I. INTRODUCTION

Disordered semiconductor alloys of the type $A_xB_{1-x}C$ can be experimentally realized for many technologically important semiconductor materials AC and BC (like GaAs and InAs, CdSe and ZnSe, GaN and AlN and many more) by substituting the cation A by the B counterpart. For a wide class of materials, the value $x$ can be adjusted over a large part of or even the whole concentration range, depending on the miscibility gap of the alloy system. As the electronic and optical properties vary continuously with $x$, the electronic properties (e.g., band gap and thus emission and absorption frequency, dielectric constant, etc.) can be tailored by choosing the appropriate concentration. Therefore, these semiconductor alloys have many applications, not only as bulk semiconductors but also in low-dimensional structures like quantum wells, quantum wires and quantum dots.

In this paper, we show that the electronic properties of such substitutional semiconductor alloys of the type $A_xB_{1-x}C$ can be described and understood on the basis of empirical tight-binding models (ETBM) for the pure semiconductors AC and BC. Once the tight-binding (TB) parameters of AC and BC are known, the ETBM for the substitutionally disordered $A_xB_{1-x}C$ alloy is obtained by choosing the AC TB parameters with probability $x$ and the BC TB parameters with probability $1-x$. The electronic eigenenergies and thus the density of states and the band gap of this disordered system can then be determined by exact diagonalization of a finite but large supercell, consisting of several thousand primitive unit cells at least. As this procedure is numerically expensive, we also considered and applied well established approximations for the treatment of disordered systems, namely the coherent potential approximation (CPA) and the virtual crystal approximation (VCA). While the CPA is a self-consistent Green function approximation, the much simpler (but still frequently applied) VCA corresponds to a static mean-field treatment of the disorder by replacing the randomly fluctuating potential by an average potential.

We apply our treatment to the zincblende phase of three interesting materials, namely to the II-VI semiconductor alloy system Cd$_x$Zn$_{1-x}$Se, to the technologically established III-V alloy In$_x$Ga$_{1-x}$As and to the III-nitride system Ga$_x$Al$_{1-x}$N. In a previous paper [1] it has already been shown that the supercell exact diagonalization method yields excellent agreement with experimental results obtained for Cd$_x$Zn$_{1-x}$Se. But as [1] was a joint paper together with experimentalists, the theoretical method was not yet described and discussed in detail and no comparison with CPA and VCA results for this material has been presented there. Whereas the VCA, in general, yields no band gap bowing, the CPA may even overestimate the bowing, as we will show in the present paper. We particularly present results obtained within combinations of CPA and VCA, treating the site-diagonal disorder in CPA and the off-diagonal disorder in VCA. Furthermore, we explicitly discuss the influence of a properly chosen basis set for the bowing results.

Also for In$_x$Ga$_{1-x}$As, reasonable results for the band gap bowing are obtained in agreement with literature values as obtained by experiment. For Ga$_x$Al$_{1-x}$N the band gap bowing is rather small and the VCA results are not too bad at all; a crossover from a direct band gap to an
indirect band gap behavior as a function of \( x \) is obtained in all three applied approaches.

This paper is organized as follows: In Section II we present the necessary theoretical background for our calculations of the electronic properties of \( A_xB_{1-x}C \) semiconductor bulk alloys. It contains a brief description of the employed tight-binding model, the CPA and the modelling on a finite ensemble of supercells. Section III contains a detailed analysis of the results that we obtained for the electronic properties of CdSe, ZnSe, CdS and \( A_xB_{1-x}C \) and discuss the applicability of the CPA and VCA to these systems.

