

# (Hyper)polarizabilities of isolated GaN nanoclusters

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## Abstract

The linear and nonlinear polarizabilities of hydrogen-terminated  $\text{Ga}_m\text{N}_n\text{H}_x$  ( $m = n = 1, 4, 7, 17$ ) clusters have been calculated by the *ab initio* time-dependent Hartree–Fock method. The calculated linear polarizability per Ga–N unit for the  $\text{Ga}_{17}\text{N}_{17}\text{H}_{38}$  cluster shows excellent agreement with the corresponding value estimated from the measured dielectric constant of bulk GaN. The calculated (hyper)polarizabilities show a strong dependence upon the size and the geometry of the cluster. For clusters containing equal numbers of Ga and N atoms but differing in geometry, the structure with a reduced symmetry has a much larger first-order NLO coefficient than that with a higher symmetry.

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## 1. Introduction

Recently, Schlect et al. [1,2] observed that the polarizabilities of atomic nanoclusters of semiconductor materials exhibited remarkable even–odd oscillation with the number of atoms. Furthermore, these authors also observed that the polarizabilities of the even/odd clusters did not, in general, scale with cluster-size. The even–odd oscillation with the size has also been reported for other properties, such as the ionization potential and electron affinities, of atomic nanoclusters [3–6]. There is, however, little information on the evolution of the nonlinear optical (NLO) properties with the size of atomic nanoclusters. In this Letter, we present a first-principles time-dependent Hartree–Fock study of the evolution and dispersion of polarizability and first-hyperpolarizability coefficients of GaN with cluster-size and shape. Our results suggest that both the linear and

NLO properties exhibit remarkable dependence on the size of the cluster; however, the latter also exhibits a strong dependence on the shape (geometry) of the cluster.

The linear and NLO of GaN *semiconductors* have been the subject of a number of experimental studies due to their applications in photonic devices [7–9]. However, the NLO properties of GaN *atomic nanoclusters*, although quite important for their potential applications in nanophotonic devices, have not received similar attention. Theoretical investigations of the NLO properties of small-to-medium size III–V atomic nanoclusters have been performed by the *ab initio* time-dependent Hartree–Fock formalism [10,11] as well as time-dependent density functional theory [12,13]. These studies suggest that the (hyper)polarizabilities vary non-monotonically with cluster-size.

Theoretical studies on the stability and structure of clusters [5,6,14–16] have shown that isomers of small  $\text{GaX}$  ( $X = \text{N}, \text{P}, \text{As}$ ) clusters may exhibit different geometrical features, with a tendency toward exhibiting bond-alternation ( $\text{Ga–X–Ga}$ ) with increasing size. Experimental and theoretical investigations on the isovalent  $\text{Ga}_m\text{As}_n$  clusters have also shown that even-numbered stoichiometric

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( $m = n$ ) clusters are most stable in a closed-shell electronic configuration with a singlet ground state [3–6]. As the focus of this study was to investigate and understand the evolution and eventual transition of the linear and NLO properties from the nanoscale to the bulk, we have only considered the clusters with  $m = n$ . Furthermore, ring structures that form the inter- and intra-plane networks have been included to represent a bulk-like atomic structure.

## 2. Calculations

Calculations were performed on  $\text{Ga}_m\text{N}_m$  clusters with  $m = 1, 4, 7,$  and  $17$ . Hydrogen atoms were added to outer atoms in order to passivate surface dangling bonds. The geometry of the GaN clusters were optimized using an *ab initio* self-consistent field (SCF) molecular-orbital (MO) approach using a double zeta-plus polarization (1p, 1d) basis set as implemented in the GAMESS electronic structure code [19]. The geometries were also optimized using polarized effective core potential (ECP) basis sets [20]. The latter geometries differed only slightly from those obtained with the all-electron basis sets. The results presented in this Letter were all obtained from the DZP (1p, 1d) optimized structures.

