PHYSICAL REVIEW B VOLUME 28, NUMBER 6 15 SEPTEMBER 1983

Structural properties of III-V zinc-blende semiconductors under pressure

Sverre Froyen and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

(Received 25 March 1983)

The pseudopotential method within the local-density approximation is used to investigate the static and structural properties of some III-V compound semiconductors. Comparisons of calculated total energies as a function of volume and structure yield information about solid-solid phase transformations. At high pressures the results indicate that several metallic structures are lower in energy than the zinc-blende structure. From our results the compounds (AlP, AlAs, GaP, and GaAs) can be divided into two classes. In the Ga compounds, we find a pressure-induced phase transformation to either rocksalt, β-Sn, or NiAs, whereas in the Al compounds rocksalt and NiAs are stabilized with respect to β-Sn. All structures except zinc blende are metallic. We discuss the electronic structure of each phase and show how it relates to structural stability.

I. INTRODUCTION

The III-V zinc-blende compound semiconductors exhibit metallic behavior under pressure. This is generally believed to be caused by a structural phase transformation where the atoms become more closely packed. Since this behavior is similar to that of the group-IV semiconductors Si and Ge, it was originally thought that the high-pressure structure would be the same; i.e., it was assumed that the high-pressure phase was the polar analog of the tetragonal β-Sn structure. However, recent advances in the diamond-anvil technique, in particular the use of *in situ* x-ray experiments, have made experiments possible that show this simple picture to be incorrect. The high-pressure structure varies with the compound as well as the temperature and preparation method.

Because of its low-transition pressure (around 2 GPa), InSb is perhaps the best studied compound. It is found to exhibit a variety of high-pressure phases[1] including rocksalt,[2] which is metastable at normal pressure. The other III-V compounds have higher transition pressures and are therefore less well studied. In particular, GaAs is found to transform to an orthorhombic structure,[3,4] although the position of the atoms in the unit cell is unknown. GaP transforms to the β-Sn structure,[3,4] and AlP has been indexed as face-centered cubic although the x-ray intensities were inconsistent with the rocksalt structure.[3] This latter compound is particularly interesting because the transition pressure[5] is much lower than predicted by Van Vechten's dielectric theory.[6] His predictions for GaAs and GaP were accurate, so the deviation for the Al compound is probably significant. As we shall see later, we believe the discrepancy is caused by differences in the nature of the high-pressure phases of the Al compounds. A similar deviation should therefore exist for AlAs; however, we have not found any experimental data for this material.

The first-principles pseudopotential method for total-energy calculations has been proven able to predict accurate structural properties for solids ranging from insulators to metals. In this paper we shall focus our attention on four compounds: GaAs, GaP, AlP, and AlAs. Since we do not include relativistic effects, we do not consider InSb where these corrections undoubtedly are important. For the four compounds studied (apart from Van Vechten's effort already mentioned), we are aware of only one previous calculation. This calculation by Soma[7] used pseudopotentials and perturbation theory to calculate the energy of GaAs, GaP, and other compounds in the rocksalt and β-Sn structures. In both cases he found β-Sn to be the preferred high-pressure structure.

In Sec. II we discuss the method used, Secs. III and IV describe the results related to structural and electronic properties, and Sec. V contains a summary and conclusions. A shorter preliminary description of our results was published earlier.[8]

II. METHOD

The pseudopotential total-energy scheme[9] is used to compute the energy differences necessary to distinguish between the various structural types. The ionic pseudopotentials needed in this scheme are generated using methods proposed by Hamann, Schlüter, and Chiang[10] and by Kerker.[11] Different potentials are used for electronic orbitals of *s*, *p*, and *d* symmetry, and the potentials are tested to give the correct atomic wave functions, energy levels, and excitation energies for a number of electronic configurations. Typically the errors are less than 1 mRy in both the energy levels and the excitation energies for atomic excitations up to 1.5 Ry. The exception is gallium where the core 3*d* states are not completely frozen. This leads to errors of around 5 mRy.

The wave function in the solid is expanded in a plane-wave basis, and the total energy for a given structure is computed as described in Ref. 9. In order to obtain a relative convergence of 2 mRy between the various structures of GaAs, we found it necessary to include plane waves up to a kinetic energy of 12 Ry. This energy cutoff was then used for the other compounds without further testing. All plane waves are treated exactly. Exchange and correlation are treated in the local-density formalism using the formulation of Hedin and Lundqvist.[12]

The Brillouin-zone integrations are replaced by discrete sums over $\vec{k}$ points. The points in the irreducible part of the zone are obtained by folding from a uniform grid in the full zone. In many cases this reproduces the special $\vec{k}$ points of Chadi and Cohen.[13] For the insulating structures we found that 10 $\vec{k}$ points in the irreducible zone are sufficient to obtain accuracy better that 2 mRy. However, the Fermi surfaces of the metallic structures create an uncertainty of about 10 mRy even with 60–100 $\vec{k}$ points.

