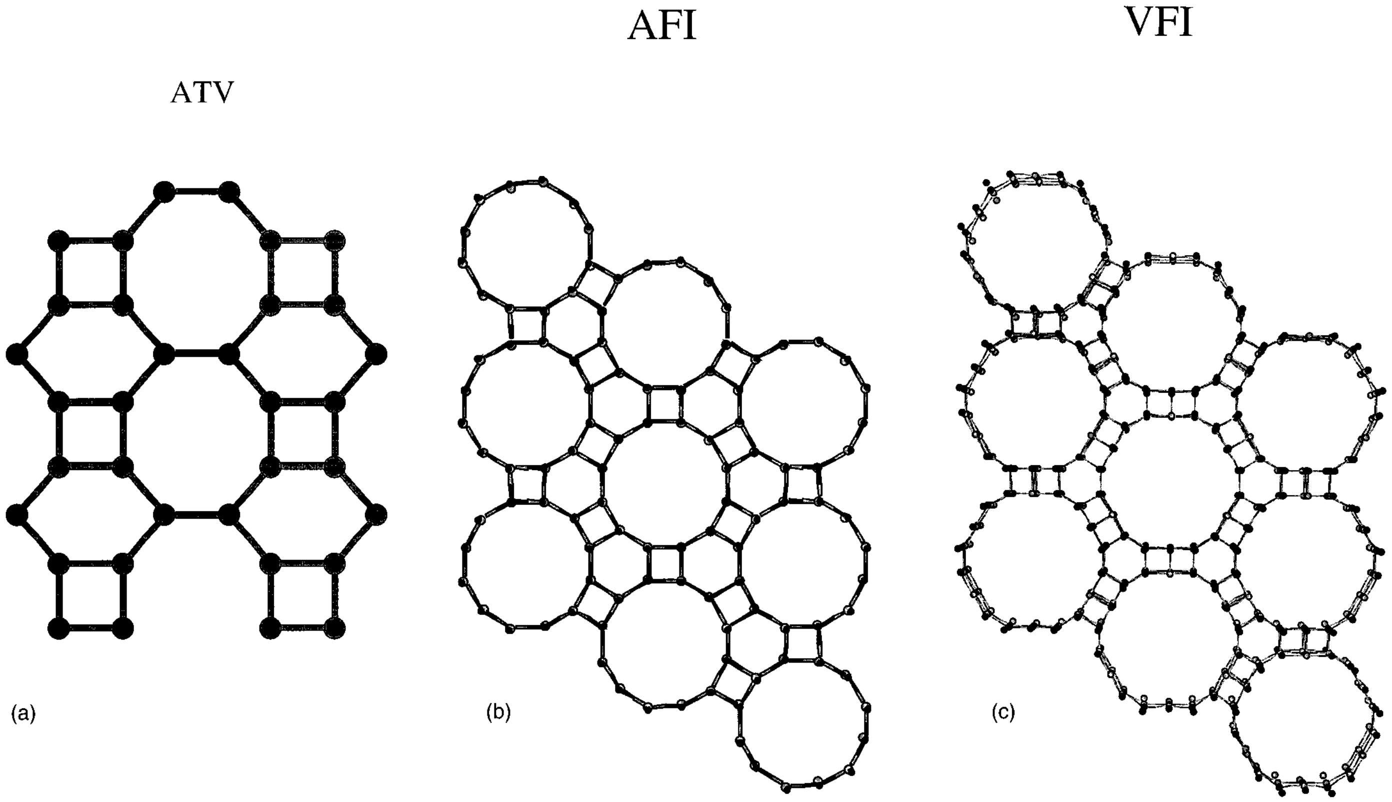


FIG. 2. A view down the *c* axis of the GaAs structure of (a) orthorhombic ATV, (b) hexagonal AFI, and (c) hexagonal VFI.

zig-zag lines along both the octagon and the square. The CrB_4-type structure is only slightly expanded relative to ZB; net 109 has nearly the same volume.