The components of the polarizability and the first-hyperpolarizability tensors,  $\alpha$  and  $\beta$ , respectively, were computed using the ‘direct’ time-dependent Hartree–Fock (TDHF) method [21]. Presented in the Letter are the values for mean polarizability,  $\langle\alpha\rangle$ , defined as [17]

$$\langle\alpha\rangle = \frac{1}{3} \sum_i \alpha_{ii}, \quad i = x, y, z \quad (1)$$

and a scalar quantity,  $\beta_{\text{vec}}$ , for the hyperpolarizability, defined as [18]

$$\beta_{\text{vec}} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)}, \quad (2)$$

where the  $\beta_i$  ( $i = x, y, z$ ) are related to the tensor components,  $\beta_{ijk}$ , of  $\beta$  by

$$\beta_i = \frac{1}{3} \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}). \quad (3)$$

In the present study,  $\beta_{\text{vec}}$  corresponding to the static hyperpolarizability,  $\beta(0;0,0)$ , the electrooptic Pockels effect (EOPE),  $\beta(-\omega;0,\omega)$ , and SHG,  $\beta(-2\omega;\omega,\omega)$ , were calculated. Two different conventions, which arise from different definitions of  $\beta$ , are used in reporting the experimental and theoretical values of hyperpolarizability [18]. In keeping with the convention for the experimental quantities, the calculated values of  $\beta_{\text{vec}}$  we report are divided by a factor of 2.

In order to assess the effect of the basis set, calculations were performed on  $\text{Ga}_m\text{N}_m\text{H}_x$  ( $m = 1-7$ ) by including (1p, 1d), (3p, 3d) and (3p, 3d, 1f) sets of polarization functions with a double-zeta basis set. The exponents of the polarization functions were taken from the GAMESS library.

The calculated values of  $\alpha$  and  $\beta$  showed only minor changes due to the basis set for smaller clusters and converged rapidly with increasing size. Here, we list the calculated results for  $\text{Ga}_m\text{N}_m\text{H}_x$  ( $m = 1-7$ ) obtained with the use of the largest polarized basis set, DZP (3p, 3d, 1f). For the largest cluster,  $\text{G}_{17}\text{N}_{17}\text{H}_{38}$ , use of the larger basis sets was not possible due to the computational cost. Therefore, for  $\text{G}_{17}\text{N}_{17}\text{H}_{38}$ , results obtained from the use of the DZP (1p, 1d) basis set are presented. This is not expected to affect our general conclusions as the calculated properties converged rapidly with respect to the basis set as the cluster-size was increased. The elements of the dynamic (hyper)polarizabilities,  $\alpha(\omega)$ ,  $\beta(-\omega; 0, \omega)$ , and  $\beta(-2\omega; \omega, \omega)$  were calculated at an input wavelength,  $\lambda = 1064$  nm.

## 3. Results and discussion

### 3.1. Structure

Figs. 1 and 2 show the energy-optimized structures of the clusters employed in this study arranged in order of increasingly bulk-like character. The clusters in Fig. 1 are what we term ‘open’ in the sense that they do not contain ring structures. By contrast, the clusters in Fig. 2 are composed of ‘closed’ network-forming rings. The clusters in Fig. 1 were taken from the previous work of Korambath et al. [14] who employed an even-tempered Gaussian (ETG) basis set in their calculations on clusters with  $m = n = 1-4$ . The  $\text{Ga}_4\text{N}_4\text{H}_x$  clusters, Fig. 1b and Fig. 2a, are related in the way that they represent the simplest open and closed alternate arrangements of Ga and N atoms derived from the bulk. These structures provide insight into the effect on the optical properties of changes in the spatial arrangements of atoms and the symmetry of the cluster. The structures in Fig. 2 all have alternating Ga and N arrangements and represent the smallest units of wurtzite

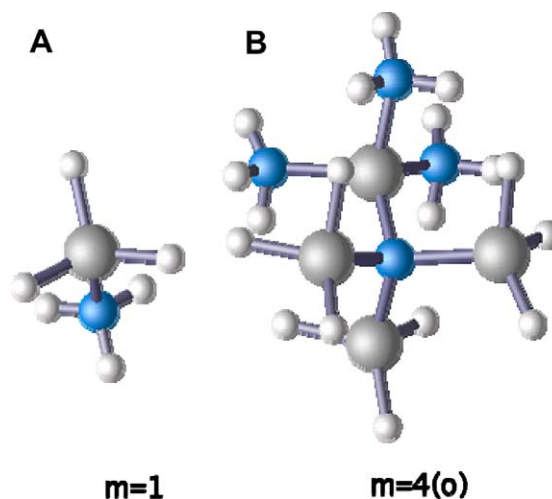


Fig. 1. Open hydrogen-terminated GaN structures: (A)  $\text{GaNH}_6$  and (B)  $\text{Ga}_4\text{N}_4\text{H}_{18}$ . Nitrogen atoms are shown in blue, gallium in silver and hydrogen in white.