The density-of-states plots shown in this paper were generated from the same $\vec{k}$-point sample that was used in the Brillouin-zone sums. The bands were interpolated linearly inside a region around each $\vec{k}$ point and the density of states was computed exactly from the interpolated bands. This made it possible to obtain the density of states without additional calculation and by using only one program independent of structure. The disadvantage of the method is that the relatively few $\vec{k}$ points that were used create spurious peaks in the density of states. This is particularly troublesome in cases where bands cross as is evident in some of the figures presented. Once the total structural energies are evaluated, the equilibrium lattice constant and bulk modulus are calculated by fitting an equation of state to the calculated energies.

III. STRUCTURAL PROPERTIES

A. Normal pressure

Experimentally, all the III-V compounds we investigated are found in the zinc-blende structure at normal pressure. This is in accord with our calculations, although we are not able to distinguish between the cubic zinc-blende structures and the hexagonal wurtzite structures, which for GaAs differ in energy by less than 1 mRy. From the total energy versus volume curves, the lattice constants and the bulk moduli are computed. We use equations of state proposed by Murnaghan[14] and by Birch.[15] Both equations fit our calculated energies equally well. They give the same lattice constants, and the bulk moduli obtained differ by less than 3%. The results given in Table I are obtained using the Murnaghan equation. Our lattice constants are about 1% smaller than those obtained by Ihm and Joannopoulos.[19] This is caused by differences in exchange and correlation functionals. Ihm and Joannopoulos used Wigner's interpolation formula[20] which generally seems to give larger lattice constants than the formulation of Hedin and Lundqvist[12] used here.

B. High pressure

As discussed before, the actual high-pressure structures of the III-V compounds are largely undetermined. Unfortunately, the present theoretical methods can only compare the stability of given structures. Using these methods, we can therefore never discount the possible existence of another structure that we have not considered and which may be even more stable. In light of these facts, we have chosen to examine some simple prototype structures, with the hope that the insights gained from the investigations will narrow down the possible choices for the high-pressure phases. The structures we studied are zinc blende, β-Sn, rocksalt, CsCl, and NiAs. The first three structures were tested for all four compounds, whereas only AlAs and GaAs were calculated in the latter two. In the initial phase of the study, we found a high degree of similarity between AlAs and AlP, and between GaAs and GaP. We therefore decided to focus our attention on the two "prototype" arsenic compounds. The major difference between the arsenic and the phosphorus compounds is the equilibrium volumes.

The results from these calculations are summarized in Fig. 1. The figure shows the total energy as a function of volume for the four compounds in the various structures. As the pressure is increased from zero we find in all cases transformations to the more closely packed metallic structures. The transition pressures and the relative volume changes are given in Table II. Focusing now on the two prototype compounds, we find that GaAs transforms to either rocksalt, β-Sn, or NiAs, whereas for AlAs the rocksalt and the NiAs phases have shifted down in energy and the transition pressure is therefore lower. The accuracy of our calculation is such that we cannot determine which of these competing structures is the more stable, and furthermore the relative stability will most likely also depend on temperature, a problem we have not addressed. We shall

TABLE I. Lattice constants and bulk moduli. The experimental lattice constants are all measured at room temperature, and the bulk moduli for AlP and AlAs have been obtained by extrapolation from other compounds.

		AlP	AlAs	GaP	GaAs	
a	calc	5.420	5.641	5.340	5.570	A
	expt.[a]	5.451	5.662	5.451	5.653	
		−0.6%	−0.4%	−2.0%	−1.5%	
B_0	calc	86.5	74.1	89.7	72.5	GPa
	expt.[b]	86.0	77.0	88.7	74.8	
				+1.1%	−3.1%	

[a] Reference 16.

[b] References 17 (AlP, AlAs) and 18 (GaP, GaAs).

