

Electronic structure of AlN

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The self-consistent electronic structure of AlN has been calculated using a first-principles linear-combination-of-atomic-orbitals method. Theoretical values for the lattice constant, internal parameter, bulk modulus, and cohesive energy were determined as well as the pressure-dependent frequency of the A_1 TO phonon. The charge density has also been calculated and is in good agreement with results from x-ray diffraction experiments which indicate the lack of a distinct bond charge.

I. INTRODUCTION

Aluminum nitride is a tetrahedrally coordinated III-V compound. It has a large band gap (6.3 eV) and forms in the hexagonal wurtzite structure (Fig. 1). Because of its piezoelectric properties it has been used recently in thin-film microwave acoustic resonator applications.¹ It also has a thermal conductivity greater than sapphire and other properties which make it an attractive candidate for applications as a substrate in thin-film devices.² Although single crystals of AlN are not easily grown, there have been measurements of several physical properties. Precise x-ray diffraction experiments have been used to determine the valence charge density,³ which suggests that the bonding is probably more ionic than covalent. The tetrahedral coordination and wurtzite structure rather than the rock-salt structure indicate, however, that some degree of co-

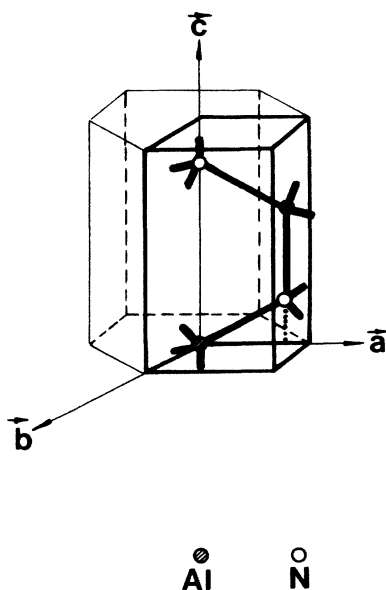


FIG. 1. Unit cell for the wurtzite structure.

valency is still present. This is consistent with the fracture toughness of AlN which is believed to be related to the residual covalent bonding. The Raman spectrum of AlN has been measured recently by two different groups with differing results.^{4,5} Finally, the photoemission spectra of AlN was measured in the last year.⁶

Several band-structure calculations have been made for AlN. An early calculation by Hejda and Hauptmanová using the orthogonalized plane wave (OPW) method;⁷ an empirical pseudopotential calculation by Bloom;⁸ a model potential calculation by Jones and Lettington;⁹ an empirical tight-binding calculation by Kobayashi *et al.*,¹⁰ and the semi-*ab initio* linear-combination-of-atom-orbitals (LCAO) calculation of Huang and Ching.¹¹ The calculations presented in this paper were largely motivated by the photoemission spectra⁶ and differ from these previous calculations by being fully self-consistent. Besides obtaining theoretical results for comparison with the above experiments we also used total energy calculations to evaluate the bulk modulus, which has not been directly measured, but may be derived from the measured elastic constants.¹² The overall agreement between the calculated and experimental values of the physical properties is excellent.

II. METHOD

The particular first-principles LCAO method used in this work has been described elsewhere.¹³ The method has been applied to Si for the evaluation of total energies with accurate results.¹⁴ In this section we limit the discussion to those aspects of the method which differ from the application to Si. The Bloch wave functions are expanded in a basis set of 18 localized atomic orbitals centered on each Al site and 9 orbitals on each N site. The radial wave functions are expanded in terms of 16 Gaussian-type orbitals with the exponents ranging from 0.15–50 000. The crystal charge density and potential are also expanded in a basis consisting of 58 independent Gaussian functions, with 16 centered on each Al site, 16 on each N site, and the remaining 26 centered at various auxiliary sites. These auxiliary sites are important for obtaining an accurate representation of the nonspherical aspects of the

charge density about the atomic positions. Four auxiliary sites were placed at interstitial positions away from the high-density regions, and the remaining auxiliary sites were placed at distances of $\frac{1}{3}$ and $\frac{2}{3}$ along each of the eight Al—N bonds in the unit cell. The coefficients for the charge density expansion are determined by a least-squares fit to the actual charge density. The fit is first performed with the total charge unconstrained so that a comparison of the fit charge to the actual number of electrons gives a measure of the fit quality. The unconstrained fit errors for the calculations in this paper are less than 0.0001 electrons for the 16 valence electrons per cell. The frozen core approximation was used in the calculations reported. Twelve special \mathbf{k} points were sampled in the irreducible $\frac{1}{24}$ th portion of the Brillouin zone and the total energy converged to better than 0.00005 Ry/cell. The Wigner interpolation formula was used in evaluating the local exchange-correlation potential.¹⁵ The calculations were performed on a Digital Equipment Corporation VAX11/785 minicomputer with each full self-consistent calculation for a particular lattice configuration taking about four and a half hours of CPU time.

