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BAND STRUCTURES OF GaN AND AlN

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Abstract—Pseudopotential band structures for GaN and AlN are calculated non-empirically by means of form factors synthesized from those of C, Ge and Ga in the case of GaN and from SiC and Al in the case of AlN. Good agreement with recent optical experiments is obtained for various gap energies.

1. INTRODUCTION

RECENT success[1] in the deposition of large, single-crystal films of GaN has spurred renewed experimental interest in this semiconductor. In particular, optical reflectivity measurements have been made up to 11 eV on both polycrystalline[2] and single-crystal [3] films, and the absorption edge has been studied[4]. This interest arises from the fact that this III–V compound has the large direct bandgap more commonly found in II–VI compounds but with, it is hoped, the easier dopability of the III–V systems. Thus GaN has potential usefulness for u.v. luminescent[5] devices and lasers. Similar considerations hold for the companion nitride, AlN, which has an even wider direct bandgap and, like GaN, has the hexagonal crystal structure. Room temperature optical absorption data [6, 7], have been taken on AlN single crystals and an OPW band structure has been estimated[8].

With new spectral data becoming available there is both the need and the opportunity for further band structure studies. In the present paper full-zone band structures for GaN and AlN are calculated by the pseudopotential method. However the commonly used empiricism, in which the form factors (Fourier transforms of the pseudopotential) are adjusted to force agreement with experimental bandgaps, is here avoided. Instead, the transferability property of the pseudopotentials of monatomic crystals is used; the form factors of GaN are synthesized from those of Ga and of the hypothetical IV–IV compound GeC, and the form factors of AlN are synthesized from those of Al and of SiC. Spin-orbit corrections[9] are neglected because of the lightness of the constituent elements.

2. METHOD AND CALCULATIONS

The pseudopotential method used here starts with that used by Bergstresser and Cohen in their well-known treatments of hexagonal[10] and cubic[11] binary compounds. The pseudopotential Hamiltonian

$$H = -(\hbar^2/2m)\nabla^2 + V(r) \qquad (1)$$

contains an effective potential which is expanded as a Fourier series in reciprocal lattice space. For binary compounds the expansion is written in two parts which are symmetric and antisymmetric with respect to interchange of the two atoms about their midpoint:

$$V(\mathbf{r}) = \sum_{G \leq G_0} [S^S(\mathbf{G})V_G{}^S + iS^A(\mathbf{G})V_G{}^A]e^{i\mathbf{G}\cdot\mathbf{r}}. \qquad (2)$$

The limited summation reflects the fact that the effective pseudopotential is sufficiently weak, because of cancellation between the kinetic and potential energies in the vicinity of atomic cores, that only a few Fourier terms suffice. The structure and form factors are given by[10]

$$S^S(\mathbf{G}) = \frac{1}{n}\sum_j e^{-i\mathbf{G}\cdot\delta_j} \qquad (3)$$

$$S^A(\mathbf{G}) = -\frac{i}{n}\sum_j P_j e^{-i\mathbf{G}\cdot\delta_j} \tag{4}$$

$$V_G^{S,A}(12) = \frac{1}{\Omega_{12}}\int \frac{1}{2}[v_1(\mathbf{r}) \pm v_2(\mathbf{r})]_{12} e^{-i\mathbf{G}\cdot\mathbf{r}} d^3\mathbf{r}. \tag{5}$$

This can be simplified through use of the transferability approximation for atomic pseudopotentials, as discussed by Phillips [12]. By writing

$$V_G(i) = \frac{1}{\Omega_i}\int v_i(\mathbf{r}) e^{-\mathbf{G}\cdot\mathbf{r}} d^3\mathbf{r}, \tag{6}$$

where Ω_i is the volume-per-atom of the monatomic solid consisting of atoms of type i, and by assuming that the atomic pseudopotential $v_i(\mathbf{r})$ is essentially independent of the particular crystalline environment of the atoms, (i.e., neglecting the dielectric screening at small G-values), we replace equation (5) by