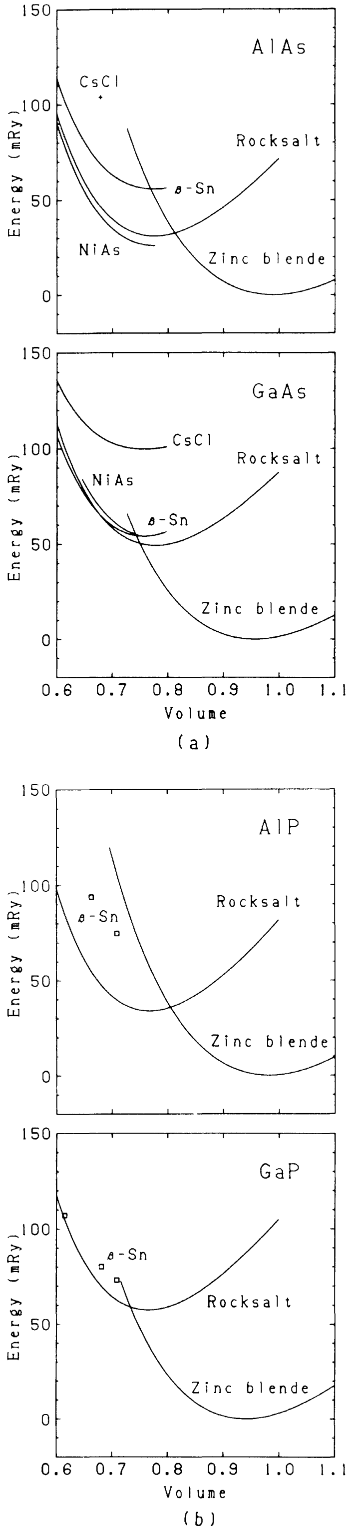

FIG. 1. Calculated total energies per molecule for (a) AlAs and GaAs, and (b) AlP and GaP in the structures indicated as function of volume.

now discuss the various structures and their characteristics.

C. β-Sn structure

The β-Sn structure can be obtained from the zinc-blende structure by compressing the crystal along one of the cubic axes. By changing the c/a ratio of the tetragonal unit cell we can therefore, at least in theory, go continuously from one structure to the other. A c/a ratio of around 0.5 gives the β-Sn structure with its sixfold coordination. Increasing c/a we obtain first the zinc-blende structure at c/a equal to $\sqrt{2}$, and then an eightfold coordinated structure for c/a of around 4. In the latter structure each atom has four neighbors of each type. In Fig. 2 we illustrate how the total energy of GaAs changes as a function of the c/a ratio when the volume is kept constant. The calculation is performed at a compressed volume where β-Sn is more stable than zinc-blende, but there is a relatively small barrier for the transition from zinc-blende to β-Sn. For larger c/a ratios there is first a large barrier and then a new minimum at the eightfold coordinated phase. The energy of this structure is close to that of the CsCl structure which has the same number of neighbors although the arrangement is different. Apart from the dip at zinc blende, the total-energy diagram has a shape similar to other related quantities such as the packing fraction of spheres and the Ewald energy.[21] The Ewald energy is the electrostatic energy of positive point ions in a uniform electron gas. The zinc-blende point at $\sqrt{2}$, which actually is an Ewald energy maximum, is stabilized by the semiconducting gap.

We now focus on the energy minimum at β-Sn. Considering only the Ewald energy with ionic charges of 3 and 5, the minimum is at c/a equal to 0.57. Our calculations place the actual minimum very close to 0.57 for compressed volumes. At larger volumes the c/a ratio increases slightly indicating a gradual transition away from a free-electron metal towards a more ionic solid. For a completely ionic solid, with charges of $+1$ and -1 at the atomic positions, the electrostatic energy has a minimum at c/a equal to $\sqrt{2}$.

D. Rocksalt structure

Although the energy barrier is too large for an actual transformation path, the transition from zinc blende to rocksalt can formally be thought of as a motion of the anion along the body diagonal from its tetrahedral position at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ to the octahedral position at the cube center. The total energy of such a displacement is shown for GaAs in Fig. 3. The curvature at the minima determine the phonon frequencies for the TO(Γ) mode, and we see that the frequency for rocksalt is much lower than zinc blende. Since this is probably typical for all phonons, it shows that the rocksalt phase has higher entropy.

From Fig. 1 we note that AlAs is relatively more stable in this structure than GaAs. We shall return to reasons for this when we discuss the electronic structure.

If the two atoms in the unit cell were the same, the rocksalt structure would be identical to simple cubic. We might then expect the crystal to be unstable with respect to distortions towards more closely packed atomic arrangements. We have investigated two such possible distortions. The first is a trigonal distortion along the [111] axis. Stretching the crystal in this direction increases the nearest-neighbor distance without changing the cell volume, eventually transforming the crystal to face-centered cubic. Calculations for GaAs show that the

TABLE II. Transition pressures, volumes, and total-energy differences for the zinc-blende to rocksalt transition. $V_t(zb,rs)$ are the transition volumes for the two phases, $V_0(rs)$ is the equilibrium volume for the (metastable) rocksalt phase, and ΔE_0 is the energy difference per molecule between the minima of the two phases. The volumes are all given as fractions of the calculated equilibrium volume for the zinc-blende phase.

		AlP	AlAs	GaP	GaAs	
P	calc	9.3	7.6	21.7	16.0	GPa
	expt.[a]	14–17		20–24	16–19	
$V_t(zb)$	calc	0.90	0.92	0.84	0.86	
$V_t(rs)$	calc	0.73	0.73	0.71	0.71	
$V_0(rs)$	calc	0.78	0.78	0.81	0.81	
ΔE_0	calc	0.46	0.43	0.78	0.67	eV

[a] References 3 and 4.

rocksalt structure is marginally stable against such a distortion. At the transition volume, the crystal can be stretched 20% with only 5 mRy per cell energy increase. Compare this to a tetragonal distortion along the [100] axis where an 8% distortion gives the same change in energy.