III. RESULTS

The band structure for AlN evaluated at the experimental lattice constants¹⁶ ($a=3.110$ Å, $c=4.980$ Å) is given in Fig. 2. The lowest bands are derived from the nitrogen $2s$ levels and are separated from the upper nitrogen $2p$ and aluminum $3s$ and $3p$ derived valence bands by the so-called ionicity gap. The calculated energy gap between the valence and conduction bands is 4.4 eV. This is 30% less than the measured optical gap of 6.3 eV,¹⁷ and reflects the well-known result that the density functional method is strictly only valid for ground-state properties. Theoretical methods for obtaining the optical gap have been developed,¹⁸ but we have not used them in this paper. The density of states corresponding to the electronic structure of Fig. 2 is given in Fig. 3 along with the experimental energy distribution curve (EDC).⁶ The calculated density of states convoluted with a Gaussian of full width

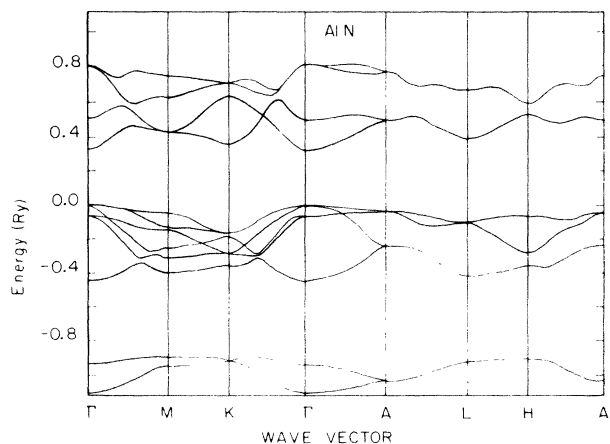


FIG. 2. Calculated band structure of AlN.

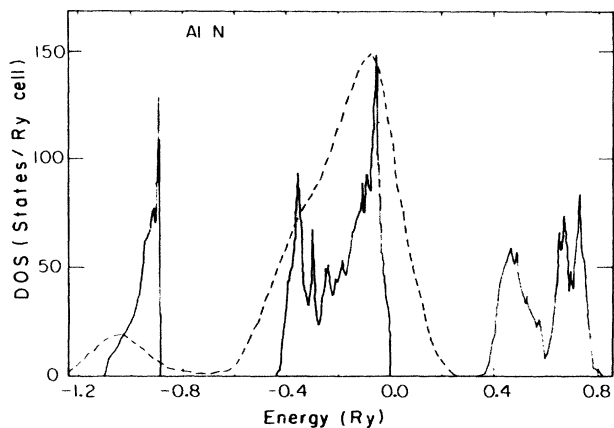


FIG. 3. Calculated electronic density of states (solid curve) and the experimental energy distribution curve obtained by the photoemission experiments of Olson *et al.* (Ref. 6) (dashed curve).

at half maximum (FWHM) of 1.3 eV is given in Ref. 6 for a more direct comparison with the same EDC. Unlike some previous non-self-consistent calculations¹⁰ the calculated shoulder near -0.4 Ry binding energy is correctly positioned and the ionicity gap is also in good agreement with experiment.

The total energy of the crystal was evaluated at 13 different volumes keeping the c/a ratio fixed at the experimental value. Figure 4 shows these values along with a third-order polynomial curve which was least squares fit to the points. The root-mean-square (rms) error of the fit was only 0.02 mRy, which is a good indication of the little noise encountered in these calculations. From this curve one derives the equilibrium volume and the bulk modulus, along with its pressure derivative. The bulk modulus has not been measured directly, but from the measured elastic constants,¹² it may be derived assuming

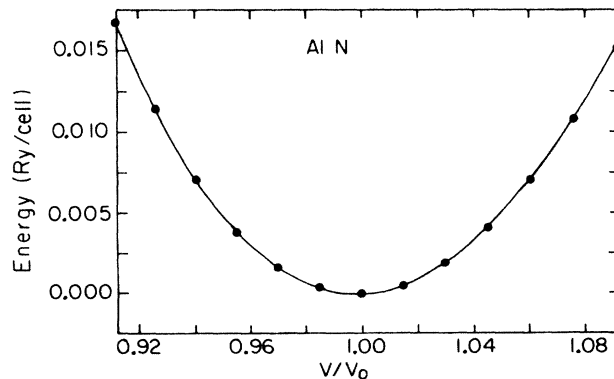


FIG. 4. Total energy versus volume for AlN. The c/a ratio was held fixed at the experimental value. The curve is a third-order polynomial which has been least squares fit to the 13 points obtained by the first-principles calculations.

