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Accurate band gaps of AlGaN, InGaN, and AlInN alloys calculations based on LDA-1/2 approach

R. R. Pelá,[1,a)] C. Caetano,[2] M. Marques,[1] L. G. Ferreira,[1,3] J. Furthmüller,[4] and L. K. Teles[1,b)]
[1]*Instituto Tecnológico de Aeronáutica, 12228-900 São José dos Campos, SP, Brazil*
[2]*Universidade Federal da Fronteira Sul, 85770-000 Realeza, PR, Brazil*
[3]*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil*
[4]*Institut für Festkörpertheorie und optik, Friedrich-Schiller-Universität, 07743 Jena, Germany*

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We present parameter-free calculations of electronic properties of InGaN, InAlN, and AlGaN alloys. The calculations are based on a generalized quasichemical approach, to account for disorder and composition effects, and first-principles calculations within the density functional theory with the LDA-1/2 approach, to accurately determine the band gaps. We provide precise results for AlGaN, InGaN, and AlInN band gaps for the entire range of compositions, and their respective bowing parameters. © *2011 American Institute of Physics*. [doi:10.1063/1.3576570]

The late 1990s mark the entrance of group-III nitride compounds and their alloys to the world of optical and electronic devices. The use of pseudobinary InGaN, AlGaN, and InAlN alloys enabled the fabrication of light-emitting diodes and laser diodes operating in the green-blue-UV spectral region and of high-frequency, high-power, and high-temperature electronic devices.[1] Alloying among the group-III nitrides allows to engineer the band gap (BG) from 0.70 eV in InN to 6.28 eV in AlN with an intermediate value of 3.44 eV for GaN.[2]

Due to their technological importance, an accurate prediction of optical properties of group-III nitride alloys is highly desirable. Theoretical studies often utilize density functional theory (DFT) within the local density approximation (LDA), or the generalized gradient approximation (GGA).[2] However, while LDA and GGA accurately predict many ground state properties, the Kohn–Sham BG's are significantly underestimated in comparison to the experimental ones. In the extreme case of InN, the predicted BG is even negative, leading to a metal instead of a semiconductor.[3] These discrepancies are caused by the lack of the discontinuity of the exchange-correlation potential. Several methods to overcome these limitations have been proposed. One of them is the GW approximation, which considers the energies of quasiparticles and calculates the electron self- energy in terms of perturbation theory.[4] This procedure achieves good accuracy, but it goes beyond the DFT, and is computationally demanding, complicating its application to complex systems, like the alloys studied here. Other procedures were also proposed, among them we may cite the hybrid functionals which allows accurate calculations of the BG and were also applied to nitride systems. One example is a recent study conducted by Moses and Van de Walle considering the hybrid exchange-correlation functional of Heyd, Scuseria and Ernezerhof (HSE), and special quasi-random structures, to obtain the BG of InGaN alloys.[5]

Another point to be considered when dealing with alloys is the statistics: for a rigorous calculation, it is imperative to take into account different configurations within a statistical scheme.[6] Therefore, to keep the computational time reasonably bounded, a reliable method for obtaining excited states at low computational costs is highly desirable. There is no theoretical work reported so far which contemplates, on an equal footing, both, a reasonably sized model supercell and the statistics of the alloy, and a method that corrects the energy gap. All of them use only one or just few alloy configurations. The method we employ here surpasses this difficulty.

Recently, Ferreira *et al.*[7] proposed a method called LDA-1/2 which approximately includes the self-energy of excitations in semiconductors, providing BG energies, effective masses, and band structures in very good agreement with experiment. The great advantages of the method are: (i) the low computational cost, comparable to a traditional LDA calculation; (ii) the simple implementation, making the method easily applicable within several *ab initio* approaches, as pseudpotential calculations,[8,9] projector augmented wave (PAW),[10] and linearized augmented plane wave (LAPW);[11] and (iii) it has no empirically adjusted parameters. These features make LDA-1/2 a promising method for studies of large and complex semiconducting systems.[12]

In this work, electronic properties of wurtzite InGaN, AlGaN, and AlInN alloys are studied by combining first-principles calculations within the LDA-1/2 approach with the generalized quasichemical approach (GQCA) to include disorder and compositional effects. The BG's and bowing parameters (BP's) are obtained for the whole range of the alloy composition.

The GQCA is well described elsewhere,[13,14] and has already been used for nitride alloys.[6,14] The macroscopic alloy $A_xB_{1-x}N$ (A and B stand for Al, Ga, or In) is divided into an ensemble of clusters independent statistically and energetically of the surrounding atomic configuration. We used sixteen-atom supercells as basic clusters to describe the fully relaxed alloys. The total energy and the BG of each cluster is calculated by adopting a pseudopotential plane-wave DFT code, as implemented in the "VIENNA *AB-INITIO SIMULATION*

a)Author to whom correspondence should be addressed. Electronic mail: rrpela@ita.br.
b)Electronic mail: ltkeles@ita.br.