The second distortion is shear along the [110] axis. Such a shear mode is the TA(X) phonon which, for very large dispacements and with a contraction along the [001] axis, takes the crystal from rocksalt to the CuAu structure. In our calculations, we find that the TA(X) phonon indeed has a very low frequency, although it is not actually unstable. In addition calculations for the CuAu structure place it above rocksalt in energy.

Again it is interesting to note the relationship between instability and the Ewald energy. Both the above distortions are unstable with respect to the Ewald energy, and we might therefore expect them to soften under pressure when the electronic structure becomes more free electron-like. This is, for example, the case for the TA(X) mode in the zinc-blende phase. For the trigonal distortion we find that this is not the case. The rocksalt structure is stabilized as the volume is compressed. The reason for this will be discussed below. We have not investigated the stability of the phonon mode as function of volume.

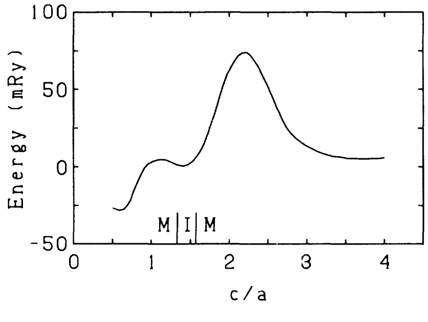

FIG. 2. Calculated total energy per molecule for GaAs in the β-Sn structure as function of the c/a ratio with constant volume. The volume is approximately 30% smaller than the observed zinc-blende equilibrium volume. The insulator-metal transition points are indicated.

E. NiAs structure

There is a well-known similarity between the cubic zinc-blende and the hexagonal wurtzite phase. The two structures can be represented as a stacking of hexagonal planes of atoms of the same type,

$$AaBbCcAaBbCcAaBbCc \text{ (zinc blende)}, \quad (1)$$

$$AaBbAaBbAaBbAaBbAa \text{ (wurtzite)}, \quad (2)$$

where upper-case characters denote the anion and lower case characters the cation. The two structures differ only in the second neighbor and beyond. Perhaps less well known is the hexagonal analog of rocksalt. Again transforming from cubic

$$AbCaBcAbCaBcAbCaBc \text{ (rocksalt)} \quad (3)$$

to hexagonal

$$AbCbAbCbAbCbAbCbAb \text{ (NiAs)}, \quad (4)$$

we obtain the NiAs structure. These structures do not correspond as closely as do zinc blende and wurtzite. In the NiAs structure the sites for the two atomic species are

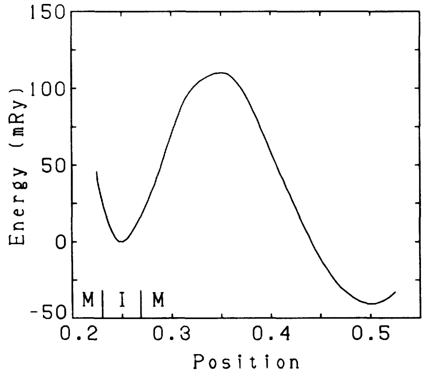

FIG. 3. Calculated total energy per molecule for the transition zinc blende to rocksalt for GaAs. Displacement refers to the position of As along the body diagonal in the cubic unit cell. The volume is approximately 30% smaller than the observed zinc-blende equilibrium volume. The insulator-metal transition points are indicated.

nonequivalent. For the ideal c/a ratio ($\sqrt{8/3}$), the anions (As) form a hexagonal close-packed lattice, whereas the cations have a simple hexagonal structure. Each cation has the same environment as in rocksalt but the anions have their six neighbors hexagonally arranged. Thus the Ni—As—Ni bond angle in the plane of the c axis is 70.5° instead of 90° (see Fig. 4). In spite of these differences we find the total energy for the two structures (rocksalt and NiAs) to be very close. For both GaAs and AlAs the difference is less than 10 mRy, which is within the accuracy of the calculation.

The calculated c/a ratio is a few percent larger than the ideal ratio indicating, as for rocksalt, an instability towards a structure where the atoms are close packed. In addition, interchanging the position of the anion and the cation we find an increase in energy of about 20 mRy per cell.

F. CsCl structure

The CsCl structure is the favored high-pressure structure of the alkali halides. In this structure each of the atomic species forms a simple cubic lattice with one lattice displaced to the body center of the other. The structure is closely packed and has a very low Ewald energy. It is therefore surprising that the calculated energies are so much higher than rocksalt and β-Sn (see Fig. 1). The structure is not a contender except possibly at very high pressures.

