Dynamics and polarization of group-III nitrides

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The group-III nitrides possess outstanding mechanical, thermal, electronic and electrostatic properties that need a deeper understanding. The compounds AlN, GaN, and InN crystallize in the wurtzite (2H) structure at ambient conditions. However, the metastable zinc-blende (3C) polytype may grow epitaxially. The deviations of the internal-strain parameter u from the ideal value 0.375 governs the electrostatic behaviour of the ion lattice in wurtzite [1]. The position of the conduction band minimum in **k** space varies with the group-III element. However, there is a controversy in the case of 3C-AlN concerning the direct or indirect character of this semiconductor [2, 3]. Strain may influence the findings for the fundamental gap. Due to sample-quality problems the phonons, in particular those of InN, are not well known experimentally [4]. The electronic and optical properties of layered wurtzite III-nitrides are remarkably influenced by spontaneous polarization fields [5]. Their magnitude seems to be extremely sensitive to the details of the atomic structure.

In this contribution we discuss and clarify these questions concerning the properties of the group-III nitrides using *ab initio* density functional theory (DFT) in local density approximation (LDA). Besides the valence electrons also the semicore Ga3d and In4d states are explicitly considered. Their interaction with the atomic cores is treated by non-normconserving *ab initio* Vanderbilt pseudopotentials. They allow a substantial potential softening also for first-row elements with the lack of core p electrons as well as for the attraction of shallow d electrons. As a consequence of the optimization the plane-wave expansion of the single-particle eigenfunctions may be restricted by an energy cutoff of 22.1 (BN), 14.4 (AlN), 16.2 (GaN), and 15.5 Ry (InN). The cutoffs have been carefully tested and successfully applied to the properties of the cleavage surfaces of zinc-blende nitrides [1]. The many-body electron-electron interaction is described within the Ceperley-Alder scheme as parametrized by Perdew and Zunger. The **k**-space integrals are approximated by sums over 10 (zinc-blende) or 12 (wurtzite) special points of the Chadi-Cohen type within the irreducible part of the Brillouin zone (BZ). Our calculations employ the conjugate gradient method to minimize the total energy. Explicitly we use the Vienna Ab-initio Simulation Package [6]. The outstanding properties of the nitrides are discussed in terms of the smallness of the nitrogen atom and the accompanying high bond strength and large bond ionicity with values $g = 0.48$ (BN), 0.79 (AlN), 0.78 (GaN), and 0.85 (InN) on the Garcia-Cohen scale [7].

The structural optimization gives an internal-cell parameter $u = 0.374$ (BN), 0.382 (AlN), 0.382 (GaN), and 0.378 (InN). Such a nonmonotoneous behaviour with respect to bond strength and ionicity is also observed for the position of the conduction-band minima. In the wurtzite crystals they are located at the Γ point in the BZ, except BN, where the minimum occurs at K. In the zinc-blende case the band minimum is still at Γ for GaN and InN. BN and AlN become indirect semiconductors with the minimum at X. The energetical position and the decrease of emission intensity is believed to imply the indirect band structure of cubic $Al_xGa_{1-x}N$ in the mid-range of composition x [2] in agreement with the theoretical findings. However, recent cathodoluminescence studies of cubic AlN and $Al_xGa_{1-x}N$ epilayers do not show a significant de-

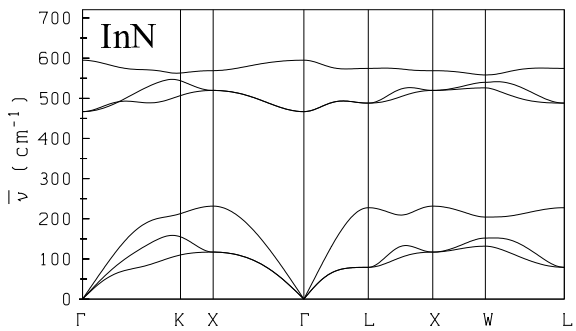

Figure 1: Calculated phonon dispersion curves of zinc-blende InN.

crease of the luminescence signal. Hence, a direct character is assumed contrary to the theoretical predictions with 1.17 eV difference in the energies of the conduction-band minima at X and Γ.
The lattice-dynamical properties are calculated using a generalization of the *ab initio* force constant method. However, also the long-range electric fields are taken into account. The screened Born effective charge is derived from an artefact of the periodic boundary conditions. As an example the vibrational branches resulting for zinc-blende InN are plotted in Fig. 1. The corresponding frequencies are 467 (TO(Γ)), 596 (LO(Γ)), 78 (TA(L)), 227 (LA(L)), 488 (TO(L)), and 573 cm^{-1} (LO(L)). In the Γ case they agree well with frequencies obtained in recent Raman measurements [8]. Assuming that the splittings of the TO(Γ) and LO(Γ) modes into E_1 and A_1 phonons of the wurtzite structure are more or less the same in GaN and InN, we derive wurtzite frequencies 449 (A_1(TO)), 475 (E_1(TO)), 594 (A_1(LO)), and 603 cm^{-1} (E_1(LO)). These values are in close agreement with recently measured values [9]. To get an impression of the effect of alloying, we study the lattice vibrations also for an ordered $In_{0.5}Ga_{0.5}N$ structure.

Instead of a Berry-phase approach we calculate the spontaneous polarization in wurtzite structures from the electric field in a 2H/3C superlattice with 30 III-N bilayers. We directly derive [4] the extrinsic or longitudinal (screened) polarization field (cf. Fig. 2). After multiplication with the electronic dielectric constant one finds the intrinsic or transverse polarization field $P_z = -120$ (AlN), -74 (GaN), and -50×10^{-3} C/m^2 (InN). In the case of BN the polarization field vanishes. These values come close to those estimated by Bernardini et al. [5]. The discrepancies are mainly a consequence of the different structural parameters u used. We predict a proportionality of the spontaneous polarization to the difference $(u - 0.375)$. Hence, the accuracy of the determination of u critically influences the value of the polarization field.

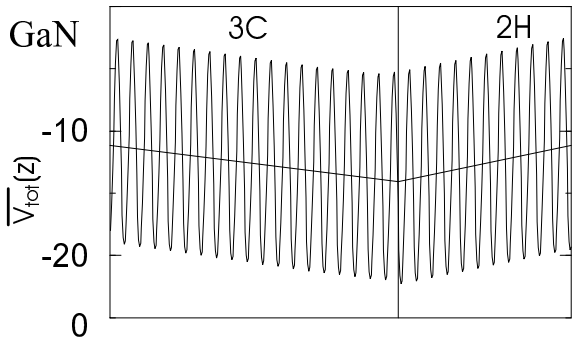

Figure 2: Averaged total one-electron potential of GaN-$(3C)_6(2H)_6$ cell.

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