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A MICROSCOPIC THEORY

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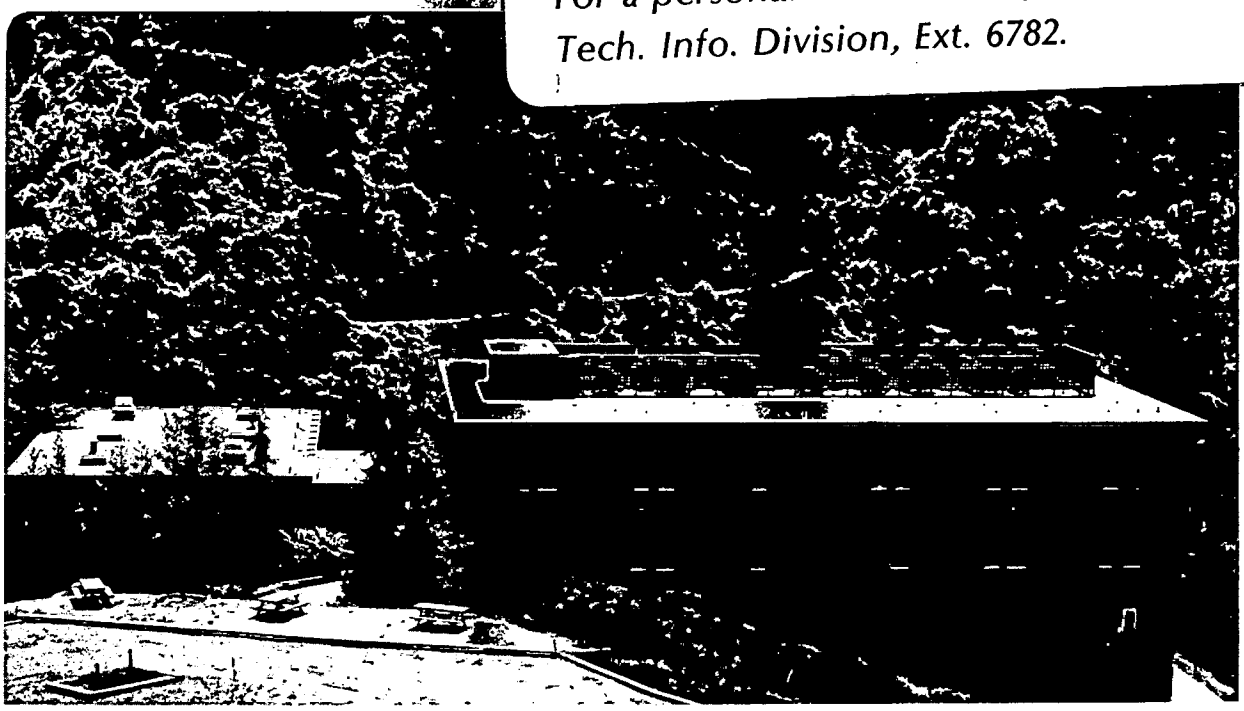

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High pressure phases of III-V semiconductors: A microscopic theory.

by

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ABSTRACT

The static structural properties and the structural stability of III-V semiconductors are investigated as a function of pressure using the pseudopotential method. At high pressures we predict a metallic rocksalt phase as the most stable structure. This phase is more stable than the ordered β-Sn structure previously thought to be the most stable form.

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It is well known that group IV semiconductors transform under pressure from an insulating diamond phase to a metallic β-Sn structure, whereas the II-VI semiconductors transform into an insulating rocksalt phase. For the III-V compounds the situation is more unclear. Neither theory [1-3] nor experiment [4] has been able to determine the structure of the high pressure phase conclusively, although it was expected that the behavior would be similar to the group IV elements. Recent experiments, however, indicate that the rocksalt structure, or distortions of it, may be important for a number of III-V compounds previously thought to transform into variations of the β-Sn structure. InSb has been crystallized in the rocksalt structure [5], and X-ray data by Baublitz and Ruoff [6] suggests that GaAs may transform into a distorted rocksalt structure. These structures are in all cases believed to be metallic.

With the recent improvements in pseudopotential total energy calculations, we are now able to confidently predict the relative stability of the various structures. Using first principles pseudopotentials, we have performed total energy calculations for AlP, AlAs, GaP, and GaAs in the zinc-blende, rocksalt, and ordered β-Sn structures. For GaAs we also include the CsCl, wurtzite, and two other structures suggested by Baublitz [6]. As a control of the method we compute the relative stability of the rocksalt and zinc-blende phase of MgS and MgSe. A more complete report of these calculations will be published elsewhere.

