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Calculated second-harmonic susceptibilities of BN, AlN, and GaN

Jian Chen, Zachary H. Levine,[a] and John W. Wilkins

Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106

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We report calculations for the dielectric constant ε_∞ and the second-harmonic susceptibility d for BN, AlN, and GaN in both zincblende and wurtzite structures within the Kohn-Sham local-density approximation (LDA). For wurtzite AlN and GaN, the computed $d^{(w)}_{xxz}$ and $d^{(w)}_{zzz}$ closely agree with experiment. For zincblende AlN and GaN as well as zincblende and wurtzite BN, we predict d. Our results show that the simple relation between the independent components of d predicted by bond-additivity works for BN, breaks down for GaN, and completely fails for AlN.

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The III-nitrides have recently attracted extensive experimental[1] and theoretical[2,3,4,5] interest. Their physical properties such as a wide band gap, low compressibility, and high thermal conductivity make them promising candidates for short-wavelength (green, blue, and ultraviolet) electroluminescent devices and high-temperature diodes and transistors.[1] There have also been efforts on measuring the second-harmonic susceptibilities for their potential use as frequency-doubling devices.[6,7] Theoretical efforts have been mainly directed towards structural properties,[2] band structures,[3,4,5,8] and linear optical properties.[5,8] The goal of the current study is to provide reliable theoretical estimates of the second-harmonic susceptibility for three of the compounds: BN, AlN, and GaN.

Our calculation uses pseudopotentials with plane-waves in the Kohn-Sham local-density approximation (LDA). After obtaining the ground-state electronic densities, we use a sum-over-states method to calculate the dielectric constants ε_∞ and the second-harmonic susceptibilities d including local-field corrections. Details of our method are provided elsewhere.[9,10]

Table I shows that our LDA dielectric constant calculations are in reasonable agreement with available experiment. Experimental data are scarce and may suffer from poor samples. Comparison with other calculations[5,8,11] are also listed in Table I. For GaN our ε_∞ agrees with a full-potential linear-muffin-tin-orbital calculation.[8] Our calculation is the only one which includes local-field corrections.

Table II gives our results for the second-harmonic susceptibility d of BN, AlN, and GaN: in wurtzite, $d^{(w)}_{xxz}$ and $d^{(w)}_{zzz}$; in zincblende, $d^{(z)}_{xyz}$. For wurtzite GaN, the measurement of Miragliotta *et al.*[12] is consistent with our predictions except for the reported overall sign. However, this overall sign was not determined experimentally relative to the atomic coordinates,[13] so there is no disagreement. For AlN we note two interesting points: (i) $d^{(z)}_{xyz}$ and $d^{(w)}_{xxz}$ almost vanish; (ii) $d^{(w)}_{zzz}$ is negative while $d^{(w)}_{zzz}$ for BN and GaN are positive. The only experiment[14] on single-crystal wurtzite AlN shows that $d^{(w)}_{xxz}$ is almost zero and that $d^{(w)}_{zzz}$ is negative, in agreement with our calculations. One experiment[6] on polycrystalline wurtzite AlN gives $|d^{(w)}_{zzz}| = 1.0$ pm/V, about 1/4 of our predictions. We believe, as suggested in Ref. 6, that this lower $d^{(w)}_{zzz}$ is caused by incomplete alignment of crystallites along the z-axis. Another experiment[7] on polycrystalline wurtzite AlN reports $d^{(w)}_{zzz}/d^{(w)}_{xxz} = 3$. But it is unclear how this ratio from polycrystallites is related to that of the single crystal without the knowledge of the orientation distribution of the crystallites. In comparison with the bond-charge model, our calculated d are four times smaller, making the III-nitride materials less attractive for frequency-doubling devices than has been predicted.[15]

In addition, we tested the validity of bond-additivity, often used as a rule-of-thumb to relate the different components of d. According to bond-additivity, the macroscopic second-harmonic susceptibilities are tensorial sums of the microscopic single-bond second-order susceptibilities. If one assumes that the bonds in the wurtzite and the zincblende crystals are identical for each compound, bond-additivity gives the following simple relations[16]

