

STRUCTURAL PHASE TRANSFORMATION OF ALUMINUM ARSENIDE.

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ABSTRACT

The electronic structure, the charge density and the total energy of AlAs in the zincblende (B3), rocksalt (B1) and nickelarsenide (B8₁) structures are studied using first-principles self-consistent local-density calculations in a plane wave basis employing soft non-local pseudopotentials. Contrary to most other III-V compounds upon applying pressure, AlAs transforms to the metallic nickelarsenide structure at a calculated pressure of 13.2 GPa, to be compared with a recent experimental value of $7. \pm 5$. GPa. The volume reduction at the transformation is calculated to be 21.0 % (experimental value 17.1 % at 7. GPa). The equilibrium lattice constant of the nickelarsenide structure is found to be $a = 3.705$ Å and $c = 5.795$ Å. From this structure no transformation appears to be possible to the rocksalt structure.

The III-V fourfold coordinated semiconductors transform under pressure to sixfold coordinated metals. This structural phase transformation leads to a closer packing of the atoms.

Recently, the first experimental observation was made of a III-V compound transforming to the hexagonal NiAs structure.¹ On the other hand, it has been shown in the past that total energy methods are capable of predicting the relative stability of semiconductor phases and of the pressure at which these transitions occur.²⁻⁷

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The calculations, reported in this paper, are performed in the framework of density functional theory together with non-local pseudopotentials. Soft ab-initio pseudopotentials are generated using the method of Troullier and Martins.⁸ These non-local potentials are then transformed into separable form by means of the Kleinman-Bylander procedure.⁹ As a consequence of this last step substantial savings in computer time and storage are achieved.

In order to ensure convergence a kinetic energy cut-off of 50 Ry is used. This corresponds to about 3000 plane waves for the NiAs structure and about 1900 for the zincblende and rocksalt structures. Because some of the high pressure phases of AlAs are expected to be metallic a large number of integration points over the Brillouin zone is necessary. We use the Monkhorst-Pack scheme¹⁰ with a (12,12,8)-division for the NiAs structure and a (8,8,8)-division for the zincblende and rocksalt structures. This corresponds to respectively 76 and 60 points in the irreducible part of the zone.

For the exchange-correlation part we use the Wigner interpolation formula. To fit the total energy and to determine the equilibrium lattice constant, the bulk modulus etc. we use the third-order Birch equation of state.¹¹ This equation is derived from the expansion of the total elastic energy to third order in the displacements.

For the hexagonal modification we determine the two lattice constants as follows: first we choose a unit-cell volume V and calculate the total energy for different values of a and c corresponding to V . These energies are then fitted to a polynomial in c/a from which the c/a ratio is determined at the minimal energy. This procedure is then repeated for 10-12 different volumes. The same number of volumes is used for the cubic structures.

Table I shows the calculated and experimental results for the three structures considered in this paper. The RMS-error of the equation of state fits is 4. 10^{-5} Ry/atom or better. The usual trends of LDA are apparent from this table : a slight overbinding (1% for zincblende and for nickelarsenide 2% for a and 4% for c) and an overestimation of the bulk modulus. It should be noted that the "experimental" value of Ref. 13 is in fact estimated using empirical relations and data from other III-V compounds.

The fact that here the deviation of the c -value is almost double that of the a -value has been observed before e.g. for graphite¹⁴⁻¹⁵ and for titaniumdiboride.¹⁶ It turns out

Table I. Calculated and experimental ground state properties of AlAs: lattice constants a and c (in Å), bulk modulus B_0 (in GPa) and the pressure derivative of the bulk modulus B'_0 .

	Zincblende		Nickelarsenide		Rocksalt	
	Calc	Exp	Calc	Exp	Calc	Exp
a	5.590	5.660 ¹²	3.705	3.791 ¹	5.201	-
c	-	-	5.795	6.054 ¹	-	-
c/a	-	-	1.564	1.597±0.008 ¹	-	-
B_0	81.1	74.±4. ¹ 77.3 ¹³	80.6	73.±7. ¹	76.9	-
B'_0	4.7	5.±1. ¹	5.0	4.6±0.7 ¹	5.2	-

Table II. Calculated and experimental values of the transition pressure, the transition volumes, the volume change at the transition pressure ΔV_t , and the energy difference ΔE_0 between the minima of the two phases.