TABLE I. Comparison of experimental and calculated values of various physical properties for AlN.

	Equilibrium volume	Bulk modulus	$\frac{dB}{dP}$	Internal parameter	Cohesive energy	A_1 TO frequency	$\frac{d\nu}{dP}$
Calc.	281.01 a.u. ³	2.07 Mbar	3.98	0.3818	12.45 eV	19.60	4.55 cm ⁻¹ /GPa
Expt.	281.51 a.u. ³	2.02 Mbar		0.3821	11.6 eV	19.77±0.02 THz	4.88 cm ⁻¹ /GPa
Ref.	3,16	19		3,16	20	4	4

either uniform strain or uniform stress (a complication necessary for noncubic crystals). These assumptions yield values of the bulk modulus of 2.02 and 2.01 Mbar, respectively, so that within experimental uncertainty it is immaterial whether the crystal undergoes uniform stress or strain. We list in Table I the values for several calculated bulk physical properties. The agreement is extremely good for the equilibrium volume and bulk modulus. The cohesive energy is off by 7%, but because this involves a separate atomic calculation, the cancellation of systematic errors within the local-density approximation (LDA) may not be as complete as for the other properties calculated.

The relative Al-N interatomic distance along the z axis is not determined by the crystal lattice parameters. Rather it is described by what is called the internal parameter u . The internal parameter can be determined theoretically by evaluating the total energy as a function of the z axis Al-N separation. This was done with the lattice constants fixed at their experimental values for 12 different separations. The result is shown in Fig. 5. The curve is a third-order polynomial with an rms error in the fit of 0.06 mRy. The minimum in the curve occurs at 0.3818 which deviates considerably from the "ideal" value of 0.375 and is in excellent agreement with experiment^{3,16} (see Table I). This means the Al-N bond along the z axis is actually 0.01 Å longer than the other three bonds.

From the second derivative of the curve in Fig. 5, one immediately obtains the A_1 TO- Γ -point-phonon frequency which involves the relative motion along the z axis

of the Al and N sublattices. The frequency of this mode has recently been reported by two different groups using Raman spectroscopy. Sanjurjo *et al.* obtain a frequency of 19.77 ± 0.02 THz (Ref. 4) while Carlone *et al.* assign a frequency of $\approx 15.4 \pm 0.5$ THz for this mode in amorphous AlN.⁵ The calculated frequency of 19.6 THz clearly favors the results by Sanjurjo *et al.* We also calculated the frequency of this phonon at three smaller volumes with the c/a ratio fixed. We find that the frequency increases linearly with pressure and $d\nu/dP = 4.55$ cm⁻¹/GPa. Sanjurjo *et al.*⁴ report a pressure derivative of 4.88 cm⁻¹/GPa.

The charge density of AlN has been determined by precise x-ray diffraction experiments.³ We show in Fig. 6 the theoretical total charge density in the x - z plane containing all the Al and N atoms in the primitive cell. The aluminum atoms have more core electrons and a higher total density near the nuclear position, while the nitrogen atoms are more spread out with the larger number of valence electrons. The charge density in the solid looks very nearly like a superposition of spherical densities. This is still true after the core has been subtracted as shown in Fig. 7. The node in the Al 3s radial function causes a minimum in the valence charge density at roughly 0.8 a.u. from the Al site. This feature, along with the nearly circular contours surrounding the N site, is in good

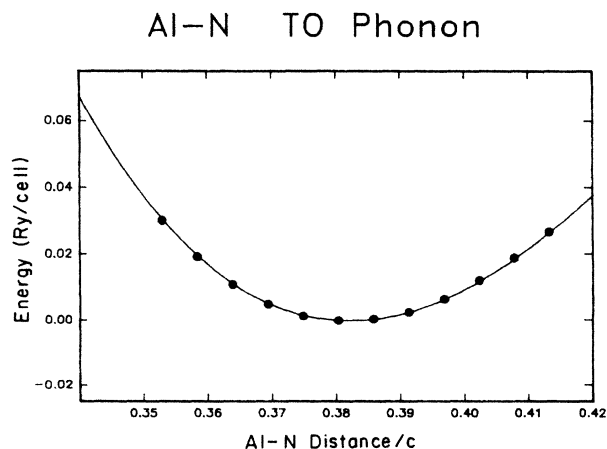


FIG. 5. Total energy as a function of the Al-N distance along the z axis. The minimum occurs at the theoretical value of the internal parameter and the second derivative yields the theoretical phonon frequency.