III. RESULTS

A. Energetics

We first discuss the total energies of the various expanded phases considered here. Since ZB is the ground state structure, we arbitrarily define this to have zero total energy, and the energy of all other phases are relative to this. The results for nine different GaAs structures computed in this study are shown in Fig. 5. Structure 7 is ZB, which is the ground state, and structure 6 is the closely related wurtzite structure. Theoretical studies have been performed on high-pressure phases.[23] Structures 1–5 are the results of recent calculations of others[24] for high-pressure phases which were also computed within a pseudopotential LDA theory, but using a plane wave basis. The consistency of such a comparison between the two slightly different techniques will be discussed below. These compressed structures are described in Ref. 24. Structure 1 (labeled *Cmcm*) is an orthorhombic structure with four atoms/cell and is a distortion of the rocksalt structure. This structure, or a very close variant, is the proposed structure[25] of the high pressure GaAs-II phase,[26] and is metallic, which is typical for high-pressure semiconductors. Structures 2 and 3 are the CsCl and NaCl (rocksalt) structures, respectively, and structure 4 is NiAs. The final compressed structure 5, denoted *sc*16, is the binary analog of the *bc*8 structure also known as γ-Si.

The expanded phases considered in this work are structures 8–15, described in the previous section. Two points are shown in Fig. 5 for each structure. The diamond indicates the ideal structure (given in Table I), and a cross (‘‘+’’) indicates the optimized structure obtained from the molecular dynamics run after dynamical quenching. We see that optimization plays only a small role in the relative energetics. A high symmetry structure such as sodalite (12) has no energy lowering at all from optimization due to relaxation, as expected.

Overall, there is an approximate 0.2 eV/atom (~20 kJ/mol) energy cost to form an expanded GaAs phase, which sets an energy scale for the formation of these structures. The lowest energy expanded phase found is ATV which is 0.146 eV above that of zinc blende. The expanded phases are generally semiconducting, and the diagonal dashed line separates insulators from metals. The set of expanded structures shown in Fig. 5 is certainly not exhaustive (the current zeolite atlas[5] lists 98 different structures), yet gives a representative set containing a variety of different classes of $AlPO_4$-like materials and other 4-ring structures.

The basic trend in the energetics, shown in Fig. 5 is similar to those found for silicas[6] and silisils.[3] The high-pressure phases rise rapidly in energy and the expanded phases (within the $AlPO_4$ framework type structures and sodalite) rise more slowly in energy with volume. However, there are two cases where this simplified trend is not obeyed. The first exceptional case is given by the structures CrB_4 and net-109 (labeled 8 and 9 in Fig. 5). These structures are metallic or semimetallic and thus forfeit the additional binding energy that accompanies an insulator because of a lowering of the

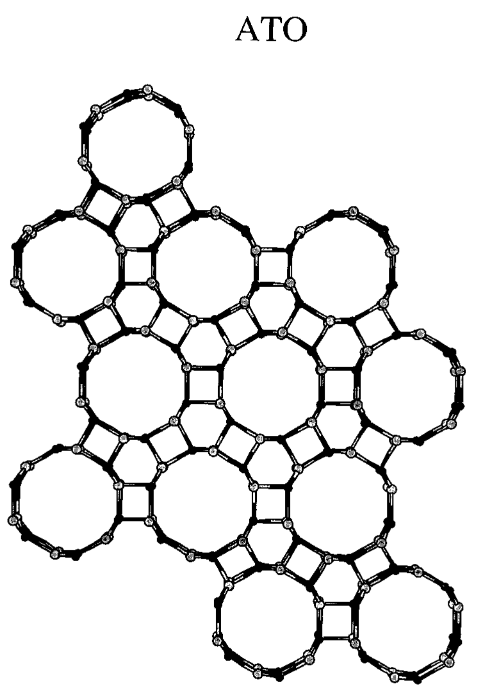


FIG. 3. A view down the *c* axis of the hexagonal GaAs structure of ATO.