$$V_G^{S,A}(12) = [\Omega_1 V_G(1) \pm \Omega_2 V_G(2)]/2\Omega_{12}. \tag{7}$$

The form factors for GaN are synthesized from the published form factors of C, Ge and Ga as follows. The symmetric form factors, V_G^S(GaN), are taken equal to those of the most closely corresponding IV–IV compound, GeC. This hypothetical cubic system would have essentially the same nearest-neighbor distance ($d = \bar{a}_{cub}\sqrt{\frac{3}{16}} = 2{\cdot}00$ Å, for a mean lattice constant $\bar{a}_{cub} = 4{\cdot}61$ Å) as has wurtzite GaN ($d = a_{hex}\sqrt{\frac{3}{8}} = 1{\cdot}95$ Å, for $a_{hex} = 3{\cdot}19$ Å). Silicon is not the appropriate choice since its nearest-neighbor separation is $d = 2{\cdot}36$ Å. The form factors for GeC are compounded graphically from a volume-weighted average of those of diamond[13] ($a_{cub} = 3{\cdot}57$ Å) and of germanium[11] ($a_{cub} = 5{\cdot}66$ Å):

$$V(\text{GeC}) = [(3{\cdot}57/4{\cdot}61)^3 V(C) + (5{\cdot}66/4{\cdot}61)^3 V(\text{Ge})]/2.$$

This is shown in Fig. 1 as V^S(GaN). The anti-

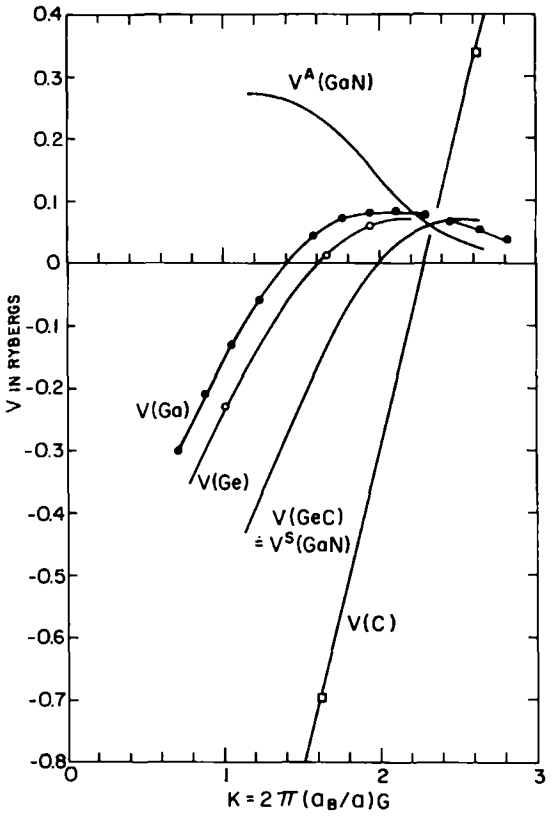

Fig. 1. Form factors for GaN, as calculated from published values for Ga, Ge and C, vs. the reciprocal lattice vector normalized with the appropriate cubic lattice constant.

symmetric form factors of GaN are then obtained from equation (7); thus

$$V^A(\text{GaN}) = (\Omega_{Ga}/\Omega_{GaN})V(\text{Ga}) - V^S(\text{GaN}), \tag{8}$$

where the volumes-per-atom are $\Omega_{Ga} = 131{\cdot}4$ and $\Omega_{GaN} = 77{\cdot}3$ a.u. The gallium form factors shown in Fig. 1 are the '$V6$' values of Inglesfield[14].

The values of $V_G^{S,A}$ for 'cubic' GaN, as determined above and plotted in Fig. 1, are replotted vs. G^2 in Fig. 3. This latter figure is then used at those values of G^2 appropriate to the actual wurtzite structure, as discussed in Ref.[10].