II. THEORY

A. Empirical tight-binding model for pure bulk semiconductors:

We know from textbook solid state physics that one complete basis set of the translationally invariant pure bulk system is given by the Wannier states \( |nR\rangle \), where \( n \) is the band index and \( R \) denotes the unit cell center where the state is predominantly localized. The Wannier states are connected to the itinerant Bloch states \( |n\mathbf{k}\rangle \), where \( \mathbf{k} \) is any wave vector in the first Brillouin zone (BZ), by means of a discrete Fourier transformation. The ETBM, as originally introduced by Slater and Koster \([2]\), uses a finite linear combination of atomic orbitals on the basis sites as ansatz for the Wannier states. The matrix elements are then fitted in order to sufficiently reproduce prominent band structure features.

Because the atomic states, and hence the Wannier states, are not explicitly used in an ETBM, one has the additional freedom to directly assume a finite basis set of localized Wannier-like states. As the Wannier basis carries the translational invariance of the crystal, these states merely have to be assigned to the sites \( R \) of the underlying Bravais lattice. This parametrization scheme is also known as effective bond-orbital model (EBOM) in the literature.

In this paper, we will use a \( sp^3 \) basis per spin direction \( \{\uparrow, \downarrow\} \) to reproduce \( N_\alpha = 8 \) bands for crystals with zincblende structure: One spin-degenerate s-like conduction band (CB) and three spin-degenerate p-like valence bands (VB), in detail the heavy hole (HH), light hole (LH) and split-off (SO) band. Thus, \( R \) labels the \( N_R \) sites of the underlying fcc Bravais lattice, and the TB matrix elements of the bulk Hamiltonian \( H^{\text{bulk}} \) are

\[
E_{\alpha \alpha'}^{RR'} = \langle \mathbf{R} \alpha | H^{\text{bulk}} | \mathbf{R}' \alpha' \rangle, \tag{1}
\]

with the orbitals

\[
| \mathbf{R} \alpha \rangle, \quad \alpha \in \{s \uparrow, p_x \uparrow, p_y \uparrow, p_z \uparrow, s \downarrow, p_x \downarrow, p_y \downarrow, p_z \downarrow \}. \tag{2}
\]

The translational invariance in the pure crystal reduces the \( N_\alpha N_R \times N_\alpha N_R \) matrix problem to a \( N_\alpha \times N_\alpha \) problem for each \( \mathbf{k} \) \([2]\), which will not be the case for disordered systems and in the later introduced supercell method. The band structure \( E(\mathbf{k}) \) is then given by the solution of the eigenproblem

\[
\sum_{\alpha'} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} E_{\alpha \alpha'}^{0\mathbf{R}} c_\alpha(\mathbf{k}) = E(\mathbf{k}) c_\alpha(\mathbf{k}). \tag{3}
\]

If one restricts the non-vanishing matrix elements, Eq. (1), up to a finite neighborhood and makes proper use of symmetry relations, the TB matrix elements can be expressed as a function of a set of material parameters of either the AC or BC material (e.g. CdSe and ZnSe). We will use the parametrization scheme of Loehr \([3]\), which includes coupling up to second nearest neighbors. The parameters are given in the appendix. Figure 1 shows the band structure and density of states (DOS) as calculated in the \( sp^3 \) EBOM for cubic CdSe and ZnSe, respectively.

Despite the small basis set, this TB model notably allows for the reproduction of a realistic bandstructure and bandwidth throughout the whole BZ. This is a typical feature of parametrizations with Wannier-like basis states \([15]\) and makes the EBOM especially suitable for the purpose of the present work, as both the CPA and the supercell calculations for the \( A_xB_{1-x}C \) will require a realistic input DOS for the pure cases \( x = 0 \) and \( x = 1 \) as starting point—the relative position of the band centers and the bandwidths will crucially influence the alloy properties. We have also already mentioned in the introduction that the inclusion of further bands would significantly increase the computational effort. Finally, the resolution on the scale of unit cells instead of atomic sites will turn out as favorable for the simulation of the ternary \( A_xB_{1-x}C \) materials, as it will allow for an unambiguous assignment of the alloy lattice sites to either AC or BC (see Sec. II D).