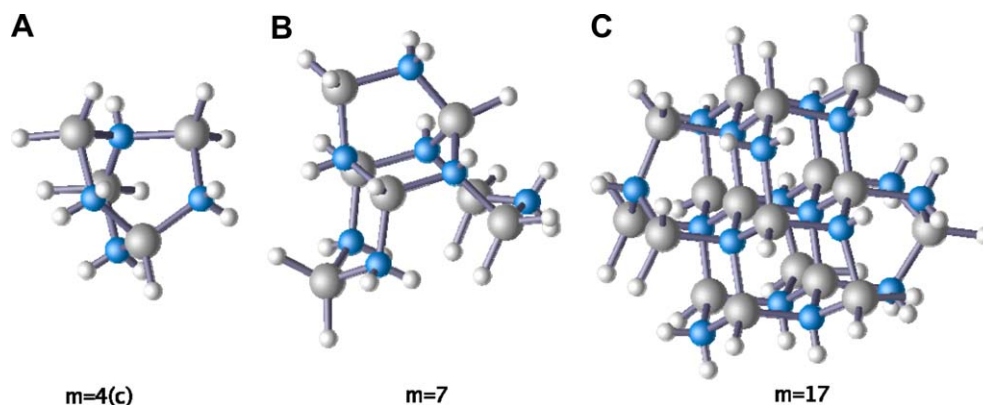


Fig. 2. Closed hydrogen-terminated GaN structures: (A)  $\text{Ga}_4\text{N}_4\text{H}_{14}$ , (B)  $\text{Ga}_7\text{N}_7\text{H}_{22}$ , and (C)  $\text{Ga}_{17}\text{N}_{17}\text{H}_{38}$ . Nitrogen atoms are shown in blue, gallium in silver and hydrogen in white.

GaN. The average Ga–N bond length for each cluster, which shows excellent agreement with the previously reported values [14–16], steadily decreased with increasing cluster-size, going from 2.157 Å for  $m = n = 1$  to 1.946 Å for  $m = n = 17$ . The latter value is in excellent agreement with the corresponding values reported for bulk GaN [22]. The bond length distribution around a single atom is generally bimodal with three bonds of nearly equal length and the fourth slightly longer by  $\sim 0.05$  Å. Such anisotropy in chemical bonds has also been reported in the case of wurtzite GaN from X-ray absorption studies [23]. The average Ga–N–Ga bond angles decrease from  $116.3 \pm 1.7^\circ$  to  $111.2 \pm 3.9^\circ$  as cluster-size increases. The bond angle distribution is also bimodal with smaller bond angles adjoining the longer bond.

### 3.2. Linear polarizability, $\alpha$

The values of calculated mean polarizability,  $\langle \alpha \rangle$  for static ( $\lambda = \infty$ ) and dynamic ( $\lambda = 1064$  nm) cases, as a function of cluster-size, are listed in Table 1. Also listed in the table is the value of  $\langle \alpha \rangle$  per Ga–N unit in the cluster. For the optical wavelength,  $\lambda = 1064$  nm used in this study, the polarizability appears to show only a weak dispersion.

The calculated values of  $\langle \alpha \rangle$  for  $m = 1$  and 4(o) are in reasonable agreement with those reported in a previous study [10], where it was also noted that the polarizability depended in an approximately linear fashion on the number

of Ga–N units in the cluster. While there is no experimental data on isolated GaN clusters to compare with, it is possible to derive useful information on the polarizability per Ga–N unit from the bulk dielectric constant,  $\epsilon(\omega)$ , and the density through the use of the Clausius–Mossotti relation,

$$\alpha(\omega) = \frac{3}{4\pi} \left( \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \right) V_m \quad (4)$$

where  $V_m$  is the volume of a Ga–N unit. Bougrov et al. [24] give  $\epsilon(0) = 8.9$  and  $\epsilon(\omega) = 5.35$ , and  $\rho = 6.15$  g/cm<sup>3</sup>. With these values, the bulk static and high frequency polarizabilities per Ga–N unit are  $3.91 \times 10^{-24}$  cm<sup>3</sup> and  $3.19 \times 10^{-24}$  cm<sup>3</sup>, respectively, which can be compared with the corresponding values of  $3.76 \times 10^{-24}$  cm<sup>3</sup> and  $3.19 \times 10^{-24}$  cm<sup>3</sup>, respectively, obtained in the present calculation for  $\text{Ga}_{17}\text{N}_{17}\text{H}_{38}$ . This suggests that with increasing cluster-size, the polarizability per unit Ga–N rapidly approaches its bulk value, as also shown in Fig. 3. It is also clear that the value of  $\alpha$  only differs slightly between the closed and open structures for  $m = 4$  clusters (see Fig. 3), indicating that linear polarizability depends mainly on the size (number of atoms) of the cluster.