A similar procedure is used for AlN. How-

ever now the corresponding IV–IV system is the real compound, SiC. This has a nearest neighbor distance of d = 1·88 Å, based on a_{cub} = 4·35 Å, while wurtzite AlN, with a_{hex} = 3·10 Å has d = 1·89 Å. The volumes-per-atom being essentially equal, the symmetric form factors V^S(AlN) can be taken equal to the published values[13] for V(SiC); these are shown in Fig. 2. Then equation (7) gives the antisymmetric values

$$V^A(\text{AlN}) = (\Omega_{\text{Al}}/\Omega_{\text{AlN}})\, V(\text{Al}) - V^S(\text{AlN}),$$

where the volumes-per-atom are Ω_{Al} = 111·3 a.u. and Ω_{AlN} = 69·7 a.u., and the aluminum form factors are from Animalu and Heine[15]. The $V^{S,A}$(AlN) values are replotted vs. G^2 in Fig. 3, for use at the wurtzite values of G^2.

The computer calculation follows that of Ref. [10]. The ratio of the wurtzite lattice constants is given its ideal value $c/a = \sqrt{8/3} = 1{\cdot}633$, which is an approximation since the actual values are c/a = 5·185/3·189 = 1·625 for GaN[1], and c/a = 4·96/3·10 = 1·60 for AlN[16]. The structure

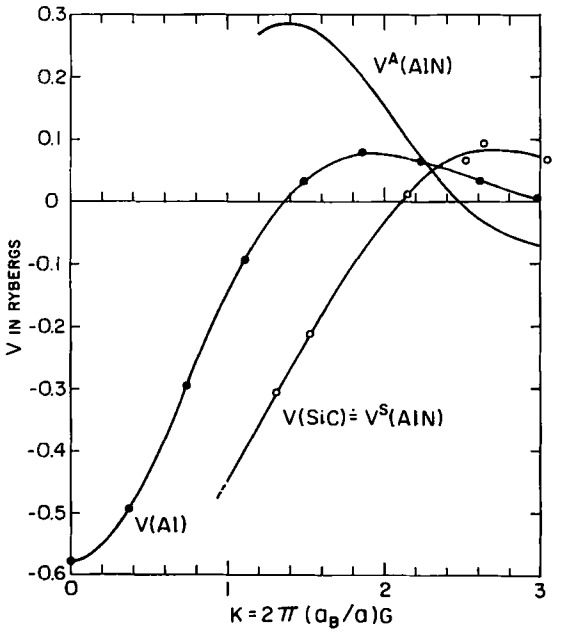

Fig. 2. Form factors for AlN, as calculated from published values for Al and cubic SiC.

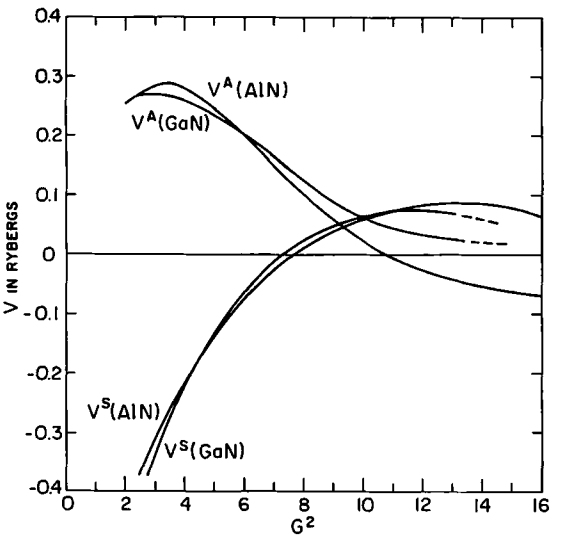

Fig. 3. Form factors for GaN and AlN vs. Square of reciprocal lattice vector.

factors of equations (3) and (4) for wurtzite are $S^S(\mathbf{G}) = \cos[2\pi(l/6 + m/6 + n/4)]\cos(\tau nu)$ and $S^A(\mathbf{G}) = \cos[2\pi(l/6 + m/6 + n/4)]\sin(\pi nu)$, where the reciprocal lattice vectors are $\mathbf{G} = 2\pi(l\mathbf{a}^* + m\mathbf{b}^* + n\mathbf{c}^*)$, in terms of the primitive translation vectors. Again, the ideal value of the wurtzite parameter, $u = \frac{3}{8}$, is used. The form and structure factors are given in Table 1, at the ideal wurtzite values of G. As in Ref.[10], all plane waves having energies $|\mathbf{G}+\mathbf{k}|^2 \leqslant 10$ eV form the basis set of the Hamiltonian matrix, and waves of energy $10 < |\mathbf{G}+\mathbf{k}|^2 \leqslant 27$ eV form the perturbation set.