$$d^{(w)}_{zzz} = -2d^{(w)}_{xxz} = 2/\sqrt{3}d^{(z)}_{xyz}. \tag{1}$$

Figure 1 compares the computed and available experimental scaled susceptibilities in Eq. (1). If bond-additivity held, they should collapse to a single point for each compound. Based on our calculations, this is true for BN, but begins to break down for GaN where $2/\sqrt{3}d^{(z)}_{xyz}$ is almost double the value of $d^{(w)}_{zzz}$. The most severe violation of Eq. (1) occurs in AlN, where the computed $d^{(w)}_{zzz}$ is -4.6 pm/V but $d^{(w)}_{xxz}$ and $d^{(z)}_{xyz}$ are almost zero. From the experiment[14] on single crystal of AlN, the ratio of $d^{(w)}_{xxz}/d^{(w)}_{zzz}$ is less than 0.04 compared to our computed ratio of 0.05. Our calculation was done for the experimental lattice geometry;[17] repeating it for the perfect tetrahedral geometry yields the ratio 0.10, which further supports our view that the bond-additivity is inadequate for these materials.

Finally we provide some technical details of our calculation. *Band gap.* We expect the calculated optical constants to be somewhat overestimated[10] because the LDA band gaps are smaller than experiment. Based on our previous study on GaP,[10] we believe that the overestimation can be up to 40% for the worst case, GaN. In BN and AlN where the band gaps are larger, the overestimation is smaller or perhaps even zero based on our studies on urea[18] and SiC.[19]

Convergence. Sufficient convergence is reached for our calculations. The only two convergence parameters for our method are the energy cut-off for the plane-waves (E_{cut}) and the number of $\vec{k}$ points to sample the integration. Using E_{cut}=25 hartree in zincblende BN we found that the eigenvalues for the lowest 50 bands have converged to about 0.1 eV compared to using $E_{cut} = 50$ hartree. The choice of E_{cut} depends on the pseudopotentials.[20] Since the $2p$ pseudopotential of N is deepest, we used $E_{cut} = 25$ hartree for all the calculations. The LDA eigenvalues reported in the literature for BN,[3,5] AlN,[4,5] and GaN[2,4,5,8] usually agree within 0.3 eV but can sometimes differ by 0.8 eV. Our calculations lie within this region. We also converged our calculations by increasing the number of $\vec{k}$ points. In the zincblende structures, we used 28 $\vec{k}$ points[21] in the irreducible Brillioun zone for BN, AlN, and GaN. In wurtzite BN and AlN, we used 2 layers of $\vec{k}$ points with 6 on each layer and for GaN 2 layers with 12 $\vec{k}$ points per layer in the irreducible Brillioun zone. The sum rules[10] associated with ε_∞ and d were used to test the convergence. With the above choices for E_{cut} and the number of $\vec{k}$ points, the sum rules are all satisfied within 2%. Decreasing the number of $\vec{k}$ points by half change the dielectric constants by 1% and the second-harmonic susceptibilities by 5%.

In summary we provide quantitative LDA calculations for the second-harmonic susceptibilities d of BN, AlN and GaN in zincblende as well as wurtzite structures. Our calculations for the dielectric constants agree with available experiments. In wurtzite AlN and GaN, our calculated values of d agree with the single-crystal measurements. We find that the bond-additivity picture fails to explain the ratios $d^{(z)}_{xyz}/d^{(w)}_{zzz}$ and $d^{(w)}_{xxz}/d^{(w)}_{zzz}$ in AlN and $d^{(z)}_{xyz}/d^{(w)}_{zzz}$ in GaN. Experimental measurement of $d^{(z)}_{xyz}$ in zincblende AlN will stringently test our predictions of a vanishingly small value.

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TABLE I. Dielectric constants ε_∞ for three III-nitride materials. Our calculated dielectric constants are generally consistent with limited experimental data. The AlN experimental values were measured from thin films of AlN crystallites. In one GaN experiment,[a] $\varepsilon_\infty^{(e)}$ was measured to be 5.8±0.4. The same experiment showed that the difference between $\varepsilon_\infty^{(o)}$ and $\varepsilon_\infty^{(e)}$ is less than 4%, which is the result listed in the table. The superscripts refer to the ordinary and extraordinary components, respectively. Results from other calculations include: an othorgonal linear-combination-of-atomic-orbital (LCAO) calculation, and two linear-muffin-tin-orbital (LMTO) calculations. Only the present calculation includes local-field corrections.

