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Electronic Band Structure of $\text{In}_x\text{Ga}_{1-x}\text{N}$ under Pressure

I. GORCZYCA^a, N.E. CHRISTENSEN^b, A. SVANE^b, K. LAAKSONEN^c
AND R.M. NIEMINEN^c

^aInstitute of High Pressure Physics, “Unipress”
Sokołowska 29/37, 01-142 Warsaw, Poland

^bDepartment of Physics and Astronomy, University of Aarhus
8000 Aarhus C, Denmark

^cLaboratory of Physics, Helsinki University of Technology, 02015 HUT, Finland

The electronic band structures of zinc-blende $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys with x varying from 0.03 to 0.5 are examined within the density functional theory. The calculations, including structural optimizations, are performed by means of the full-potential linear muffin-tin-orbital and pseudopotential methods. The effects of varying the composition, x , and of applying external pressure are studied. A composition-dependent band gap bowing parameter in the range of 1.6–2 eV is obtained. A strong nonlinearity in the composition dependence of the pressure coefficient of the band gap is found.

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1. Introduction

InGaN alloys have attracted substantial attention during the last decade due to their technological applications in optoelectronic devices, utilizing the fact that the band gap can be tuned in a wide spectrum of wavelengths from the red to the ultraviolet.

Early experimental studies of InN , up to year 2000, suggested a direct band gap E_g of about 2 eV. Then, some experiments performed on high quality samples with low free-electron concentration, mostly grown by molecular beam epitaxy (MBE), revealed that the fundamental gap is much smaller. Recently, optical studies at room temperature showed that the InN gap is in the range of 0.6–0.7 eV [1–4]. The discovery of the low band gap of InN has extended the range of available direct band gaps of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys into the near-infrared part of the spectrum, causing an increased interest in these alloys.

Consequently, it has become necessary to reexamine the band structure models of InN and InGaN. Knowledge of the electronic band structures of these materials is crucial for improving the laser characteristics. This motivated us to perform a detailed analysis of the band structure of $\text{In}_x\text{Ga}_{1-x}\text{N}$ for a wide range of indium concentrations.

Although InGaN crystallizes at ambient conditions in the wurtzite structure, the calculations are performed for the zinc-blende structure due to their simplicity, and also because the zinc-blende structure of InGaN is interesting from the technological point of view due to some advantages (larger optical gain, lower threshold current density, compatibility with GaAs substrates) over the wurtzite structure. On the other hand, as it was already shown [5], all the conclusions regarding the behavior of energy bands as a function of composition and external, hydrostatic pressure are practically the same.

2. Method

The electronic structures of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys have been analysed by *ab initio* calculations in a supercell geometry. The indium concentrations, $x = 0.031, 0.062, 0.124, 0.25,$ and 0.50 have been realized by substituting 1, 2, 4, 8, and 16 Ga atoms, respectively, by In in a 64-atom supercell.

The calculations were performed in two steps using different approaches based on the local density approximation (LDA) [6] to the density functional theory, with the Perdew–Zunger [7] parameterization of the Ceperley–Alder exchange correlation [8]. We applied two computational schemes. The first one used pseudopotentials [9] as implemented in the Vienna *ab initio* simulation package (VASP) [10]. This code is well suited for calculations of the atomic relaxations in the whole supercell by minimizing the Hellman–Feynman forces. A cutoff energy of 30 Ry for the plane wave basis set was sufficient to obtain converged results. The k -space integrals were approximated by sums over $3 \times 3 \times 3$ Monkhorst–Pack special points folded within the irreducible part of the Brillouin zone (BZ) [11].

For each value of x and a given configuration of indium atoms the relaxed atomic positions were determined. Then the $\text{In}_x\text{Ga}_{1-x}\text{N}$ band structure was obtained by the second approach — the linear-muffin-tin-orbital (LMTO) method [12]. We chose this method because it allows for adjustment of the band gap, as will be described below. A full-potential (FP) version of the LMTO was applied [13]. The semi-core cation d states were included as local orbitals [14]. As usual, in open structures, empty spheres were included for the accuracy of interpolation of the charge density [15].

It is well known that the LDA underestimates the band gaps of semiconductors. We applied a simple procedure for correcting the band gaps and conduction band dispersion by introducing, at the sites of the atoms and the empty spheres, additional external potentials sharply peaked at the nuclear positions [16]. In compound semiconductors we choose different values of the external potential parameters at anion and cation sites. By introducing extra potentials also on the

empty sites we can make a gap correction not only at the Γ point, but also at other points in the BZ. The potentials are transferable [16, 17]. They were determined for GaN and InN at ambient conditions by adjusting to experimental gap values, and subsequently applied, with the same parameters, to InGaN. They were kept unchanged while the volume was varied.

3. Results and discussion

The energy band structures of GaN and InN were calculated with the band gap adjustment, as described in the previous section. We adjusted the fundamental band gaps at the Γ point to the experimental values, for GaN: 3.28 eV [18] and for InN: 0.62 eV, which is an average of the values found in the literature (0.60–0.65 eV) [1–4]. Then we obtained the band structure of InGaN using the same external potential parameters for real atoms and empty spheres as determined for GaN and InN by the adjusting procedure.