3. RESULTS

The calculated band structures are shown in Figs. 4 and 5. In both compounds we find the Γ_1 to be higher than the Γ_6 valence band edge. For GaN, the fundamental, direct bandgaps are calculated to be 3·5 eV (‖) and 3·7 eV(⊥). The average agrees well with the various room-temperature experimental bandgaps of 3·4 eV[1], 3·5 eV[4], 3·6 eV[3] and 3·8 eV[2]. The bandgap calculated in the dielectric two-band model[17] is 4·8 eV. We calculate the $E_1 = \Gamma_{5v} \rightarrow \Gamma_{3c}$

Table 1. Wurtzite reciprocal lattice vectors, structure factors and form factors (in Ry*) for* GaN *and* AlN

G	G^2	$\lvert S^S(G)\rvert$	$\lvert S^A(G)\rvert$	GaN V^S	GaN V^A	AlN V^S	AlN V^A
000	0	1	0				
001	$\frac{3}{4}$	0	0				
100	$2-\frac{3}{8}$	$\frac{1}{2}$	0	−0·38		−0·34	
002	3	0·71	0·71	−0·34	0·27	−0·31	0·28
101	3−5/12	0·33	0·80	−0·29	0·26	−0·27	0·28
102	$5-\frac{3}{8}$	0·35	0·35	−0·09	0·21	−0·09	0·22
003	$6-\frac{3}{4}$	0	0				
210	8	1	0	0·02		0·01	
211	$8-\frac{3}{4}$	0	0				
103	9−5/12	0·80	0·33	0·05	0·07	0·04	0·05
200	$10-\frac{3}{8}$	$\frac{1}{2}$	0	0·07		0·07	
212	11	0·71	0·71	0·07	0·04	0·07	−0·01
201	11−5/12	0·33	0·80	0·07	0·03	0·08	−0·02
004	12	0·00	1·00		0·03		−0·03
202	$13-\frac{3}{8}$	0·35	0·35	0·06	0·02	0·09	−0·05
104	$14-\frac{3}{8}$	0·00	0·50		0·01		−0·06
213	$14-\frac{3}{4}$	0	0				

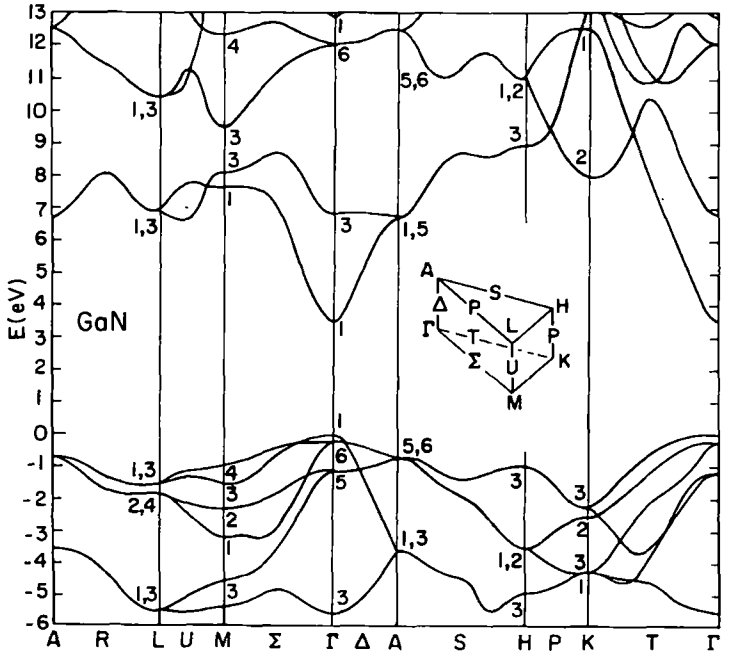

Fig. 4. Band structure of GaN. The numbers along the bands at the various symmetry points denote the irreducible representations of the particular point groups.