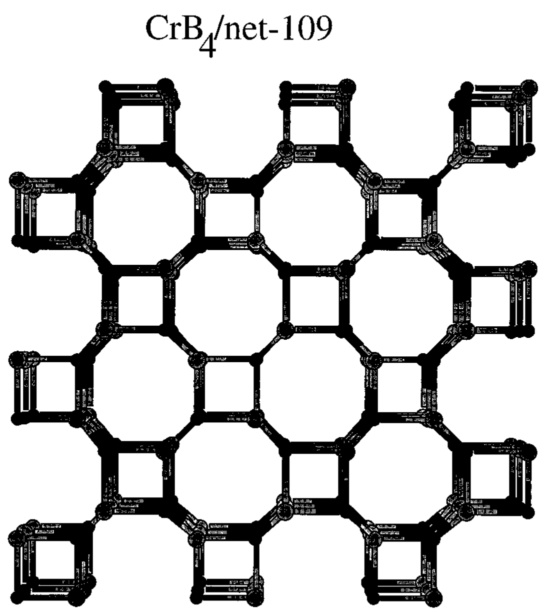


FIG. 4. A view down the *c* axis of the tetragonal GaAs structures of CrB$_4$ or net-109. In projection both of these structures look the same—the atoms in a single square are at the same z value in CrB$_4$, but are at two different heights in net-109.

bonding bands. It is a curious coincidence that these two structures have nearly the same density as the ground state zinc-blende structure yet are metallic. The second exception is that of LTA (labeled 1 in Fig. 5) which has a very high energy because of the presence of *double* 4-rings. This shows that structures with double 4-rings (which form a cube) are not very good candidate structures for compound semiconductors. LTA (15) is grossly off scale (signified by the vertical arrow) and has an energy of 2.3 eV.

The typical energy cost of 0.15–0.2 eV above the ground state is about twice that for the elemental expanded Si phases, which had structures ~0.075 eV/atom above the diamond ground state. Thus there is a significant energy cost to form an expanded compound semiconductor material (GaAs) compared to elemental semiconductors. Thus while the energy of Si expanded phases are about 0.075 eV (3 kT at room temperature) making their formation at high temperatures with the proper guest possible, the formation of GaAs phases requires 0.15 eV (~6 kT at room temperature) which is more problematical. The present calculations indicate that expanded GaAs phases are likely to be more difficult to synthesize than elemental semiconductor forms, but at the same