For each value of x the $\text{In}_x\text{Ga}_{1-x}\text{N}$ band structure was calculated for different volumes to find the equilibrium volume and the hydrostatic pressure dependence. The obtained values of equilibrium lattice constants and bulk moduli are for GaN: 4.465 Å, 204 GPa and for InN: 4.96 Å, 148 GPa, respectively. In $\text{In}_x\text{Ga}_{1-x}\text{N}$ they are found to be almost linearly dependent on x . It means that to a good approximation the Vegard law is fulfilled, i.e., the lattice constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$ can be approximated by the formula: $a(x) = xa_{\text{InN}} + (1-x)a_{\text{GaN}}$ within the accuracy of the calculations. The band structure of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ is next investigated, and band gap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ as a function of indium content is plotted in Fig. 1.

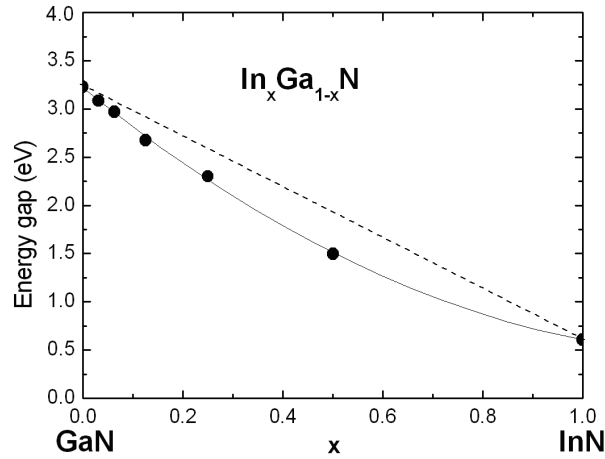


Fig. 1. Energy gap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ as a function of composition, x . Solid line: spline fit to the calculated values (filled circles) in comparison with the linear dependence (dashed line).

The band gap of the alloy can be expressed as a function of x by the following formula: $E_g(x) = xE_{g,\text{InN}} + (1-x)E_{g,\text{GaN}} - bx(1-x)$, where b is the band gap bowing parameter. Our calculated band gap bowing is found to be composition dependent ranging from 1.95 eV for $x = 0.031$ to 1.65 eV for $x = 0.25$ and 1.63 eV for $x = 0.5$. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ bowing parameter is still a subject of discussion. An anomalously large bowing (≈ 3 eV) was reported before the discovery of low InN band gap. The new values found in the literature are in the range between 1.37 eV [19] and 1.89 eV [20]. The composition dependence of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ gap bowing was obtained by Bechstedt et al. [21], where the calculated values for wurtzite $\text{In}_x\text{Ga}_{1-x}\text{N}$ vary between 2.5 and 1.5 eV within the interval $0 \leq x \leq 0.25$ and decrease further to 1.4 eV for $x = 0.5$ and 1.3 eV for $x = 0.75$. On the other hand, constant band gap bowing parameters were reported by Li et al. [22] ($b = 1.43$ eV) and by Kuo et al. [20] ($b = 1.89$ eV).

Next, we consider the hydrostatic pressure dependence of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ energy gap. In Fig. 2 the band gap pressure coefficient is shown as a function of x . We can see from the figure that the bowing is large and strongly composition dependent. Starting from the value of 39 meV/GPa for GaN we observe a very strong decrease in the band gap pressure coefficient up to $x \approx 0.25$; then it decreases more slowly, having at $x = 0.50$ the value 26 meV/GPa, essentially as in pure InN, 27 meV/GPa, as we estimate our calculational error to be about ± 1 meV/GPa. Our calculated pressure coefficients for varying In content are in good agreement with the experimental data obtained from absorption measurements [3], where similar tendencies are observed.

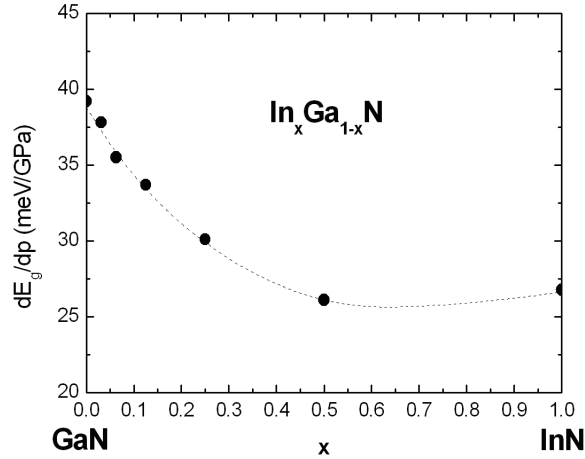


Fig. 2. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ band gap pressure coefficient as a function of composition, x .

It is suggestive to associate a strong nonlinear behavior of the band gap pressure coefficient of InGaN with In-induced changes of the states at the valence band top [5].

Summarizing, the band structure of zinc-blende $\text{In}_x\text{Ga}_{1-x}\text{N}$ was studied for different values of x in the range from 0.03 to 0.5 and for different hydrostatic pressure values. The significant composition dependent bowing of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ band gap was found. The pressure coefficient of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ energy gap exhibits a very strong nonlinearity as a function of x , decreasing rapidly for small x and being almost constant for $x > 0.25$. These conclusions are in agreement with available experimental data.

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