B. The coherent potential approximation

The basic principle of the CPA has independently been developed by several groups in the late sixties of the last century \([4][5][6]\). The best known formulation is certainly the work of Soven \([3]\), which explicitely dealt with the calculation of the electronic DOS of substitutionally disordered one-dimensional systems. An excellent and comprehensive general introduction into the CPA formalism can be found in \([7]\).

The simplest form of the CPA for an alloy assumes uncorrelated substitutional disorder of the respective species. If all sites are indistinguishable (i.e. no division into sublattices is necessary), as it is the case in the spatial discretization in the EBOM, the probability of finding either species is just given by the concentrations \( x \) and \( 1-x \).
For the sake of clarity, we will suppress the band and orbital indices until further notice. In order to be consistent with the common CPA literature, let us denote the site diagonal ($\mathbf{R} = 0$) TB matrix elements of the AC or BC material as $v_{AC/BC}$:

$$v_{AC/BC} = E^{00}_{AC/BC} = \left\langle 0 | H_{AC/BC}^{bulk} | 0 \right\rangle.$$

We will now briefly specify the most important assumptions that enter the CPA (see e.g. [7] for details of the derivation):

1. The disorder is confined to the diagonal elements. The off-diagonal (or hopping) matrix elements with $\mathbf{R} \neq \mathbf{R}'$ are either identical for both species or can approximately be replaced by a common value, e.g. the VCA average. If we now separate the TB Hamiltonian of the alloy $H$ into a diagonal part $V$ and an off-diagonal part $W$, such that $H = V + W$, only $V = \sum_{\mathbf{R}} v^R | \mathbf{R} \rangle \langle \mathbf{R} |$ is site-dependent, as $v^R = v_{AC/BC}$, depending on the species on the site $\mathbf{R}$. The operator $W$ is still translationally invariant under translations by $\mathbf{R}$ and therefore remains diagonal with respect to Bloch states $| \mathbf{k} \rangle$.

2. The configurational average $\left\langle \ldots \right\rangle$ over the resolvent of $H$ defines an effective Hamiltonian $H_{\text{eff}}(z)$:

$$\langle (z\mathbf{1} - H)^{-1} \rangle \equiv \langle z\mathbf{1} - H_{\text{eff}}(z) \rangle^{-1} \equiv \langle z\mathbf{1} - \Sigma(z) - W \rangle^{-1}. \quad (4)$$

Here, $\mathbf{1}$ is the identity operator and $z$ is in the complex energy plane, containing the energy axis $E = \text{Re} (z)$. The self-energy operator $\Sigma(z) = H_{\text{eff}}(z) - W$ absorbs the influence of the disorder on the microscopic scale. Note that $H_{\text{eff}}$ will in general be non-hermitian.

3. Due to the single-site nature of the CPA, the self-energy is diagonal in every representation. Furthermore, its matrix elements $\Sigma^0(z)$ are neither dependent on $\mathbf{k}$ nor on $\mathbf{R}$.

In order to obtain the self energy matrix elements $\Sigma^0(z)$, which uniquely define the effective medium, we have to solve the CPA equation for two constituents:

$$\frac{x \left[ v_{AC} - \Sigma^0(z) \right]}{1 - v_{AC} - \Sigma^0(z)} G_{\mathbf{R}}(z) + \frac{(1-x) \left[ v_{BC} - \Sigma^0(z) \right]}{1 - v_{BC} - \Sigma^0(z)} G_{\mathbf{R}'}(z) = 0. \quad (5)$$