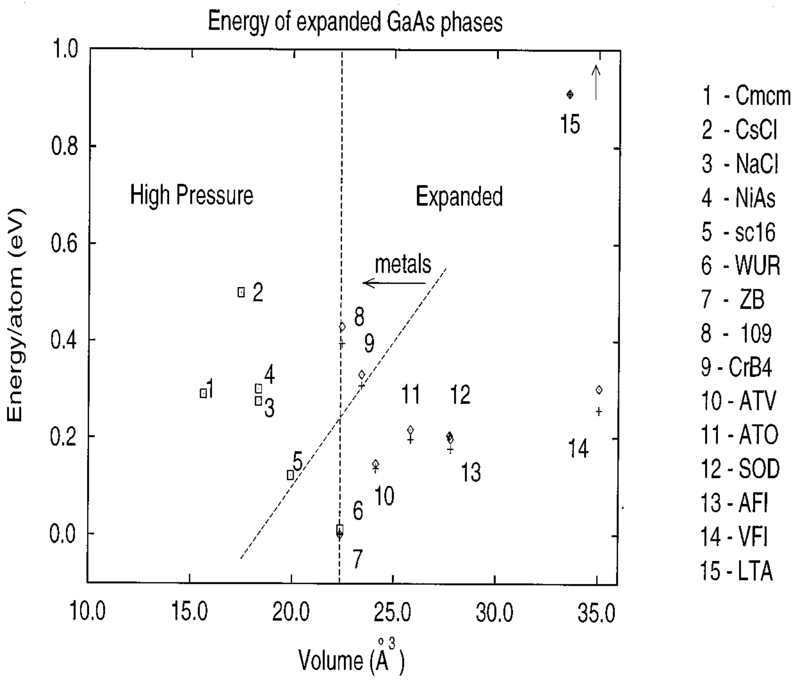


FIG. 5. The total energy of hypothetical compressed phases and expanded phases of GaAs as a function of volume. Structure 7 is zinc blende (ZB) which is the ground state and is defined to be zero energy. The energies of the compressed structures were taken from Ref. 24. Structure 1 is the high-pressure GaAs-II phase observed experimentally. Structures 8 through 15 are the expanded phases of this work. The energies of the expanded phases are given both for ideal coordinates (diamonds) and QMD-optimized internal coordinates (+). The LTA structure (15) has an energy off scale.

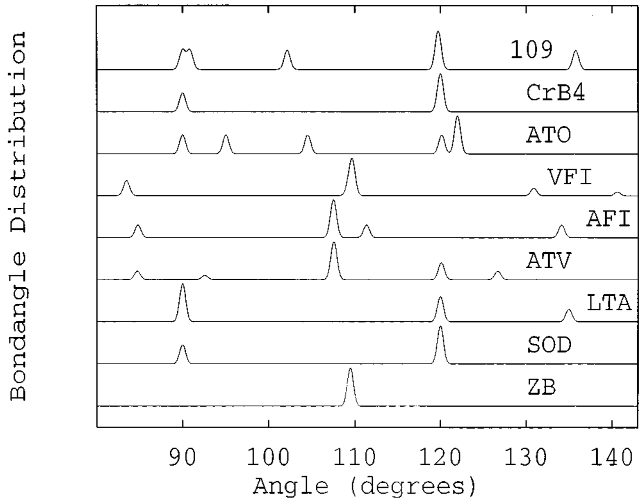


FIG. 6. The bond angle distribution for zinc-blende (ZB) and expanded phases for the ideal structures. The perfect tetrahedral angle is 109.5°, and occurs for ZB. A small Gaussian broadening has been given to the peaks. The relative heights of the peaks within a structure give the relative proportion of bond angles within that structure.

TABLE II. Electronic band gaps for various expanded GaAs phases. VBM and CBM identify the *k* point in the Brillouin zone corresponding to the valence band maximum and conduction band minimum, respectively.

Structure	E_g (eV)	VBM-CBM
ZB	1.346	Γ-Γ
SOD	1.391	Γ-Γ
LTA	1.410	Γ-Γ
ATV	0.658	Γ-Γ
AFI	0.716	Γ-Γ
VFI	0.741	Γ-Γ
ATO	1.261	Γ-Γ
CrB_4	metal	
Net-109	semimetal	

time, they also show that expanded GaAs phases are not totally out of the question either. This may be particularly true if the guest species has a small energy stabilizing effect.

We believe the origin of the higher energy of expanded phases for compound semiconductors is the occurrence of four rings in the structures. We show in Fig. 6 the distribution of bond angles for the expanded phases. The *average* bond angle in all structures is very near θ_{Tet}, and falls between 107.5° and 110.0° over all eight structures. One notices that ATV has the smallest RMS deviation from θ_{Tet}, and also has the lowest energy. Also LTA has the highest fraction of 90° bond angles (associated with the high proportion of four rings) and has the highest energy. An attempt was made to correlate the energy with the RMS deviation from θ_{Tet}, but no clear trend was found. Perhaps the simplest indicator of the total energy is just the fraction of four rings in a structure (obtained from Table I). This indicator predicts 10 (ATV) to be lowest in energy, 15 (LTA) to be highest, that 11 (ATO) and 13 (AFI) should be equal in energy, and that 14 (VFI) should be slightly above 11 and 13. All of these qualitative predictions are in accord with Fig. 5. It fails however to properly order 8 (net-109) and 9 (CrB_4) relative