gap to be 7·9 eV, compared to 7·0 eV by Van Vechten; experimentally, Kosicki[2] sees a reflectivity peak near 6·8 eV whereas Harbeke[3] sees one at 7·2 at room temperature. Reflectivity peaks are also measured at 9·5 and 10·7 eV. This calculation would assign the 9·5 eV peak to transitions near symmetry points M and/or H, rather than near Γ for

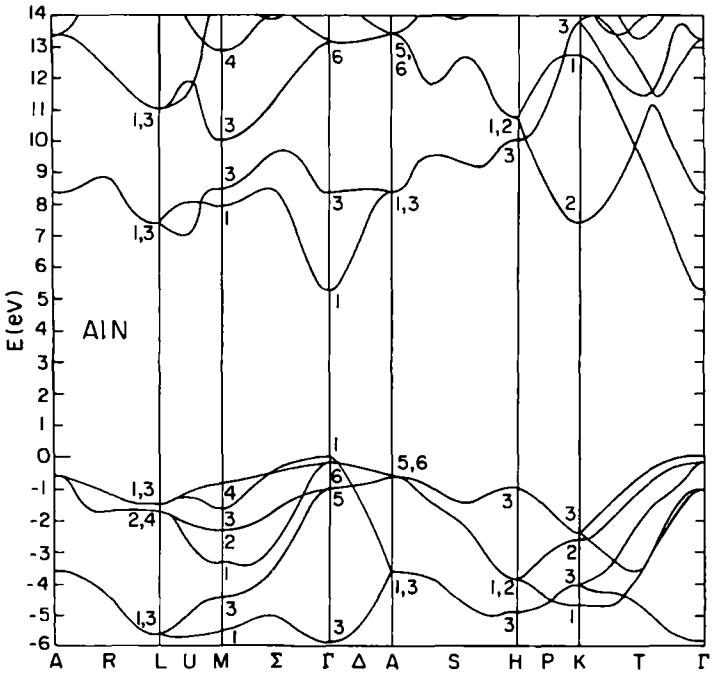

Fig. 5. Band structure of AlN.

which $E_0' = \Gamma_{1,6v} \rightarrow \Gamma_{1,6c}$ is over 12 eV here, although it is only 9·08 eV in the dielectric model[17]. The 10·7 eV peak corresponds to a calculated value at point K of $E_{2B} = K_{2v} \rightarrow K_{2c} = 10{\cdot}5$ eV, in agreement also with Van Vechten's[17] value of 10·96 eV. Other values calculated here are $E_{2A} = K_{3v} \rightarrow K_{2c} = 10{\cdot}2$, $E_1' = \Gamma_{5v} \rightarrow \Gamma_{6c} = 13{\cdot}3$, $E_{\text{ind}X} = \Gamma_{1v} \rightarrow H_{3c} =$ 8·9 eV; the dielectric model[17] values are 9·9, 12·2 and 6·4 eV, respectively. The calculated valence band is 23·2 eV wide, (the lowest band is not shown in Figs. 4 and 5).

For AlN the top of the valence band again has Γ_1 above Γ_6, the calculated bandgaps being 5·25 eV ($\|$) and 5·4 eV ($\perp$), in essential agreement with room temperature absorption data[6] of 5·74 eV ($\|$) and 5·88 eV ($\perp$). Thus both the ordering and the crystal-field splitting of 0·15 eV agree with experiment. The dielectric model[17] yields a value for this gap as high as 10·4 eV and Hejda's OPW calculation[8] gives a gap of only 2·4 eV, although Hejda, too, finds Γ_{1v} to be 0·15 eV above Γ_{6v}. Although the ordering and splitting of the $\Gamma_{1v,6v}$ bands agree with experiment for AlN, this is evidentally not so for GaN [3, 18]. However, not too much importance should be attached to this calculated ordering in either case; a slight empirical adjustment in one, or at most two, critical form factor is enough to re-order these two valence bands without affecting the other bands significantly. In fact Γ_{1v} is the most sensitive of all bands to form factor changes. With Γ_{6v} above Γ_{1v}, the band structure of GaN would have the connectivity of that of ZnS [10]. Other values calculated here for AlN are $E_1 = 9{\cdot}3$, $E_{2A} = 9{\cdot}8$, $E_{2B} = 10{\cdot}0$, $E_1' = 14{\cdot}2$ and $E_{\text{ind}X} = 10{\cdot}0$ eV; the dielectric model[17] gives 9·3, 10·0, 11·0, 12·2 and 8·4 eV, respectively. The valence band is calculated to be 22·1 eV wide, in essential agreement with Hejda's value of 20 eV.