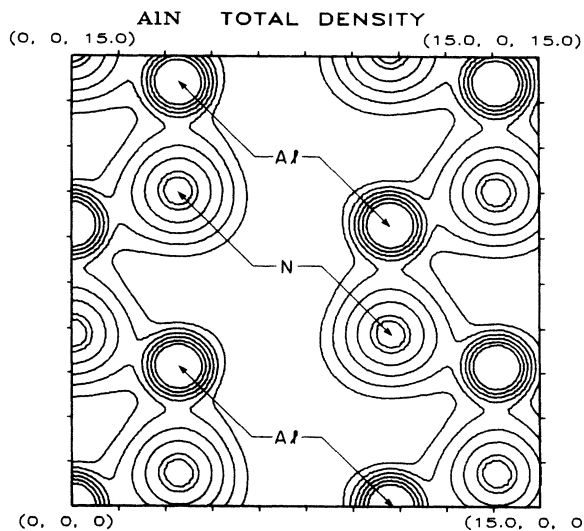


FIG. 6. Total charge density of AlN in the x - z plane. The contours in $e/(a.u.^3)$ are at 0.035, 0.070, 0.140, 0.280, 0.560, and 1.12.

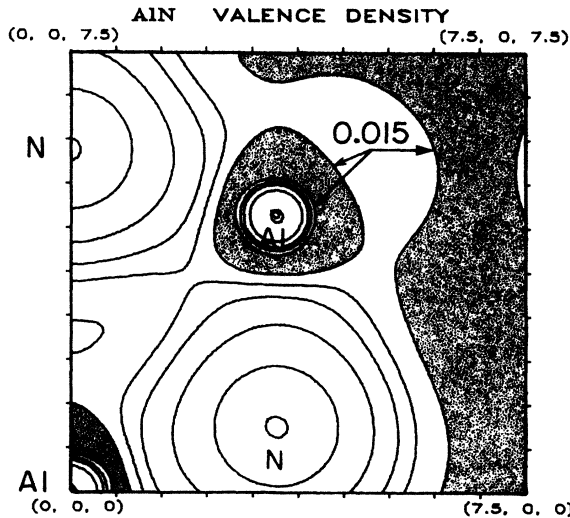


FIG. 7. Valence charge density of AlN. The shaded area indicates the region where the charge density falls below $0.015 e/a.u.^3$. The contours in $e/a.u.^3$ are drawn at 0.015, 0.031, 0.050, 0.100, 0.300, and 0.800.

quantitative agreement with experiment (see Fig. 3 of Ref. 3). The lack of a distinct bond charge between the two atoms is certainly an indication of the more ionic bonding found in this compound than in, say, InSb.³ We also note a very low-density channel parallel to the z axis which could provide a diffusion path in AlN.

IV. CONCLUSIONS

Using a first principles LCAO method we have calculated a number of the physical properties of AlN. The excellent agreement with experiment for the somewhat complicated wurtzite structure is another indication that modern electronic structure calculations can be very accurate in the evaluation of crystalline ground-state properties. Within the adiabatic approximation phonon frequencies can also be accurately calculated with these same methods²¹ as our results for the frequency and pressure dependence of the A_1 TO mode indicate. We should remark that the accuracy obtained in these calculations for AlN is probably better than one may expect in general. At least we can see no compelling reason why the local density approximation should be so extremely accurate for AlN, although for a compound with a relatively large bulk modulus, like AlN, the energy minimum is at the bottom of a steep well and small errors in energy will not significantly change the position of the minimum.

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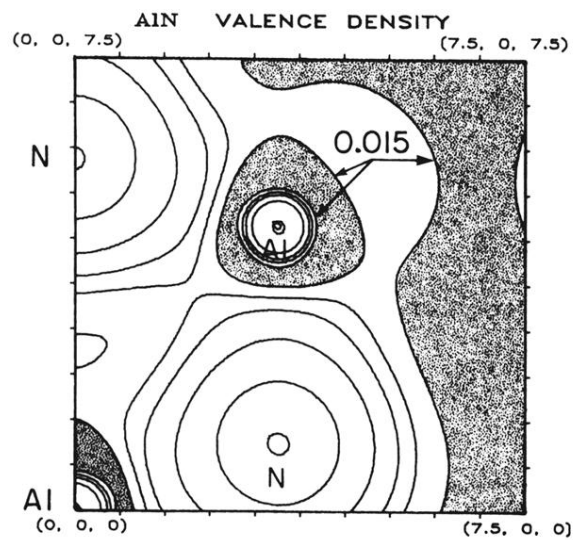


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