IV. ELECTRONIC PROPERTIES

A. Normal pressure

In Table III we tabulate the band energies at some symmetry points. The zero of energy is the valence-band maximum, and the calculations were performed using the experimental zero-pressure lattice constants tabulated in Table I. To ensure convergence, we increased the plane-wave energy cutoff to 20 and 30 Ry. The only state significantly affected is the Γ_{1c} state which is reduced in energy by approximately 0.3 eV when the cutoff energy is increased from 12 to 20 Ry. The second increase to 30 Ry did not modify any state. Our results for GaP and GaAs are all within 0.1 eV of those obtained by Wang and Klein.[26] This is despite the fact that they used a different method (linear combination of Gaussian orbitals and including the core electrons), and a different correlation density (Wigner interpolation).

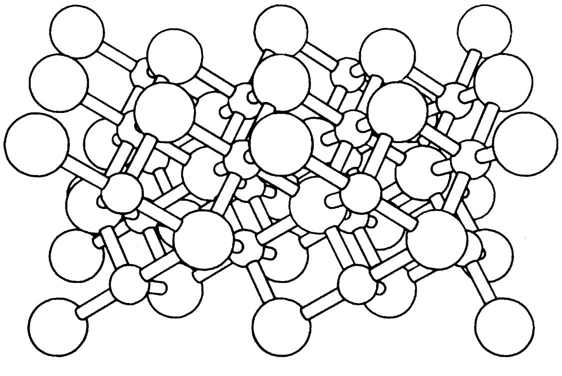

FIG. 4. NiAs structure with ideal c/a ratio. The larger atoms (As) form a close-packed hexagonal lattice interpenetrated by chains of Ni atoms. The local environment of each Ni is the same as in the rocksalt structure.

GaP and GaAs are the only materials for which angle-resolved photoemission results are available. The agreement is good except for the lowest s band in GaAs which we place about 1 eV too high. As is usual in local-density calculations, the conduction bands are placed too low. The largest discrepancy is for the X point in AlP which is off by 1 eV.

B. High pressure

Below we shall discuss the electronic properties of the various structures that we have investigated. Again we choose to study the arsenic compounds with an emphasis on differences and similarities between AlAs and GaAs. Unless otherwise stated, all numerical values quoted are calculated for a cell volume equal to 208 a.u., which is about 30% smaller than the equilibrium volume of the zinc-blende phase.

C. Zinc-blende structure

Since the zinc-blende phase has been extensively studied, we will point out only a few relevant facts. At normal pressure zinc blende is stabilized by a semiconducting gap produced by the arrangement of the electrons into bonding orbitals. As the phase is compressed the bonding region becomes smaller. This increases the kinetic energy of the electrons in the bond, and the energy difference between the bonding valence bands and the antibonding conduction bands decreases. The behavior of the lowest conduction band at X reflects this change. It is localized in the octahedral region between the anions, and as the volume is compressed, the state drops in energy and reduces the band gap (see Fig. 5). In the case of GaAs, which has a direct gap at normal pressures, the gap changes from direct to indirect. Therefore, at very high pressure, the zinc-blende phase would be metallic. However, before this can occur, the crystals transform into other structures. The gap, which stabilizes zinc blende at low pressures, is responsible for the instability at high pressures. In order to move away from the bond region, the electrons must first transfer to conduction-band states, and this is prevented by the gap. This is clearly seen in Fig. 6 where we show the total and differential valence charge density along the Ga—As bond. The latter is defined as the difference between the self-consistent charge density and that from overlapping atomic charge densities. The figure shows the charge densities for GaAs at both normal and compressed volumes. The units are electrons per unit cell and give a measure of integrated charge. Although there is a reduction in the total charge, the differential charge densities are very similar. In particular the peak in the charge, which is localized in the bond region and can be taken to represent the bond charge, is still present at the compressed volume. Recent experiments on Si and InSb

TABLE III. Band energies at symmetry points at normal pressure. All energies are in eV, referenced to the top of the conduction band.

	AlP		AlAs		GaP		GaAs	
	theory	expt.[a]	theory	expt.[a]	theory	expt.[b]	theory	expt.[c]
Γ_{1v}	−11.46		−11.60		−12.26		−12.33	−13.1
X_{1v}	−9.05		−9.53		−9.43	−9.5	−9.88	−10.75
X_{3v}	−5.37		−5.42		−6.60	−6.4	−6.62	−6.70
X_{5v}	−2.14		−2.17		−2.68	−2.9	−2.61	−2.80
L_{1v}	−9.73		−10.11		−10.32		−10.64	−11.24
L_{1v}	−5.50		−5.56		−6.50		−6.46	−6.70
L_{3v}	−0.78		−0.83		−1.09		−1.11	−1.30
Γ_{1c}	3.25	3.63	2.29	3.13	2.09	2.86	1.10	1.63
X_{1c}	1.51	2.50	1.46	2.23	1.62	2.32	1.51	2.18
L_{1c}	2.76		2.20		1.85	2.67	1.30	1.85

[a] Reference 22.
[b] References 23 and 24.
[c] Reference 25.

indicate that the phase transformation is preceded by a vanishing of the bond charge.[27] We observe that both calculations for Si (Ref. 28) and our calculations for the III-V compound semiconductors show no sign of this.