The pseudopotential total energy scheme [7], which has been successful both for elemental [8] and compound semiconductors [9-10], was used to compute the energy differences necessary to distinguish between various structural types. The ionic pseudopotentials needed in this scheme were generated using

the method of Hamann, Schlüter and Chiang [11]. Different potentials were used for orbitals of s, p, and d symmetry, and the potentials were tested to give the correct atomic wavefunctions, energy levels, and excitation energies for a number of electronic configurations. Exchange and correlation were treated in the local density formalism using the formulation of Hedin and Lundqvist [12]. The wavefunction in the solid was expanded in a plane wave basis and the total energy for a given structure was computed as described in reference 7. The size of the basis set was expanded until a relative convergence of better than 2×10^{-3} Rydberg was obtained. Typically we used 230 plane waves for the structures with one molecule per unit cell, and twice that for wurtzite which has four atoms per unit cell. The number of k points used in the integration over the Brillouin zone was also increased until a similar convergence was obtained.

To obtain the static properties, the total energy was calculated for a number of different volumes and then fitted with an equation of state. The best overall fit was obtained using

$$B = -V\frac{dP}{dV} = B_o + B'_o P \tag{1a}$$

$$P = -\frac{dE}{dV}, \tag{1b}$$

which give the Murnaghan equation [13] when integrated. The deviation from the fit is typically less than 10^{-3} Rydberg.

As a test of quality for the calculation we have computed the static and dynamic properties listed in table I. The various ways of computing the bulk modulus, using different functions to fit our data, gave values with a 10% variation. Our lattice constants are slightly smaller than those reported by Ihm and Joannopoulos [9], this does not reflect numerical errors in the

calculation, but is a result a different type of correlation energy functional.

Fig. 1 shows the total energy of AlAs and GaAs as a function of volume for the structures indicated. The observed equilibrium structures at zero pressure are zincblende. This is in agreement with our calculation, although the calculated energies for GaAs in the wurtzite structure coincide with the zincblende curve. As the crystals are compressed (fig.1), they undergo phase transitions to a metallic rocksalt phase at pressures of 76 and 160 kbar respectively. However, for GaAs (and GaP) at the transition volume, the energy difference between the rocksalt and the ordered β-Sn structures is of the order of the accuracy of the calculation. Therefore at this point we cannot rule out this structure. At larger volumes the rocksalt structure is definitely the more stable of the two. Of course at these volumes the crystal would phase separate, and the equilibrium structure would be a mixture of zincblende and the high pressure phase. The CsCl structure, which is also metallic, is not a contender except possibly at very high pressures.

In fig. 1 we also give the total energies for two structures suggested by Baublitz [6]. They are both orthorhombic with the same lattice parameters; 4.946, 4.628, and 5.493 A. The lower energy structure has symmetry Fmmm and is a distorted rocksalt. In the other structure, the atoms in each [001] plane are arranged as in rocksalt, but the planes are not staggered, giving rise to chains of atoms of the same type in the z direction. The symmetry of the latter structure is Cmmm. Both of the structures are considerably higher in energy than the ideal rocksalt.

The total energy curves for AlP and GaP are very similar to those for AlAs and GaAs. The major difference is that the phosphorus compounds have a

smaller lattice constant. However, scaled by the equilibrium volume, the energies for AlP are very close to those of AlAs, and those of GaP are very close to GaAs. This is reflected in table II were we give the transition pressures and volumes.

Since our calculations consistently place rocksalt below the β-Sn phase in energy, and since we get a transition pressure for AlP that is quite a bit lower than the experimental value, one may ask if the method somehow overestimates the stability of the rocksalt phase. To explore this question, we calculated the total energies for the II-VI semiconductors MgS and MgSe in the rocksalt and zincblende structure. Both compounds are observed in the rocksalt phase at standard pressure, but it is believed that the energy difference between the two phases is very small [1]. Our calculation indeed gives rocksalt as the more stable structure, less than 10^{-3} Rydberg below the zincblende phase in energy.

Assuming that our results are correct, we can only speculate that the differences between theory and experiment arise from superstress effects or metastable phases. In fact, for GaAs, we calculate a barrier of 1.5 eV for the motion of the anion along the diagonal from its tetrahedral position at 1/4, 1/4, 1/4 in the zincblende structure to the octahedral position at the center of the unit cube in the rocksalt phase. The barrier prevents a transformation along this path, and a rocksalt phase must probably nucleate from a surface or some defect. This is in accord with the experiments on InSb where the rocksalt phase was obtained from an amorphous phase.