The complex-valued $G_{\mathbf{R}}(z)$ is the configurationally averaged one-particle Green function in Wannier representation (more precisely its $\mathbf{R}$-diagonal element). Although $G_{\mathbf{R}}(z)$ does not depend on $\mathbf{R}$ in the CPA, we will keep the index to clearly distinguish it from its Bloch representation $G_k(z)$. The two representations are connected by

$$G_{\mathbf{R}}(z) = \frac{\left\langle \mathbf{R} | (z\mathbf{1} - H)^{-1} | \mathbf{R} \right\rangle}{\frac{1}{N_k} \sum_{\mathbf{k}} \left\langle \mathbf{k} | (z\mathbf{1} - H)^{-1} | \mathbf{k} \right\rangle},$$

$$\text{Eq.}(4) \quad \frac{1}{N_k} \sum_{\mathbf{k}} \left[ z - \Sigma^0(z) - \langle \mathbf{k} | W | \mathbf{k} \rangle \right]^{-1} \equiv \frac{1}{N_k} \sum_{\mathbf{k}} G_k(z), \quad (6)$$

with $N_k$ as the number of wave vectors in the first BZ or the corresponding irreducible wedge (as $N_k = N_\mathbf{R}$ and $G_{\mathbf{R}} = G_{\mathbf{R}+\mathbf{R}'}$, this relation follows directly from the invariance of the trace under unitary transformations).

Under certain conditions, the summation over all $\mathbf{k}$-values can be avoided by the introduction of a sufficiently smooth DOS $g_W$ for the off-diagonal part $W$:

$$g_W(E) = \frac{1}{N_k} \sum_{\mathbf{k}} \delta(E - \langle \mathbf{k} | W | \mathbf{k} \rangle). \quad (7)$$
Now the calculation of \( G_R(z) \) can be performed as a one-dimensional integration/summation over the energy axis:

\[
G_R(z) = \frac{1}{N_k} \sum_k \frac{1}{z - \Sigma^0(z) - \langle k | W | k \rangle}
\]

\[
\approx \sum_i g_W(E_i) \int_{E_i}^{E_{i+1}} \frac{1}{z - \Sigma^0(z) - E} \, dE
\]

\[
= \sum_i g_W(E_i) \left\{ \ln \left[ z - \Sigma^0(z) - E_i \right] - \ln \left[ z - \Sigma^0(z) - E_{i+1} \right] \right\}.
\]

The approximation holds if \( g_W(E) \) is approximately constant on the interval \([E_i, E_{i+1}]\).

The equations (5) and optionally (6) or (8) can be solved in a self-consisted manner in order to obtain \( \Sigma^0(z) \) and \( G_R(z) \). We can then directly obtain further quantities for the effective medium; e.g. the configurationally averaged DOS \( g(E) \) per lattice site is given as

\[
g(E) = -\frac{1}{\pi} \lim_{z \to E^+} \text{Im} \frac{1}{N_R} \text{Tr} \left\{ [z \mathbb{1} - \mathbb{H}_{\text{eff}}(z)]^{-1} \right\}
\]

\[
= -\frac{1}{\pi} \lim_{\delta \to 0^+} \text{Im} G_R(E + i\delta).
\]

As a rule of thumb, the CPA is known to yield very good results in two limit cases [2]:

1. The weak scattering limit, where the difference of the first moments of the substituents (aka the centers of gravity of the bands) is smaller than the respective bandwidths.

2. The split band limit or atomic limit, where the substituents’ first moments are either sufficiently far apart or the bandwidths are small, so that the respective bands do not overlap.

Additionally, it of course also gives the correct pure limit for \( x \to 0 \) and \( x \to 1 \). Also, in the limit case of vanishing difference of the moments, the CPA reduces to the VCA.

### C. Multiband CPA + ETBM

The formal extension of the CPA to multiband TB models is straightforward and has been used in different levels of detail to qualitatively examine the electronic properties of disordered alloys (see e.g. [8] for Si\(_x\)Ge\(_{1-x}\), [10] for Pd\(_x\)H\(_{1-x}\), [11] for Cd\(_x\)Hg\(_{1-x}\)Te or [12] for palladium-noble-metal alloys).