	Calculated	Experimental ¹
p_t (GPa)	13.2	$7. \pm 5.$
$V_t(\text{zb})/V_0(\text{zb})$	0.885	0.887
$V_t(\text{na})/V_0(\text{zb})$	0.699	0.734
ΔV_t (%)	21.0	$17. \pm 1$
ΔE_0 (eV/atom)	0.35	-

that energy differences due to sizeable changes in c are very small (which is not the case for a) so that the uncertainty in the numerical determination of c is a lot bigger than of a . It should be remarked that the c/a ratio is almost constant as it only changes from 1.564 at zero pressure to 1.551 at 54 GPa and 1.531 at 100 GPa. The bulk modulus obtained from Cohen's empirical formula¹⁷ is 79.0 GPa and falls right in between our calculated and the experimental value. Figure 1 shows the total energy versus the atomic volume for the three structures. It is clear that the zincblende form is the most stable of the three and that the rocksalt form is always unstable. No transformation ap-

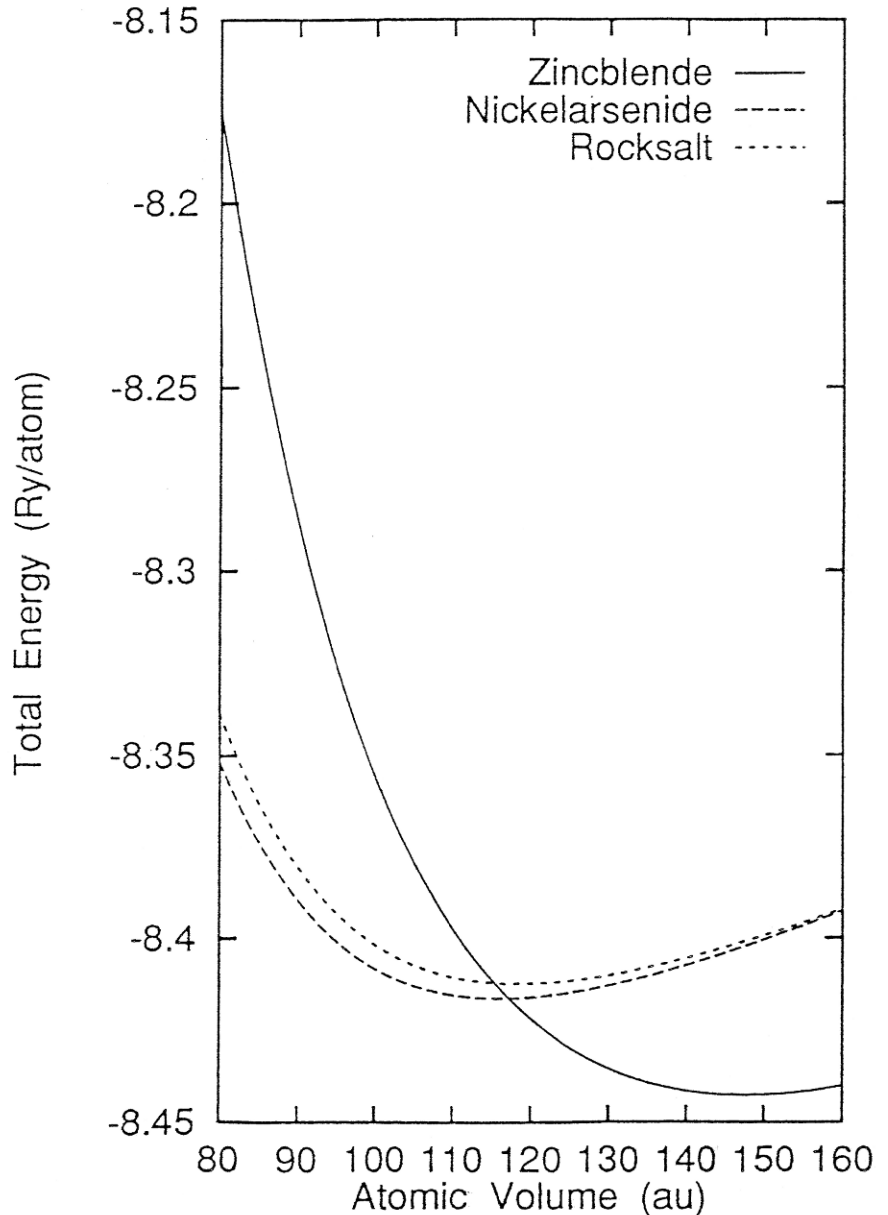


Figure 1. Total energy (in Ry per atom) versus the atomic volume (in au) for the zincblende, nickelarsenide and rocksalt structures of AlAs.

pears to be possible to the rocksalt structure. The energy difference between the minima of the nickelarsenide and rocksalt phases is only 0.054 eV per atom. The common tangent to the zincblende and nickelarsenide curves determines the transition path between both structures. The slope of this line is 13.2 GPa, to be compared with the measured transition pressure of $7. \pm 5$. GPa.¹ Table II gives the calculated and experimental data regarding the transition. According to Van Vechtens' interpolation formula,¹⁸ the volume change at the transition pressure (ΔV_t) is related to the ionicity of the compound. In the present case his formula gives (with for AlAs an ionicity of 0.274) $\Delta V_t = 19.4 \%$, which is in good agreement with both the experimental and theoretical values. It also should be remarked that the experimental transition volumes, shown in Table II, were determined from the equation of state at 12 GPa.

In summary, the ground state properties of AlAs in the zincblende, rocksalt and nickelarsenide structure are determined in the plane wave local density approximation. The calculated lattice constant, bulk modulus and the transition pressure from the zincblende to the nickelarsenide structure are in good agreement with recent experimental values.

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