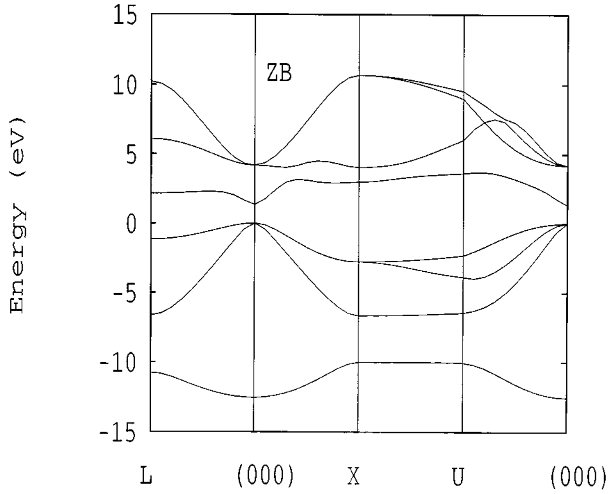


FIG. 7. Band structure for the zinc-blende GaAs structure.

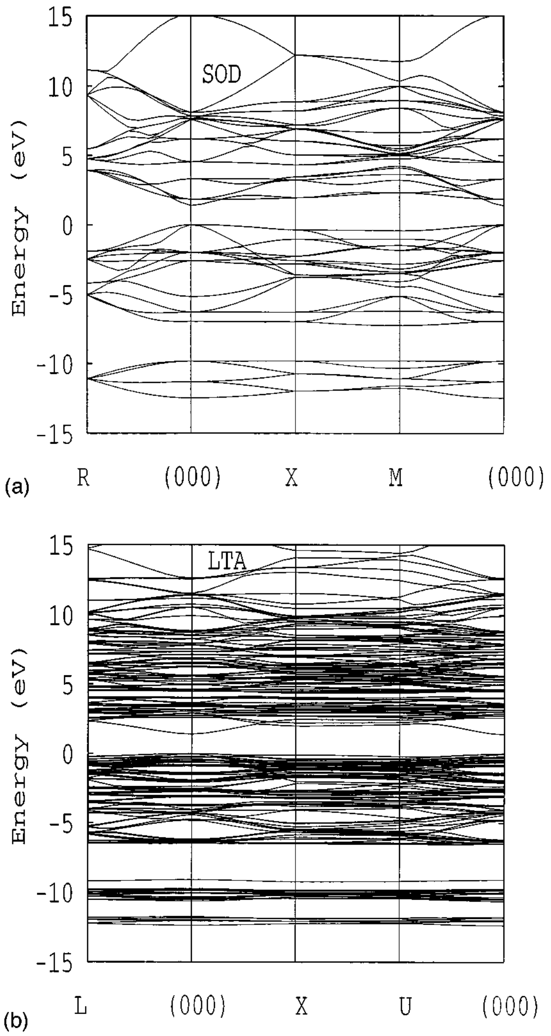


FIG. 8. Band structures of (a) simple cubic GaAs sodalite and (b) face-centered cubic GaAs Linde type *A*.

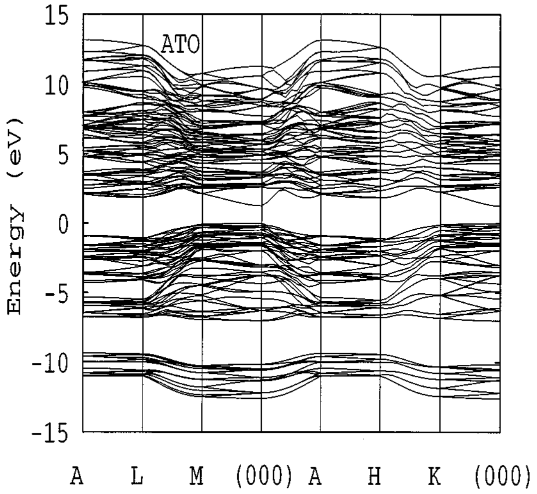


FIG. 9. Band structure for the hexagonal structure ATO of GaAs.

to the rest. However, these are the only structures that are found to be metallic or semimetallic (see next section) which might explain why they are more energetically unfavorable than expected. The most important failure of energy ordering by counting four rings is for sodalite (12). Sodalite has $\frac{1}{3}$ of its rings four rings, so $\frac{1}{3}$ of its bond angles are 90°. This makes it the second worst candidate (followed by LTA), but clearly Fig. 5 shows that its energy fits in with the other lower energy structures.