1. \( \text{sp}^3 \) representation

In the \( \text{sp}^3 \) EBOM, the localized basis is now given by the TB orbitals \(|R\alpha\rangle\). Hence, Eq. (5) has to be replaced by the corresponding matrix equation, with

\[
v_{\text{AC/BC}} \rightarrow v^{\text{sp}^3}_{\text{AC/BC}} \equiv \begin{bmatrix} E_{00}^{00} \end{bmatrix},
\]

\[
\Sigma^0(z) \rightarrow \Sigma^{\text{sp}^3}(z) \equiv \begin{bmatrix} \Sigma^{\alpha\alpha'}(z) \end{bmatrix},
\]

\[
G_R(z) \rightarrow G^{\text{sp}^3}_R(z) \equiv \begin{bmatrix} G^{\alpha\alpha'}_R(z) \end{bmatrix}
\]

as \( 4 \times 4 \) matrices per spin direction (here, the square brackets denote matrices). The effective Hamiltonian matrix \( \mathbb{H}_{\text{eff}}^{\text{sp}^3}(z) \) in the \( \text{sp}^3 \) TB scheme can be obtained by the substitutions

\[
E_{\text{AC/BC}} \rightarrow \Sigma^{\alpha\alpha'}_R(z),
\]

\[
E^{\text{RR'}}_{\text{VCA}} \rightarrow x E^{\text{RR'}}_{\text{AC}} + (1 - x) E^{\text{RR'}}_{\text{BC}, R'},
\]

i.e. the hopping matrix elements are approximated in the VCA. Like in Eq. (6), we then obtain the Green function via BZ summation,

\[
G^{\text{sp}^3}_R(z) = \frac{1}{N_k} \sum_k \left\{ z \mathbb{1} - \mathbb{H}_{\text{eff}}^{\text{sp}^3}(z) \right\}^{-1},
\]

where \( \mathbb{1} \) is the \( 8 \times 8 \) identity matrix. The matrix \( G^{\text{sp}^3}_R(z) \) has non-vanishing off-diagonal elements \( G^{\alpha\alpha'}_R(z) \), as the TB Hamiltonian is not diagonal in the orbital basis \(|R\alpha\rangle\).

2. Band-diagonal (Wannier) representation

Alternatively, we can again calculate Green’s function via energy integration. In a band-diagonal (Wannier-like) TB representation, the site-diagonal TB matrix element \( E^0_n = \langle 0n | H_{\text{bulk}} | 0n \rangle \) of the \( n \)-th band can be calculated from the first moment

\[
E^0_n = \int dE \, g^n(E),
\]

with \( g^n(E) \) as the DOS of band \( n \) (normalized to unity). Therefore, we can assign the moments of the AC or BC system to a corresponding self-energy:

\[
E^0_{\text{AC/BC}} \rightarrow \Sigma^n(z).
\]

The analogon of equation (8) is then the band-diagonal Green function matrix \( G^0_R(z) \) (denoted by “\( \text{wn} \)” for “Wannier” from now on) with elements

\[
G^{\text{wn}}_R(z) \approx \sum_i g^0_W(E_{n,i}) \left\{ \ln \left[ z - \Sigma^n(z) - E_{n,i} \right] - \ln \left[ z - \Sigma^n(z) - E_{n,i+1} \right] \right\} \delta_{nn'}(16)
\]

with \( g^0_W(E) = g^\text{VCA}(E - E^0_0) \) as the VCA DOS of the \( n \)-th band, shifted by \( E^0_0 \). This procedure allows us to calculate the DOS of the off-diagonal operator \( W \) in the Wannier basis by diagonalization of the EBOM Hamiltonian in the VCA. Notably, we do not have to explicitly know the corresponding matrix elements \( \langle Rn | W | R'n \rangle \).
3. Calculation of electronic properties

Finally, the CPA + ETBM DOS of the alloy can be calculated by either tracing over the orbital index (in the \( sp^3 \) basis) or the band index (in the Wannier basis) of the matrix elements:

\[
g^{sp^3}(E) = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} \sum_{\alpha} G^{\alpha}_{\alpha_R}(E + i\delta), \quad (17)
\]

\[
g^{wn}(E) = -\frac{1}{\pi} \lim_{\delta \to 0} \sum_{n} G^{wn}_{n_R}(E + i\delta). \quad (18)
\]

Although the trace of a matrix is of course independent of the representation used, it should be noted that \( g^{sp^3} \) and \( g^{wn} \) are not identical: The self-energies, which define the effective medium, replace different quantities [see Eqs. (11) and (15)], which results in different operators \( H_{\text{eff}} \).