		Zincblende	Wurtzite	
		ε_∞	$\varepsilon_\infty^{(o)}$	$\varepsilon_\infty^{(e)}$
BN	LCAO (Ref. 11)		3.98	4.23
	LMTO[b] (Ref. 5)	4.14	4.19	4.06
	Present	4.56	4.51	4.69
	Exp. (Ref. 22)	4.5		
AlN	LCAO (Ref. 11)		3.88	5.06
	LMTO[b] (Ref. 5)	3.90	3.91	3.77
	Present	4.61	4.42	4.70
	Exp. (Ref. 23)		4.84	
	Exp. (Ref. 24)		4.68	
GaN	LCAO (Ref. 11)		8.72	11.16
	LMTO[b] (Ref. 5)	4.78	4.71	4.62
	LMTO[c] (Ref. 8)	5.96	5.48	5.65
	Present	5.74	5.54	5.60
	Exp. (Ref. 25)		5.35±0.20	$\varepsilon_\infty^{(o)} \pm 4\%$

[a] Ref. 26.

[b] LMTO with atomic sphere approximation, Ref. 5

[c] Full-potential LMTO, Ref. 8

TABLE II. Second-harmonic susceptibilities d of three III-nitride materials. Our calculations closely agree with experiments on wurtzite AlN and GaN. The magnitudes of d from our calculations are four times smaller than the bond-charge model estimates.[a] The experimental data for AlN is corrected by using a new reference for d of quartz.[b] All the experimental values for d are our extrapolation to ω=0 using Miller's rule.[c] The superscript (z) and (w) refer to zincblende (cubic) and wurtzite (hexagonal), respectively. See text for discussions of additional experimental results for AlN.

		Zincblende	Wurtzite	
		$d_{xyz}^{(z)}$	$d_{xxz}^{(w)}$	$d_{zzz}^{(w)}$
BN	Present (LDA)	2.80	-1.46	2.92
AlN	Present (LDA)	0.01	-0.24	-4.61
	Bond-charge model[a]			-17
	Exp. (Ref. 14)		$\leq \|0.26\|$	-6.3 ± 3.5
GaN	Present (LDA)	8.47	-3.45	5.76
	Bond-charge model[a]			-26
	Exp. (Ref. 12)		2.66	-5.35

[a] Ref. 15.

[b] Ref. 27.

[c] Ref. 28.

FIG. 1. Rescaled second-harmonic susceptibilities — using Eq. (1) — d for BN, AlN, and GaN in zincblende (z) and wurtzite (w) structures. If one assumes bond-additivity, the rescaled d should collapse to a single point. This is not the case for AlN or GaN. The hollow symbols report our calculations and the solid symbols experiment.

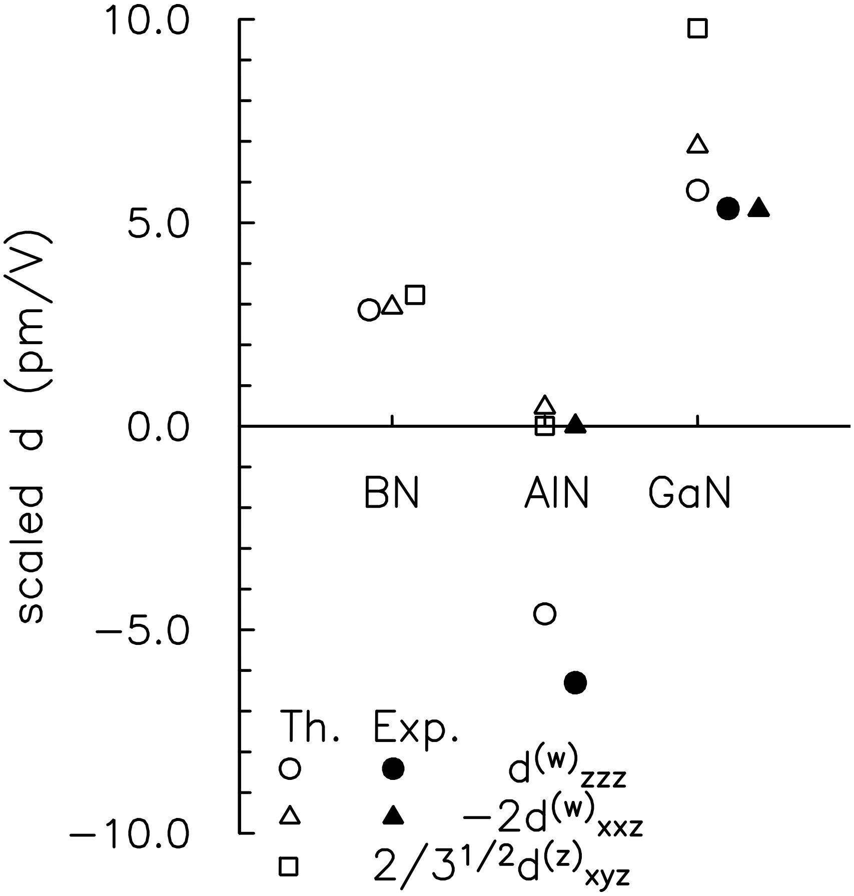

Fig. 1

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REFERENCES

[a] Present address: Bldg. 221/A253, National Institute of Standards and Technology, Gaithersburg, MD 20899.