Finally, we have repeated the calculations of zinc blende and sodalite phases using the self-consistent pseudopotential plane wave LDA method. The plane wave method is generally considered to be quite reliable for the structural energy difference since it makes no assumptions concerning the basis (a complete set is used) nor the shape of the potential. Of course we still use the approximations of pseudopotentials and the LDA. We perform these more accurate calculations on these two systems in order to obtain an estimate of the errors that we make in our local-orbital Harris functional method, and as a check that our conclusions are sensible. For the plane wave calculations we use an energy cutoff of 220 eV and four special k points in 1/24th of the Brillouin zone. The special k points are obtained using the Monkhorst-Pack[14] scheme. The density of k points is approximately equivalent to about 16 for irreducible wedge of the zinc-blende lattice where it is known that 10 k points is quite sufficient for an insulator as GaAs. The energy cutoff is chosen so that the convergence on an absolute scale is approximately 0.1 eV, but the energy differences from reasonably similar structures will be far better converged than this. The pseudopotential is a soft Kerker-Troullier-Martins[27] type with matching radii of the wave functions at 2.15, 2.25 a_{Bohr} for Ga s and p potentials, and 1.85 and 2.00a_{Bohr} for the As s and p orbitals, and the exchange/correlation functional is from Ceperley *et al.*[28] We chose the sodalite phase as the expanded phase in our test since it has no internal coordinates to be optimized. We find that the expanded GaAs sodalite phase is 0.196 eV/atom higher in energy than that of the zinc-blende phase. This compares well with the energy difference of 0.204 eV/atom that we obtain using the local orbital method. One generally would not expect these two methods to be in this close agreement—however, this test suggests that the trends we obtain with the local-orbital method are reliable.

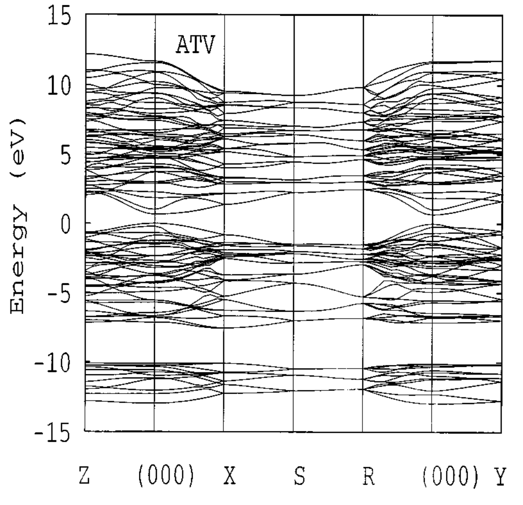


FIG. 10. Band structure for the orthorhombic ATV structure of GaAs.