D. β-Sn structure

Although the charge density of the β-Sn phase resembles a distortion of that of the zinc-blende phase, there are important differences. The charge-density peak in the bond region is reduced by more than 20%, and is much closer in magnitude to what we find in the rocksalt phase (see Fig. 7). The change is even more dramatic if we consider the differential charge density. The bond charge, i.e., what is left of it, is reduced by 50% and is almost identical to rocksalt.

The band structure and the density of states for GaAs in the β-Sn structure with a c/a ratio of 0.57 are shown in Fig. 8. The density of states still show traces of a gap, although the structure is metallic except for a small region around the zinc-blende value at c/a equal to $\sqrt{2}$. When the c/a value is changed slightly from this value, the increased dispersion, along the c axis for smaller values and perpendicular to the c axis for larger values, quickly erase the gap as indicated in Fig. 2. For β-Sn at c/a equal to 0.57, we find a conduction-band minimum around H 3.8 and 4.3 eV below the Fermi level for AlAs and GaAs, respectively. This fifth band is approximately 20% occupied, and there is very little difference between GaAs and AlAs. This is in contrast to rocksalt as we shall see below.

E. Rocksalt structure

The major difference between Ga and Al compounds is the relative stability of the rocksalt (and NiAs) phase (see Fig. 1). We believe that this is caused by differences in the valence s states. The $3d$ core electrons in Ga are only partially able to screen the nuclear charge which therefore binds the s electrons more strongly. This makes the Ga compounds less ionic and the rocksalt phase less stable.

The charge density in rocksalt shows about the same amount of bond charge as in β-Sn (Fig. 7), much less than in zinc blende. Comparing GaAs to AlAs (not shown in the figure), we see a shift of charge towards the As atom in the latter. This is in accord with the argument above,

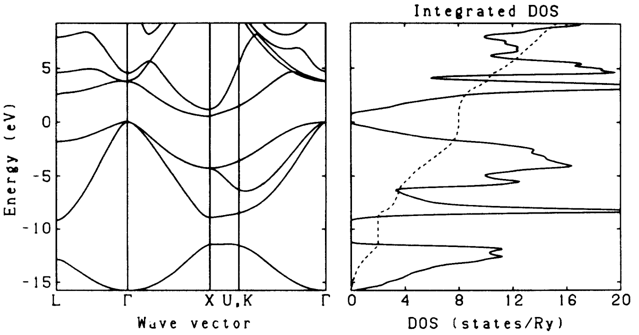

FIG. 5. Band structure and density of states for zinc blende GaAs at a volume approximately 30% smaller than the observed zinc-blende equilibrium volume.

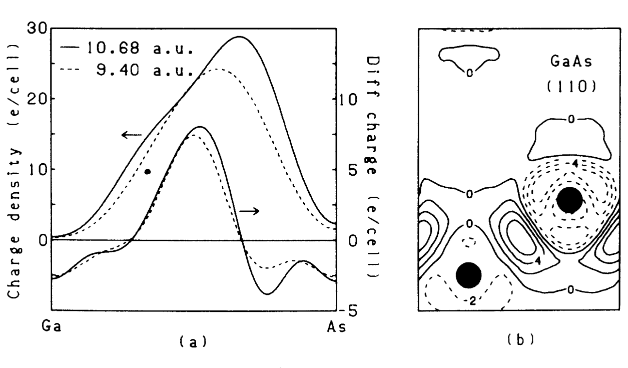

FIG. 6. (a) Total and differential valence charge densities for zinc blende GaAs along the Ga—As bond at two different volumes. The larger correspond to the observed zinc-blende equilibrium volume and the smaller correspond to a compression of approximately 30%. (b) The differential charge density in the (110) plane for the compressed volume. The contour interval is 2 electrons per unit cell. Dashed lines indicate negative contour levels.

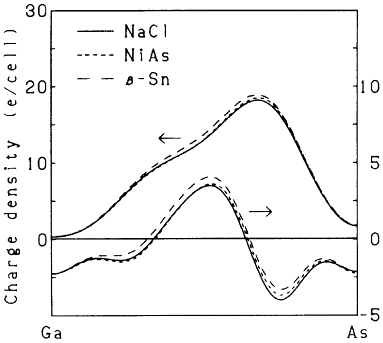

FIG. 7. Total and differential valence charge densities for GaAs along the Ga—As bond for the structures indicated at a volume approximately 30% smaller than the observed zinc-blende equilibrium volume.