TABLE I. LP's as recommended in Ref. 16 and band energy gaps (eV) obtained with the LDA-1/2 compared with pure LDA and experimental results of Ref. 16

	a (Å)	c (Å)	E^{LDA}	$E^{\mathrm{LDA-1/2}}$	E^{exp}
AlN	3.112	4.982	4.50	6.06	6.23
GaN	3.189	5.185	2.02	3.52	3.507
InN	3.545	5.703	−0.03	0.95	0.7–1.9

PACKAGE" code.[9,15] We employed the LDA exchange-correlation potential and the LDA-1/2 approach.[7] For a given composition x of the alloy, each cluster j with a certain number of A and B atoms is realized with a certain probability $p_j(x)$. The configurationally averaged BG, $E(x)$, results from a sum over all individual cluster BG's E_j, weighted by the probability $p_j(x)$ of occurrence of each cluster: $E(x) = \Sigma p_j(x) E_j$. One could argue that the prediction of the optical transition energy, the peak which is observed in a photoluminescence (PL) measurement, could come from the cluster with smallest BG. But this cluster may have a small probability to occur, which might give a very low intensity in the PL spectrum, so the consideration of alloy statistics is crucial to obtain a good prediction of the PL peak.

The lattice parameters (LP's) of the studied alloys follow the linear interpolation of Vegard's law.[6,14] Thus, for the binary compounds AlN, GaN, and InN, we use the values for the LP's recommended by Vurgaftman and Meyer[16] (Table I) and for clusters with mixed cations, the LP's are obtained from Vegard's law. To demonstrate the accuracy of the LDA-1/2 method,[7] calculated BG's for the binaries are also shown in Table I, in which they are compared to LDA values and experimental data.

Figure 1 shows results for the $In_xGa_{1-x}N$ alloy, together with LDA and experimental results (the data were extracted from a broad range of works). The LDA-1/2 results show a remarkable agreement with experimental data, only differing slightly within the In rich region ($x > 0.5$); which is not a surprise, because of the difficulties for a perfect experimental characterization.[16]

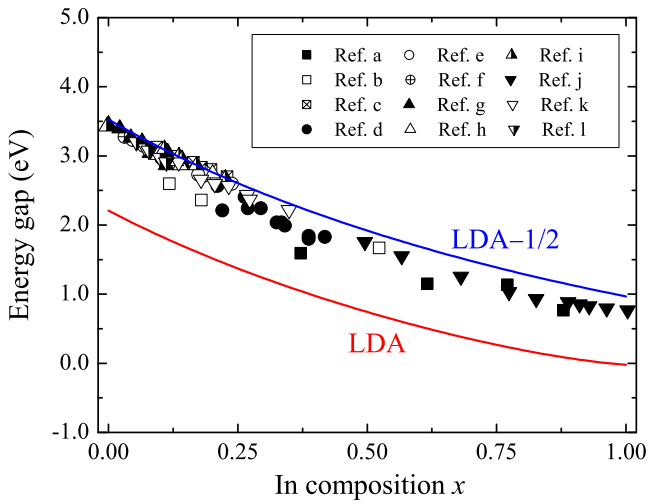

FIG. 1. (Color online) Comparison between the energy gap of the $In_xGa_{1-x}N$ alloy calculated through the ordinary LDA exchange-correlation potential (red line) and the LDA-1/2 method (blue line). The symbols represent experimental results, as follows: a (Ref. 17), b (Ref. 18), c (Ref. 19), d (Ref. 20), e (Ref. 21), f (Ref. 22), g (Ref. 23), h (Ref. 24), i (Ref. 25), j (Ref. 26), k (Ref. 27), and l (Ref. 28).

TABLE II. BG bowing parameter (eV) for the studied alloys: results obtained from LDA and LDA-1/2 calculations, compared with those recommended by Vurgaftman *et al.*[16]

	LDA	LDA-1/2	Ref. 16
$In_xGa_{1-x}N$	1.4	1.3	1.4
$Al_xGa_{1-x}N$	0.4	0.8	0.7
$Al_xIn_{1-x}N$	2.7	$3.4x+1.2$	2.5

The LDA and LDA-1/2 curves share the same shape, discounted by a rigid shift, fact verified by comparing the BP's (Table II). The BP b determines the deviation from the linear tendency predicted by Vegard's law. It is defined mathematically by

$$E(A_xB_{1-x}N) = xE(AN) + (1-x)E(BN) - bx(1-x), \quad (1)$$

where $E(X)$ is the energy gap of the X compound.