Convergence toward the bulk limit is not seen in other properties either. For example, the energy difference,  $\Delta\epsilon$  between the highest occupied (HO) and the lowest unoccupied (LU) molecular orbitals (MOs), in principle should decrease as a function of cluster-size, and in the bulk limit approach the bandgap ( $\Delta E_{\text{bg}}$ ) of the bulk material. However,  $\Delta\epsilon$  (HOMO–LUMO) (eV) = 13.58, 10.85/12.03, 13.41 for  $m = 1$ , 4(o)/4(c), 7, and 17, respectively, obtained with the DZP (1p, 1d) basis set suggests that its approach to the bulk limit ( $\Delta E_{\text{bg}}$ ) is slow and depends non-trivially on the shape (geometry) of the cluster. The corresponding values obtained with the largest basis set, DZP (3p, 3d, 1f) are slightly smaller in magnitude, but the qualitative trend does not change. A slow convergence in the  $\Delta\epsilon$  (HOMO–LUMO) with increasing cluster-size suggests that yet larger clusters and incorporation of electron correlation effects in the calculations are needed to reach the bandgap limit of the bulk GaN.

Table 1  
Mean polarizability,  $\langle \alpha \rangle$  ( $10^{-24}$  cm<sup>3</sup>) and polarizability per GaN unit,  $\langle \alpha \rangle/m$ , for  $\text{Ga}_m\text{N}_m$  clusters<sup>a</sup>

$m$ , $\text{Ga}_m\text{N}_m$	$\langle \alpha(0) \rangle$	$\langle \alpha(\omega) \rangle$	$\langle \alpha(0) \rangle/m$	$\langle \alpha(\omega) \rangle/m$
1	6.26	6.32	6.26	6.32
4(o)	22.35	22.59	5.59	5.65
4(c)	19.25	19.44	4.81	4.86
7	31.94	32.23	4.56	4.60
17	63.97	64.48	3.76	3.79

<sup>a</sup> Results for the  $m = 1$ –7 clusters were obtained with DZP (3p, 3d, 1f) basis set while those for  $m = 17$  were obtained with a smaller DZP (1p, 1d) basis set. See text for details.

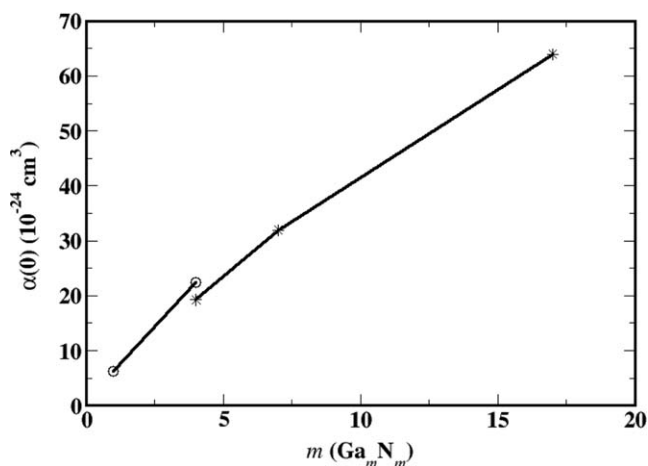


Fig. 3. Static mean polarizability,  $\langle\alpha(0)\rangle$ , of hydrogen-terminated GaN clusters as a function of the number of GaN units.