For the zincblende phase at the observed volume, we calculate gaps of 1.6, 1.4, 1.7, and 1.4 eV for AlP, AlAs, GaP, and GaAs respectively. As is usual in the local density approach, these values are smaller than the

experimental numbers at 0 K [14], 2.6, 2.3, 2.40, and 1.53 eV. The experimental value for AlP has been obtained by adding 6% to the gap at room temperature. All the gaps are indirect from Γ to X, except GaAs which has a direct gap Γ to Γ. The calculated values of the gaps are not as well converged as the total energies and the fully converged values are smaller. As the zincblende phase is compressed the direct gap increases slightly and the conduction band at X is lowered to make the gap indirect for all the compounds. The probability density of this state has an approximate octahedral symmetry, and has a maximum at the center of the octahedron formed by the anions (As,P). This is where the total charge density has a minimum, and where a state can gain potential energy from the increasing overlap of the ionic potentials without having to contribute by an increase in the electron-electron repulsion and the kinetic energy. With the anions at the corners and face centers of the cubic unit cell, this region is at the center of the cube. This is where the cation is located in the rocksalt phase, and as the crystal transforms, it is therefore not surprising that the state at X drops in energy. For the III-V compounds this state falls below the valence band maximum, making the structure metallic. For GaAs, at the transition volume, it is 3.4 eV below the valence band maximum at Γ. Note that although the crystal transforms from semiconducting to metallic, there are no transitions within each phase. The zincblende phase stayed semiconducting and the rocksalt metallic in the volume range we investigated. The wavefunction at the valence band maximum in the rocksalt structure is mostly made up from the p states on the anions, whereas the X state wavefunction consists mainly of s states from the cations. This explains why the rocksalt structure is metallic for the III-V's. In more polar materials, the anion states will drop in energy compared to the cation states, and a gap will open up. In fact, we find that the amount of overlap,

or lack of such, corresponds roughly to the difference in the atomic term values for the elements in question. The rocksalt phase will be metallic if the order of the term values is s-s-p-p, and insulating if it is s-p-s-p. Neglecting the carbon row, this would predict all the III-V's to be metallic, all the II-VI's to be semiconducting, and among the II-VI's, CdSe and CdTe should have the smallest gaps.

Aside from the change in energy at the X point just described, the band structures of the zincblende and the rocksalt phases are remarkably similar [17]. This is also born out in the density of states, which for the rocksalt phase shows a large dip just above the fermi level. For this reason we believe the rocksalt phase should be thought of as ionic when considering structural properties. This also helps explain why the Al compounds are relatively more stable in the rocksalt phase than the Ga compounds. The atomic s term value is about 1.3 eV higher in energy for Al than for Ga. This leads to a larger average gap in the Al compounds that makes them more ionic and favors the rocksalt phase. The higher ionicity of Al was also observed by Ihm and Joannopoulos [9] in the charge densities of AlAs and GaAs in the zincblende structure.

The similarity in the band structure of the two phases is not reflected in the charge density. The bond charge, characteristic of the zincblende phase, is almost absent in the rocksalt phase, where the charge distributes itself spherically around the anion. As a function of volume, however, we see very little change in the charge density of each structure. In particular the bond charge of the zincblende phase, as measured by the phase of the <222> fourier components of the charge density, is still present at the volume where rocksalt is the more stable phase. The presence of bond charge in the zinc-

blende phase has been used to indicate the relative stability of the two structures at zero pressure [18]. From the above it follows that this argument cannot be extended to structural stability as function of pressure.

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Table I. Lattice constants, bulk modulus, B'_o, and the frequency for the transverse optical phonon at Γ. The experimental lattice constants are measured at room temperature.

		AlP	AlAs	GaP	GaAs	
a	calc	5.420	5.641	5.340	5.570	A
	exp +	5.451	5.662	5.451	5.653	
		-0.6%	-0.4%	-2.0%	-1.5%	
B_o	calc	8.65	7.41	8.97	7.25	$\times 10^{10}$ Jm^{-3}
	exp *			8.87	7.48	
				+1.1%	-3.1%	
B'_o	calc	3.73	3.50	4.14	3.82	
ν (TO at Γ)	calc				7.84	THz
	exp ‡				8.19	
					-4.3%	

+ Reference [14], * compiled by reference [15], ‡ reference [16].

Table II. Transition pressures, volumes, and total energy differences for the zincblende to rocksalt transition. V_t(zb,rs) are the transition volumes for the two phases, V_o(rs) is the equilibrium volume for the (metastable) rocksalt phase, and ΔE_o 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 zincblende phase.

		AlP	AlAs	GaP	GaAs	
P	calc	93	76	217	160	kbar
	exp +	140-170		200-240	160-190	
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_o(rs)	calc	0.78	0.78	0.81	0.81	
ΔE_o	calc	0.46	0.43	0.78	0.67	eV

+ References [4,6].