Due to the translational invariance of the self energy matrix elements and thus \( H_{\text{eff}} \), we can define a complex band structure of the medium. The electronic excitations of the effective medium can be assigned to quasiparticles with a modified dispersion relation

\[
E^{\alpha}_{n_R}(k) = \langle k|W|kn \rangle + \text{Re} \Sigma^n(\varepsilon^{\alpha}_{n_R}). \quad (19)
\]

The corresponding CPA one-particle spectral function

\[
S^{\alpha}_{k}(E) = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} G^{\alpha}_{k_R}(E + i\delta), \quad (20)
\]

will in general be broadened in case of disorder \((0 < x < 1)\), as the non-vanishing imaginary part of \( \Sigma^n \) accounts for a finite lifetime \( \tau \propto 1/\text{Im} \Sigma^n(\varepsilon) \) of the excitation. As an example, Fig. 2 visualizes the complex band structure \( E^{\alpha}_{n_R}(k) \) of Cd\(_{0.5}\)Zn\(_{0.5}\)Se on the left, calculated in the combination of the CPA and the \( sp^3 \) EBOM. On this energy scale over the whole bandwidth, the results from the Wannier and the \( sp^3 \) representation are not distinguishable. The color-coding clearly shows the \( k \)-dependent broadening of the band structure due to finite lifetime effects. The figure on the right additionally shows the corresponding CPA DOS and the spectral function at the BZ center for all four spin-degenerate bands, i.e.

\[
S_{k=0}(E) = -\frac{1}{\pi} \lim_{\delta \to 0} \sum_{n} G^{wn}_{k=0}(E + i\delta).
\]

Note that we have chosen a relatively large imaginary part \( \delta = 0.05 \text{ eV} \) for the energy axis, which leads to a small but non-vanishing DOS in the band gap region. We furthermore used \( \# k \approx 10^6 \) values in the irreducible BZ of the fcc lattice. The peak structure of the \( k = 0 \) quasiparticle excitations at the edges of the band gap region is clearly visible. A qualitative and quantitative discussion of the electronic structure in comparison with VCA and supercell results will follow in Section II A.

D. Supercell tight-binding calculation in the EBOM

If the Hamilton operator \( H \) is no longer translationally invariant, the TB approach is not reducable to the form [9] and we are left with the \( N_c N_R \times N_c N_R \) matrix eigenvalue equation

\[
\sum_{\alpha_R} \langle R\alpha | H | R'\alpha' \rangle c_{\alpha R} = E c_{\alpha R}. \quad (21)
\]

We will now use a finite supercell with periodic boundary conditions. Like in calculations for zero-dimensional nanostructures [13][14][15][16], we will furthermore assume that

\[
\langle R\alpha | H | R'\alpha' \rangle \approx \langle R\alpha | H_{\text{bulk}} | R'\alpha' \rangle = E^{RR'}. \quad (22)
\]

Again assuming uncorrelated substitutional disorder in the \( \text{A}_x\text{B}_{1-x}\text{C} \) alloy, each primitive cell will be occupied by the AC or BC basis, where the probability of finding either an AC or BC pair in the unit cell at \( R \) is directly given by the concentrations \( x \) and \( 1-x \). Building the Hamilton matrix for the supercell, we will therefore use the matrix elements of the pure AC or BC material for the corresponding lattice sites. The valence band offset between the two materials is incorporated by shifting the respective site-diagonal matrix elements by a value \( \Delta E_{vb} \). Hopping matrix elements between unit cells of different material are approximated by the arithmetic average of the corresponding AC or BC values. Although this approach for the incorporation of the energy offset and the hopping between two materials is very simple, it gives the correct limit in the pure case. In the phase separation case (a limit of which the probability is practically zero in case of uncorrelated disorder), it would furthermore lead to an interface treatment that has been extensively tested in calculations for low-dimensional heterostructures [13][14][15]. Specifically, the results turn out to be insensitive to small variations of the hopping between two materials (e.g. the usage of a geometric instead of an arithmetic average).