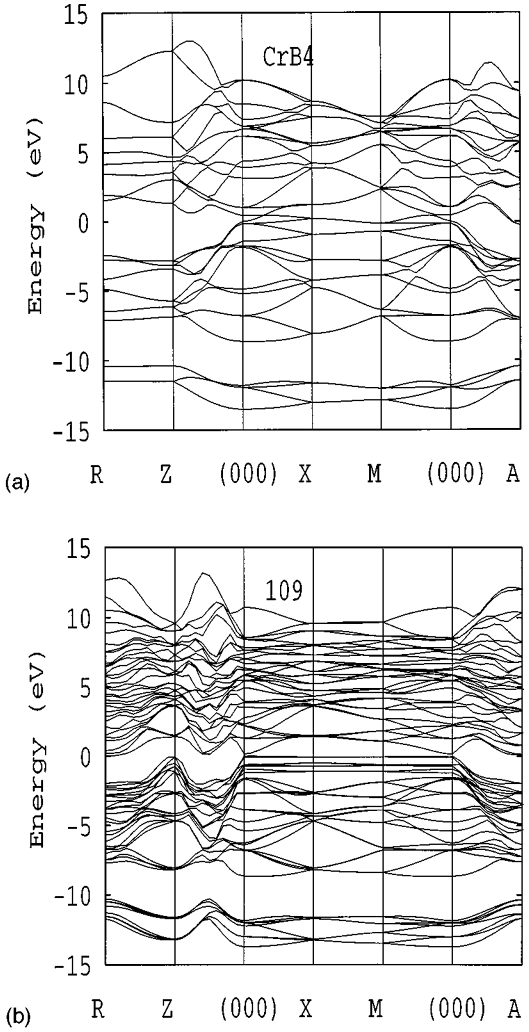


FIG. 11. Band structure for the tetragonal structures (a) CrB_4 and (b) net-109 of GaAs.

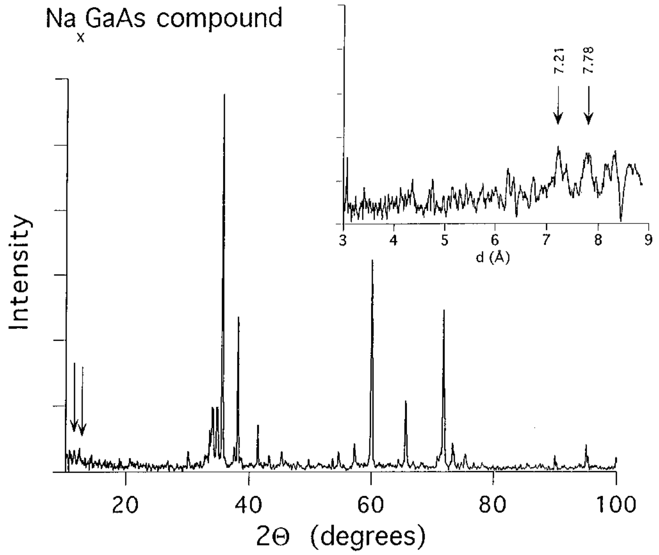


FIG. 12. The x-ray pattern of the Na$_x$GaAs compound. Two low-angle peaks, marked with the arrows, correspond to two sets of planes with the spacings of 7.21 Å and 7.78 Å marked in the inset.

B. Electronic structure

We have computed the electronic band structure for all the expanded GaAs phases reported here, and for the zinc-blende phase. All phases are found to be semiconducting with direct band gaps, except for net-109 and CrB_4. A summary of the band gaps is given in Table II.

The band structure of GaAs zinc-blende phase from our method is shown in Fig 7. The *k* point labels for all structures are those for symmetry points in the Brillouin zone by Koster.[29] We find a direct Γ-to-Γ gap of 1.35 eV. The LDA typically underestimates band gaps, while the minimal basis set tends to open up gaps. These two errors partially compensate giving a gap in reasonable agreement with the experimental value of 1.5 eV. The top of the valence band is defined to have zero energy and we see that the width of the valence band is about 12.5 eV. The lower portion of the valence band is separated from the rest of the valence states by the ''antisymmetric'' gap of 3 eV. The top of the valence band is triply degenerate because of the neglect of the spin-orbit interactions [an inclusion of spin-orbit interactions would split the degeneracy by 0.3 eV (Ref. 30)].