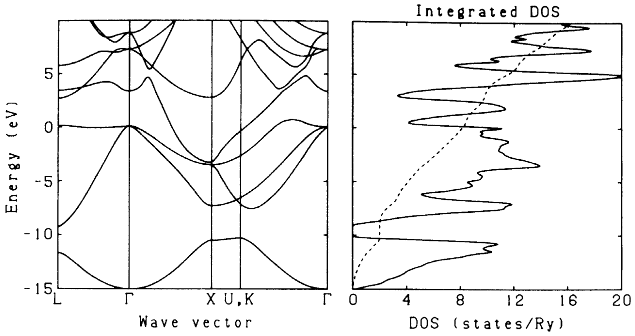

FIG. 9. Band structure and density of states for GaAs in the rocksalt structure at a volume approximately 30% smaller than the observed zinc-blende equilibrium volume.

but is not by itself sufficient to explain the stability of rocksalt, since we see a similar shift, although smaller, for the other structures.

The band structures give a better indication. In Fig. 9 the band structure and the density of states for GaAs are given. The density of states has a well-developed "gap" at the Fermi level, and the band structure, which is very similar to that of zinc blende, confirms this. The major difference between the two structures is that the conduction-band state around X has dropped below the valence-band maximum at Γ and this makes the rocksalt phase metallic. A decomposition of the fifth band shows it to be composed mostly of s states on the cation, and this accounts for the difference between Al and Ga. At a compression of 30%, the occupation of this band is 15% in GaAs and only 5% in AlAs whereas in β-Sn the occupation is 20% for both.

Interestingly, the pressure dependence of the X point in rocksalt is the opposite of the behavior in zinc blende, i.e., the band overlap in rocksalt decreases with increasing pressure. The stability of the trigonal distortion we studied in the preceding section is related to this. When the crystal is stretched, states are moved from the peak just below to the gap region just above the Fermi level. We also find that under changes in volume, the density of states remain the same if the energy is scaled with the inverse second power of the lattice constant. This enlarges the gap at small volumes and should, if the gap is stabilizing, give rocksalt additional stability. The trigonal distortion seems to confirm this.

F. NiAs structure

In the preceding section we showed that the NiAs structure can be thought of as a structural analog of rocksalt. The electronic structure also show similarities, although the correspondence is not exact. The general shape of the density of states (Fig. 10) are the same for the two structures, and they both have the pronounced gap feature just above the Fermi level; we believe this helps stabilize the structures. The Brillouin zone of the two structures can be mapped onto each other,[29] but aside from Γ at the center of the zone the levels do not correspond very closely (Fig. 10). We would expect the conduction-band minimum in NiAs to be at the hexagonal M point which maps to fcc X. Instead we find it at hexagonal K which corresponds to a point close to fcc K on the Σ symmetry line. Albeit the difference in position, however, the nature as well as the energy of the two minima are the same. Both are mainly s states on the cations approximately 2.0 and 3.5 eV below the Fermi level for AlAs and GaAs, respectively.

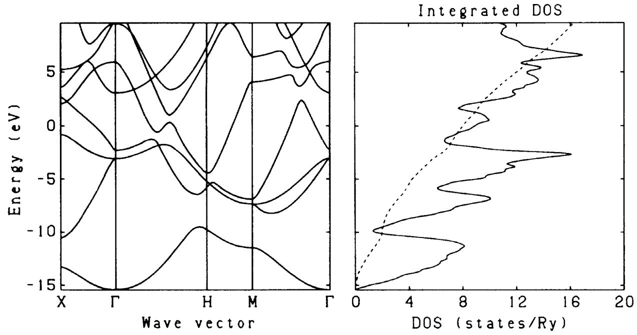

FIG. 8. Band structure and density of states for GaAs in the β-Sn structure with a c/a ratio of 0.57 and a volume approximately 30% smaller than the observed zinc-blende equilibrium volume.

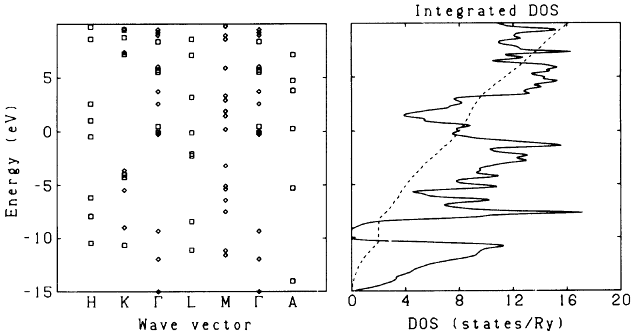

FIG. 10. Band structure and density of states for GaAs in the NiAs structure with a c/a ratio of 1.70 and a volume approximately 30% smaller than the observed zinc-blende equilibrium volume. The diamonds indicate singly degenerate states whereas the squares are states with degeneracies of 2 or more.