Predicted gap values (together with experimental data) for $Al_xGa_{1-x}N$ are depicted in Fig. 2. In this case, the LDA-1/2 BG fits the experimental values even better than before. Again, comparing LDA and LDA-1/2 curves, both curves present the same shape, but now with a slighter difference, which can be verified with the aid of the BP (Table II).

BG energies for $Al_xGa_{1-x}N$ appear in Fig. 3. This alloy covers one of the widest ranges in energy gaps among all semiconductor alloys, varying from 0.70 eV for InN to 6.28 eV for AlN. Although experimental results are more dispersive for this alloy, probably because of the greater lattice mismatch between InN and AlN, LDA-1/2 predictions much better accommodate measured values, in comparison to LDA predictions, which as expected, are underestimated. The BP for LDA is found to be 2.7 eV agreeing well with 2.5 eV, which is the recommended value by Vurgaftman *et al.* (Table II). On the other hand, the BP obtained from LDA-1/2 is composition dependent, as shown in Table II. The average value, throughout all compositions is 2.9 eV, which is also in nice agreement with the recommended value.

In summary, we provided BG calculations for InGaN, AlGaN, and AlInN alloys, considering the approach called

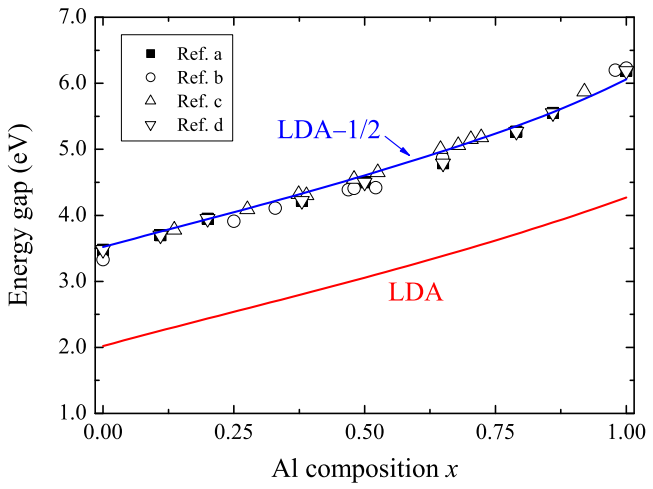

FIG. 2. (Color online) BG of the $Al_xGa_{1-x}N$ alloy: comparison between LDA (red line) and LDA-1/2 (blue line) calculations. Experimental results: a (Ref. 29), b (Ref. 30), c (Ref. 31), and d (Ref. 32).

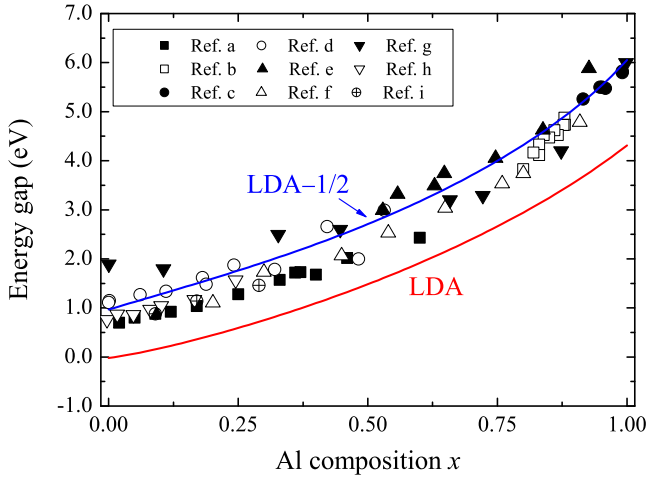

FIG. 3. (Color online) Energy gap of the $Al_xIn_{1-x}N$ alloy: comparison between LDA (red line) and LDA-1/2 (blue line) calculations. Experimental results: a (Ref. 33), b (Ref. 34), c (Ref. 35), d (Ref. 36), e (Ref. 37), f (Ref. 38), g (Ref. 39), h (Ref. 40), and i (Ref. 41).

LDA-1/2 for obtaining excited states within the DFT at a low computational cost. We compared our results with LDA and experimental data. The results were surprisingly good: LDA-1/2 predictions for the BG and respective BP fit remarkably well with experimental results for all alloys studied. This study shows that LDA-1/2 is a promising parameter-free method to study the properties of excited states of large and complex semiconducting systems, but at a very small computational price.

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