1. For a review, see S. Strite, M. E. Lin, and H. Morkoc, Thin Solid Films **231**, 197 (1993).

2. A. F. Wright and J. S. Nelson, Phys. Rev. B **50**, 2159 (1994).

3. M. P. Surh, S. G. Louie, and M. L. Cohen, Phys. Rev. B **43**, 9126 (1991).

4. A. Rubio, J. L. Corkill, M. L. Cohen, E. L. Shirley, and S. G. Louie, Phys. Rev. B **48**, 11810 (1993).

5. N. E. Christensen and I. Gorczyca, Phys. Rev. B **50**, 4397 (1994).

6. P. M. Lundquist, W. P. Lin, Z. Y. Xu, G. K. Wong, E. D. Rippert, J. A. Helfrich, and J. B. Ketterson, Appl. Phys. Lett. **65**, 1085 (1994).

7. W. P. Liu, P. M. Lundquist, G. K. Wong, E. D. Rippert, and J. B. Ketterson, Appl. Phys. Lett. **63**, 2875 (1993).

8. M. Alouani and J. Willis, unpublished.

9. Z. H. Levine and D. C. Allan, Phys. Rev. B **44**, 12781 (1991); **48**, 14768 (E) (1993).

10. For an overall review of our methods, see Z. H. Levine, Int. J. Quantum Chem., in press.

11. Y. N. Xu and W. Y. Ching, Phys. Rev. B **48**, 4335 (1993).

12. J. Miragliotta, D. K. Wickenden, T. J. Kistenmacher, and W. A. Bryden, J. Opt. Soc. Am. B, **10**, 1447 (1993). [GaN]

13. J. Miragliotta, private communication. [GaN]

14. Y. Fujii, S. Yoshida, S. Misawa, S. Maekawa, and S. Sakudo, Appl. Phys. Lett. **31**, 815 (1978). [AlN] The authors speculated that the lattice distortion from perfect tetrahedron could strongly modify the susceptibilities of the bonds, thus causing a vanishing ratio of $d^{(w)}_{xxz}/d^{(w)}_{zzz}$. Our calculation was done for the experimental lattice geometry;[17] repeating it for the perfect tetrahedral geometry yields the ratio 0.10, which further supports our view that the bond-additivity is inadequate for these materials.

15. B. F. Levine, Phys. Rev. Lett. **25**, 440 (1970).

16. F. N. H. Robinson, Phys. Lett. **26A**, 435 (1968).

17. H. Schultz and K. H. Thiemann, Solid State Commun. **23**, 815 (1977).

18. Z. H. Levine and D. C. Allan, Phys. Rev. B **48**, 7783 (1993).

19. J. Chen, Z. H. Levine, and J. W. Wilkins, Phys. Rev. B **50**, 11514 (1994).

20. The reported calculations were done using the norm-conserving pseudopotentials generated by the method of N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991). We also tested some of the calculations using the hardness-conserving pseudopotentials by M. Teter, Phys. Rev. B **48**, 5031 (1993). The differences between the results are small.

21. H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

22. Numerical Data and Functional Relationships in Science and Technology, edited by K.-H. Hellwege, Landoldt-Bornstein Tables, Group III, Vol. 17a (Springer-Verlag, New York, 1982).

23. A. T. Collins, E. C. Lightowlers, and P. J. Dean, Phys. Rev. **158**, 833 (1967).

24. L. Akasaki and M. Hashimoto, Solid State Commun. **5**, 851 (1967).

25. A. S. Barker and M. Ilegems, Phys. Rev. B **7**, 743 (1973).

26. D. D. Manchon, A. S. Barker, J. P. Dean, and R. B. Zetterstrom, Solid State Commun. **8**, 1227 (1970).

27. D. A. Roberts, IEEE J. Quant. Electron, **28**, 2057 (1992).

28. R. C. Miller, Appl. Phys. Lett. **5**, 17 (1964).