It is of interest to note that form factors for nitrogen can be estimated through the use of the present results in the equation $\Omega_N V(N) = \Omega_{\text{GaN}}[V^S(\text{GaN}) - V^A(\text{GaN})]$, or in the similar AlN equation. We find $\Omega_N V(N) = -36{\cdot}0, 0{\cdot}0,$

3·0 Ry via GaN, and $\Omega_N V(N) = -35{\cdot}5$, 0·0, 5·2 Ry via AlN, at points $K = 1{\cdot}5$, 2·3 and 2·5 respectively, which is the important range for K. The agreement is a measure of the internal consistency.

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REFERENCES

1. MARUSKA H. P. and TIETJEN J. J., *Appl. Phys. Lett.* **15**, 327 (1969).
2. KOSICKI B. B., POWELL R. J. and BURGIEL J. C., *Phys. Rev. Lett.* **24**, 1421 (1970).
3. HARBEKE G. and MEIER E. (unpublished).
4. PANKOVE J. I., MARUSKA H. P. and BERKEYHEISER J. E., *Appl. Phys. Lett.* **17**, 197 (1970).
5. PANKOVE J. I., BERKEYHEISER J. E., MARUSKA H. P. and WITTKE J. P., *Solid State Commun.* **8**, 1051 (1970).
6. PASTERNAK J. and ROSKOVCOVA L., *Phys. Status Solidi* **26**, 591 (1968).
7. COX G. A., CUMMINS D. O., KAWABE K. and TREDGOLD R. H., *J. Phys. Chem. Solids* **28**, 543 (1967). Also, YIM W. M., STOFKO E. J., ETTENBERG M. and GILBERT S. L. (to be published).
8. HEJDA B., *Phys. Status Solidi* **32**, 407 (1969).
9. BLOOM S. and BERGSTRESSER T. K., *Phys. Status Solidi* **41**, 1 (1970).
10. BERGSTRESSER T. K. and COHEN M. L., *Phys. Rev.* **164**, 1069 (1967).
11. COHEN M. L. and BERGSTRESSER T. K., *Phys. Rev.* **141**, 789 (1966).
12. PHILLIPS J. C., *J. phys. Soc. Japan* **21** (supp.), 3 (1966).
13. JUNGINGER H. -G., van HAERINGEN W., *Phys. Status Solidi* **37**, 709 (1970).
14. INGLESFIELD J. E., *J. Phys. C. (Proc. Phys. Soc.)* **1**, 1337 (1968).
15. ANIMALU A. O. E. and HEINE V., *Phil. Mag.* **12**, 1249 (1965). Also, HARRISON W. A., *Pseudopotentials in the Theory of Metals*, Table 8–4, W. A. Benjamin, New York (1966).
16. JEFFREY G. A. and PARRY G. S., *J. chem. Phys.* **23**, 406 (1955).
17. VAN VECHTEN J. A., *Phys. Rev.* **187**, 1007 (1969).
18. DINGLE R., SELL D. D., STOKOWSKI S. E., DEAN P. J. and ZETERSTROM R. B., *Phys. Rev.* (to be published). *Note added in proof*: A small adjustment of a single GaN form factor, $V^s(103)$, from the value of 0·05–0·06 Ry has subsequently been made, as suggested in Section 3. This was found sufficient to put Γ_{6v} *above* Γ_{1v} (by 0·11 eV), in agreement with experiments. The bandgap values that result are now 3·7 eV ($\perp$) and 3·8 eV ($\parallel$R); the other energy differences throughout the zone are unchanged to within 0·1 eV, and the K_{3v}, K_{2v} bands reverse positions.