V. CONCLUSIONS

The stability of the high-pressure structures for the four compounds that we have investigated fall into two different classes as determined by the cations. For the Ga compounds we find that β-Sn, rocksalt, and NiAs are all possible high-pressure structures. For the Al compounds the ionic structures (rocksalt and NiAs) are stabilized with respect to β-Sn, and the transition pressures are therefore lowered. Although they are all metallic, we find that these ionic structures are stabilized by ionic gaps over most of the Brillouin zone. The relative stability of the Ga versus the Al compounds can therefore be understood in terms of atomic energy levels.

For GaAs we find that several structures lie within a narrow energy range at the transition point. With this many competing structures, it is likely that several more possibilities exist; both combinations of the ones we have considered and others. Thus in an experimental situation, the structure obtained will be sensitive to the conditions under which the experiment takes place. In particular the possibility of phase mixtures is present.

The pressures that we obtain for the phase transformations compare well with the experimental values for GaAs and GaP. For AlP our calculated pressure is 30% lower than the experimental value. However, since the observed transition is quite sluggish,[5] indicating a transformation by nucleation and growth process, there is little reason to believe that the experimental pressure should be equal to the calculated equilibrium pressure. The fact that for many compounds, the high-pressure phases remain metastable at low temperature and normal pressure, further illustrates this. As far as we know there has been no attempt to observe the transition in AlP while reducing the pressure, but experiments on InSb (Ref. 30) indicate that the hysteresis can be considerable. It should also be very interesting to see an experimental comparison of AlP and AlAs.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant No. DMR-78-22465 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

[1] S. C. Yu, I. L. Spain, and E. F. Skelton, J. Appl. Phys. 49, 4741 (1978).

[2] K. Asaumi, O. Shimomura, and S. Minomura, J. Phys. Soc. Jpn. 41, 1630 (1976).

[3] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. 25, 49 (1978) and references therein.

[4] A. L. Ruoff and M. A. Baublitz, Jr., in *Physics of Solids Under Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, New York, 1981), p. 81; M. A. Baublitz, Jr. and A. L. Ruoff, J. Appl. Phys. 53, 6179 (1982).

[5] J. Wanagel, V. Arnold, and A. L. Ruoff, J. Appl. Phys. 47, 2821 (1976).

[6] J. A. Van Vechten, Phys. Rev. B 7, 1479 (1973).

[7] T. Soma, J. Phys. C 11, 2681 (1978).

[8] S. Froyen and M. L. Cohen, Solid State Commun. 43, 447 (1982); Physica (Utrecht) 117B, & 118B, 561 (1983).

[9] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979); 13, 3095 (Corrigendum) (1980).

[10] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[11] G. Kerker, J. Phys. C 13, L189 (1980).

[12] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[13] D. J. Chadi and M. L. Cohen, Phys. Rev. B 8, 5747 (1973).

[14] F. D. Murnaghan, Proc. Nat. Acad. Sci. USA 30, 244 (1944); O. L. Anderson, J. Phys. Chem. Solids 27, 547 (1966).

[15] F. Birch, J. Geophys. Res. 83, 1257 (1978).

[16] R. C. Weast, *Handbook of Chemistry and Physics*, 62nd ed. (CRC, Boca Raton, 1981), p. E99—103.

[17] J. D. Wiley, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1975), Vol. 10, p. 134.

[18] R. M. Martin, Phys. Rev. B 1, 4005 (1970).

[19] J. Ihm and J. D. Joannopoulos, Phys. Rev. B 24, 4191 (1981).

[20] E. Wigner, Phys. Rev. 46, 1002 (1934).

[21] M. T. Yin and M. L. Cohen, Phys. Rev. B 26, 5568 (1982).

[22] B. Monemar, Phys. Rev. B 8, 5711 (1973).

[23] F. Houzay, G. M. Guichar, and R. Pinchaud (unpublished).

[24] D. S. Kyser and V. Rehn, Phys. Rev. Lett. 40, 1038 (1978), and references therein.

[25] T.-C. Chiang, J. A. Knapp, M. Aaono, and D. E. Eastman, Phys. Rev. B 21, 3513 (1980). The conduction-band energies are inferred from optical transitions [D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975) and references therein].

[26] C. S. Wang and B. M. Klein, Phys. Rev. B 24, 3393 (1981).

[27] D. R. Yoder-Short, R. Colella, and B. A. Weinstein, Phys. Rev. Lett. 49, 1438 (1982).

[28] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. 50, 1172 (1983).

[29] J. L. Birman, Phys. Rev. 115, 1493 (1959).

[30] B. Okai and J. Yoshimoto, J. Phys. Soc. Jpn. 45, 1880 (1978).