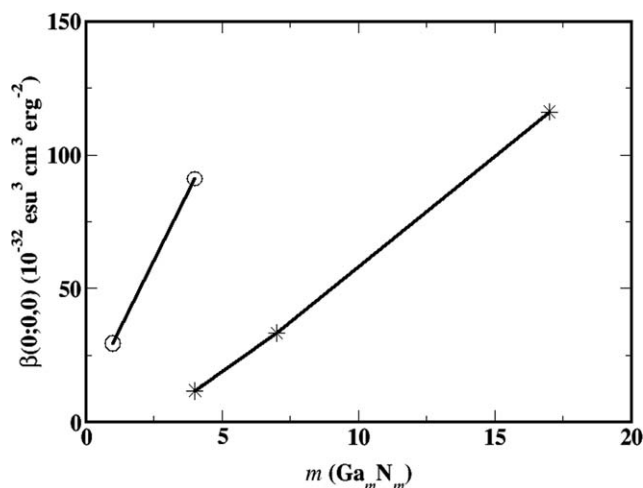


Fig. 4. Static first-hyperpolarizability,  $\beta_{\text{vec}}(0; 0, 0)$ , of hydrogen-terminated GaN clusters as a function of the number of GaN units.

Table 2

Calculated dipole moment,  $\mu$  (D), and first-hyperpolarizability coefficient,  $\beta_{\text{vec}}$  ( $10^{-32}$  esu<sup>3</sup> cm<sup>3</sup> erg<sup>-2</sup>) for Ga<sub>m</sub>N<sub>m</sub> clusters<sup>a</sup>

$m$ , Ga <sub>m</sub> N <sub>m</sub>	$\mu$	$\beta(0; 0, 0)$	$\beta(-\omega; 0, \omega)$	$\beta(-2\omega; \omega, \omega)$
1	5.15	29.61	30.35	31.91
4(o)	18.34	90.94	96.02	107.98
4(c)	5.80	11.74	11.99	12.48
7	2.62	33.32	33.93	35.16
17	13.19	116.14	119.93	128.10

<sup>a</sup> See the footnote to Table 1 for the description of the basis set and geometry employed.

### 3.3. Nonlinear polarizability, $\beta$

Table 2 lists the calculated  $\beta_{\text{vec}}$  for static, EOPE, and SHG processes along with the calculated dipole moment of the Ga<sub>m</sub>N<sub>m</sub>H<sub>x</sub> clusters. For the purpose of illustration, the static  $\beta_{\text{vec}}$  as a function of the cluster-size is also shown in Fig. 4. It is clear from Table 2 that  $\beta$  values for different NLO processes strongly depend on the cluster-size. Unlike the linear polarizability,  $\beta$  cannot be accounted for in terms of a simple additivity model. For example, the calculated  $\beta$  values (Table 2) vary roughly over an order of magnitude between  $m = 1$  and  $m = 17$  clusters. It is also clear from Table 2 and Fig. 4 that  $\beta$ , in addition to a strong size-dependence, shows a remarkable dependence on the geometry of the GaN clusters. For example, in the case of Ga<sub>4</sub>N<sub>4</sub>H<sub>x</sub> clusters, the value of  $\beta_{\text{vec}}$  decreases by a factor of over 9 in going from a less symmetric open structure, Fig. 1b, to a rather symmetric closed structure, Fig. 2a. Similar observation has been made from a semiempirical tight-binding study on Si<sub>n</sub> clusters [25]. A strong-correlation of  $\beta$  with cluster-geometry is also reflected in the dipole moment,  $\mu$ , which decreases by a factor of 3 in going from the open (Ga<sub>4</sub>N<sub>4</sub>H<sub>18</sub>) to the closed structure for Ga<sub>4</sub>N<sub>4</sub>(Ga<sub>4</sub>N<sub>4</sub>H<sub>14</sub>).

## 4. Conclusion

In order to understand the evolution of linear and NLO properties in nanostructures, we have calculated the (hyper)polarizabilities of a series of Ga<sub>m</sub>N<sub>m</sub>H<sub>x</sub> clusters of varying size and geometry by *ab initio* TDHF method. The calculated properties appear to have converged at the DZP (3p, 3d) level of basis set. The value of  $\langle\alpha\rangle$  for a Ga–N unit in a cluster is found to slowly vary with cluster-size and appears to be well accounted for by a simple atom additivity model. The linear polarizability,  $\alpha(\omega)$ , exhibits small frequency dispersion. Other properties appear to converge more slowly with the cluster-size. The hyperpolarizabilities are found to oscillate strongly with cluster-size owing to the competing effects of size and geometry. For equal numbers of Ga and N atoms (e.g., Ga<sub>4</sub>N<sub>4</sub>), the structure with reduced symmetry gives a substantially enhanced value of  $\beta$  as compared with the more symmetric structure. Since the range of energetically accessible structures of atomic nanoclusters depends upon temperature, our results suggest that the variation of hyperpolarizabilities with cluster-size will exhibit a strong temperature-dependence. The magnitude of  $\beta_{\text{vec}}$  for various second-order effects shows the expected order:  $\beta(-2\omega; \omega, \omega) > \beta(-\omega; 0, \omega) > \beta(0; 0, 0)$ , as was also reported previously [10].