FIGURE CAPTION.

Fig. 1. Total energy diagrams for AlAs and GaAs as a function of volume relative to the experimental equilibrium volumes. The triangle and the square give the energy for two orthorhombic structures suggested in reference 6 and described in the text.

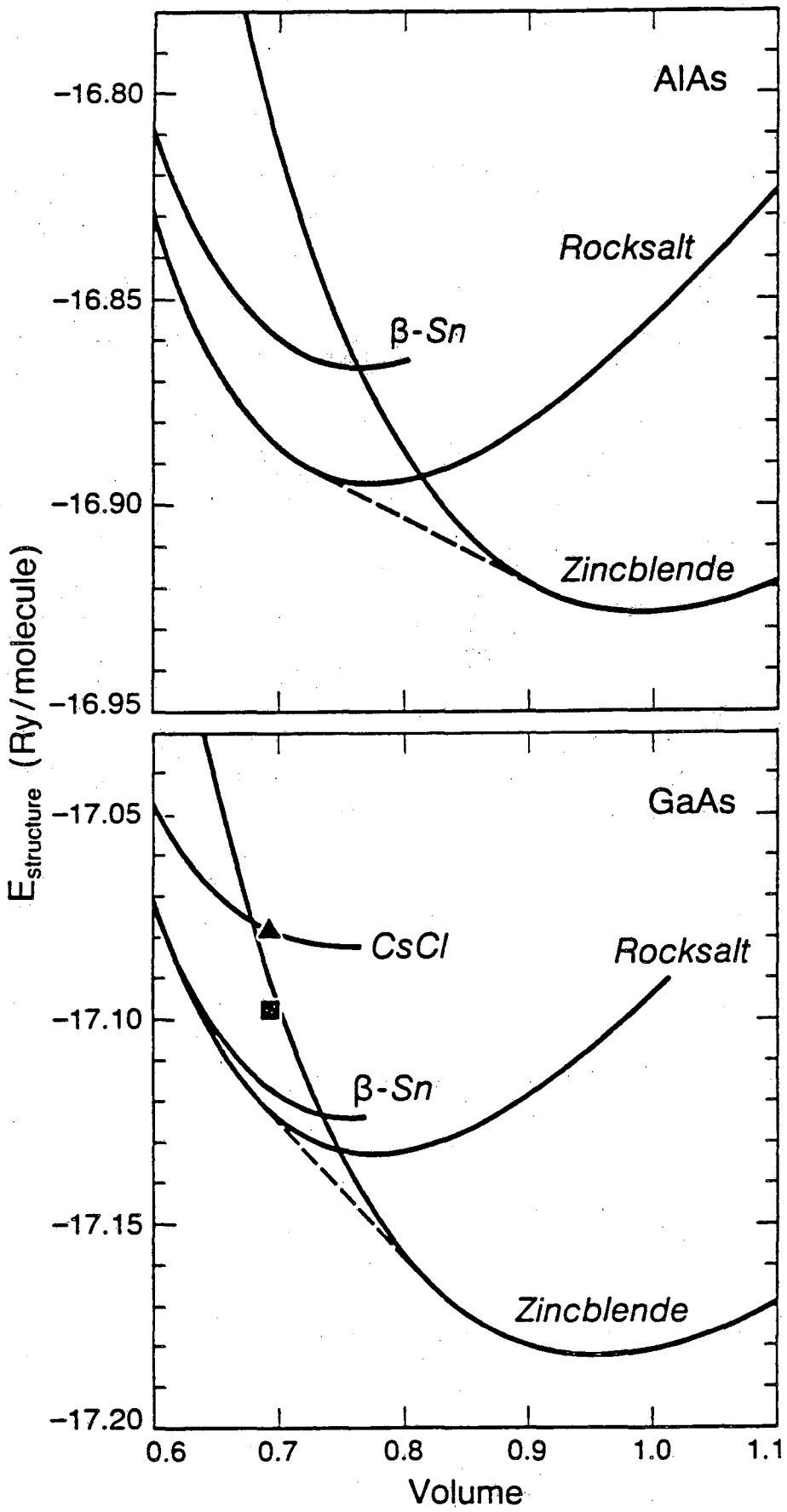
AlAs
Rocksalt
β-Sn
Zincblende
GaAs
CsCl
Rocksalt
β-Sn
Zincblende
−16.80
−16.85
−16.90
−16.95
−17.05
−17.10
−17.15
−17.20
0.6
0.7
0.8
0.9
1.0
1.1
Volume
E_structure (Ry/molecule)

FIG. 1

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