There are three classes of structures under consideration in this paper. We begin our discussion of their electronic structures with frameworks built from the β cage of sodalite—Sodalite (SOD) and Linde *A* (LTA). The band structure of SOD and LTA are shown in Fig. 8(a) and Fig. 8(b), respectively. The width of the valence band and the band gaps are very similar to those of the zinc-blende structure. The band gaps open slightly compared to zinc blende. Curiously, LTA has the largest band gap in spite of the fact that it has the largest total energy. The top of the valence band for SOD and LTA remains triply degenerate and these materials are direct gap (Γ-to-Γ) semiconductors.

The three hexagonal phases (AFI, VFI, and ATO) are found to be semiconducting with band gaps from 0.63 to 0.09 smaller than that of zinc blende. The band structure of ATO is shown in Fig. 9. The width of the valence band is again similar to that of the zinc-blende structure. The 1.261 eV gap is direct and at the Γ (000) point.

The lowest energy structure (among the expanded phases) is ATV which is found to be a fairly narrow direct gap semiconductor with a band gap of 0.658 eV. The corresponding band structure of ATV is shown in Fig. 10. The valence band is slightly widened comparatively to the zinc-blende structure. It is interesting that the gap is changed by a factor of two with only an 8% change in volume, which suggests a possible role for such expanded volume materials in band gap engineering, if they could be synthesized.

The remaining two structures are the CrB_4 net and net-109. These nets are only slightly expanded compared to zinc blende and are high energy structures. These related structures are the only ones which are found to be metallic or semimetallic. Their band structures are shown in Figs. 11(a) and 11(b) for CrB_4 and net-109, respectively. The width of the valence band increased by almost an electron volt compared to that of the zinc-blende structure. The net-109 band structure has a very small overlap which makes it semimetallic, and may make this material an interesting ''marginal metal'' superconductor.

IV. DISCUSSION AND CONCLUSION

We have theoretically examined various expanded phases of GaAs structurally derived from $AlPO_4$ molecular sieves and other nets. This work follows previous work involving group-VI zeolites and elemental semiconductors. In this paper, we assessed the relative energetics of expanded phases of compound semiconductors, and have predicted their electronic properties.

The total energy calculations have been performed for eight expanded structures: two cubic (SOD and LTA), an orthorhombic (ATV), three hexagonal (AFI, VFI, and ATO), and two tetragonal (CrB_4 and net-109). The largest volume structures (VFI, LTA) have volumes 60% greater than that of ZB GaAs. Among the $AlPO_4$-derived structures (ATV, ATO,AFI,VFI) and sodalite (SOD), the energy increases rapidly with volume, to 14% expansion (ATO), then shows little change with a further increase in volume. This behavior is analogous to the silica zeolites.[6] The LTA structure, based on β cages with a high portion of four rings, lies at much higher energy than other materials. Although the energy of the most stable expanded phase (ATV) is roughly half that of the GaAs-II high-pressure phase, most of the GaAs expanded phases lie ~0.15–0.2 eV/atom above the zinc-blende structure. This is a factor of nearly three larger than the corresponding silisils, compared with diamond Si, and suggest that synthesis of expanded volume GaAs materials might be correspondingly more difficult. In the case of Si expanded phases, these are obtained as alkali metal clathrates by the metastable heating of the Zintl compounds MSi ($M=$ Na, K, Rb) (Refs. 4,31), or by ablation/deposition methods.[32] We have attempted pilot synthesis of Na$_x$GaAs expanded volume phases: materials of an unknown structure with evidence of a large unit cell have been obtained.[33] The x-ray pattern for one of these phases is shown in Fig. 12, although it does not correspond to any specific clathrate-type structure, the interplanar distances are similar to those of ATV and CrB_4. It may be possible to obtain expanded phases of

GaAs by supersonic cluster beam techniques.[34] Another method of synthesis of these phases is from chemically designed precursors. This has been exploited in the synthesis of a low-density (sp^2) structure of C_3N_4.[35]

Almost all expanded phases reported here are found to be semiconducting with direct band gaps ranging from slightly above that of zinc-blende structure, to about 0.6 eV below it. Two structures, net-109 and CrB_4, are metallic or semimetallic. All form interesting synthesis targets for future experimental studies.

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