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## References

- [1] S. Schlecht, R. Schäfer, J. Woenckhaus, J.A. Becker, Chem. Phys. Lett. 246 (1995) 315.

- [2] R. Schäfer, S. Schlecht, J. Woelckhaus, J.A. Becker, *Phys. Rev. Lett.* 76 (1996) 47.
- [3] Y. Liu, Q.-L. Zhang, F.K. Tittel, R.F. Curl, R.E. Smalley, *J. Chem. Phys.* 85 (1986) 7434.
- [4] C. Jin, K.J. Taylor, J. Conceicao, R.E. Smalley, *Chem. Phys. Lett.* 175 (1990) 17.
- [5] L. Lou, L. Wang, L.P.F. Chibante, R.T. Laaksonen, P. Nordlander, R.E. Smalley, *J. Chem. Phys.* 94 (1991) 8015.
- [6] L. Lou, P. Nordlander, R.E. Smalley, *J. Chem. Phys.* 97 (1992) 1858.
- [7] B.F. Levine, *Phys. Rev. Lett.* 22 (1969) 787.
- [8] J.C. Phillips, J.A. Van Vechten, *Phys. Rev.* 183 (1969) 709.
- [9] J. Miragliotta, D.K. Wickenden, *Phys. Rev. B* 53 (1996) 1388.
- [10] P.P. Korambath, S.P. Karna, *J. Phys. Chem. A* 104 (2000) 4801.
- [11] Y.-Z. Lan, W.-D. Cheng, D.-S. Wu, X.-D. Li, H. Zhang, Y.-J. Gong, *Chem. Phys. Lett.* 372 (2003) 645.
- [12] I. Vasiliev, S. Ögüt, J.R. Chelikowsky, *Phys. Rev. B* 60 (1999) R8477; I. Vasiliev, S. Ögüt, J.R. Chelikowsky, *Phys. Rev. Lett.* 78 (1997) 4805.
- [13] R. Natarajan, S. Ögüt, *Phys. Rev. B* 67 (2003) 235326.
- [14] P.P. Korambath, B.K. Singaraju, S.P. Karna, *Int. J. Quant. Chem.* 77 (2000) 563.
- [15] A.K. Kandalam, M.A. Blanco, R. Pandey, *J. Phys. Chem. B* 105 (2001) 6080; A.K. Kandalam, M.A. Blanco, R. Pandey, *J. Phys. Chem. B* 106 (2002) 1945.
- [16] A. Costales, A.K. Kandalam, R. Franco, R. Pandey, *J. Phys. Chem. B* 106 (2002) 1940.
- [17] N. Bloembergen, *Nonlinear Optics*, Benjamin, New York, 1965.
- [18] S.P. Karna, M. Dupuis, E. Perrin, P.N. Prasad, *J. Chem. Phys.* 92 (1990) 7418.
- [19] M.W. Schmidt et al., *J. Comput. Chem* 14 (1993) 1347.
- [20] W.J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.* 81 (1984) 6026.
- [21] S.P. Karna, *Chem. Phys. Lett.* 214 (1993).
- [22] J. Neugebauer, C.G. Van de Walle, *J. Appl. Phys.* 85 (1999) 3003.
- [23] K. Lawniczak-Jablonska et al., *J. Alloy. Compd.* 328 (2001) 77.
- [24] V. Bougrov, M.E. Levinshtein, S.L. Rumyantsev, A. Zubrilov, in: M.E. Levinshtein, S.L. Rumyantsev, M.S. Shur (Eds.), *Properties of Advanced Semiconductor Materials*, John Wiley & Sons Inc., New York, 2001, p. 1.
- [25] T.T. Rantala, M.I. Stockman, D.A. Jelski, T.F. George, *J. Chem. Phys.* 93 (1990) 7427.