The usage of the EBOM, i.e. the usage of Wannier-like orbitals situated at the sites of the Bravais lattice in the supercell approach, has several advantages over similar approaches which use an ETBM with discretization on atomic sites:

1. Even when introducing disorder on a microscopic scale, each lattice site can be unambigously assigned to one site-diagonal TB matrix element and the corresponding band structure parametrization for either AC or BC. In ETBM supercell calculations with atomic resolution, each anion of the type C will locally be surrounded by a different number of A or B cations, thus making an assignment of the diagonal elements of the anions to the band structure of either AC or BC impossible.

It is common to then use either a concentrationally averaged VCA value or to determine this matrix
FIG. 2: (Color online) Complex band structure (left), DOS and spectral function at \( k = 0 \) (right) for \( \text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se} \), calculated in the combination of the CPA and the \( sp^3 \) EBOM. To enhance contrast, we have color-coded the logarithm of \(- \text{Im} \, G_k\). The spectral function and the DOS are normalized to a common scale.

element as a weighted average of the C matrix elements for AC and BC, depending upon the number of nearest-neighbour atoms A or B [17][18]. This will lead to an effectively more coarse-grained resolution as in the case of the EBOM, as the latter model only has to average the intersite hopping matrix elements (which typically differ on a scale of 10 meV in materials with moderate lattice mismatch). In the \( \text{Cd}_x\text{Zn}_{1-x}\text{Se} \) system for example, the site diagonal matrix elements for the Se anions in CdSe and ZnSe (see e.g. Refs. [17] and [19]) differ to a larger extent than the EBOM hopping matrix elements when using a congruent set of input parameters.

2. All influences which originate from effects on a smaller length scale, like the difference in the AC and BC bond lengths, are absorbed into the values of the corresponding TB matrix elements between the effective orbitals.

3. As the results are not sensitive to the exact treatment of the hopping between AC and BC sites, further effects that basically result in minor variations of the hopping matrix elements (like small bond angle changes due to relaxation) can be neglected in a first approximation.

The numerical diagonalization (e.g. using standard numerical libraries like ARPACK/PARPACK) of the corresponding Hamiltonian for a fixed concentration and a finite number \( N \) of microscopically distinct configurations gives the density of states (DOS) of the finite ensemble. In order to obtain a meaningful DOS from the supercell calculations, we must first appropriately define it. Strictly speaking, a macroscopic alloy crystal represents just one realization; by dividing it into small portions, we can nevertheless get subsystems that differ from each other on a microscopic scale. In this sense, the DOS for one fixed concentration \( x \) is then obtained by the average of the DOS for each finite ensemble.

To eliminate the influence of finite size effects, the number of lattice sites \( N_R \) as well as the ensemble size \( N \) must be sufficiently large. We point to previous work [1] for a careful analysis of the convergency behaviour and will use the recommendations throughout this paper. In a nutshell, a resolution of the band edges up to 0.01 eV, which is the typical input accuracy for the material parameters, will require supercells with \( N_R \approx 2000–4000 \) lattice sites and \( N \approx 50 \) microscopically distinct configurations per concentration. For a discussion of properties on a larger energy scale, e.g. a comparison of the DOS over the whole bandwidth, smaller supercells and ensemble sizes can be chosen.

In contrast to the CPA, the supercell approach can easily be augmented to simulate effects not only of configurational, but also of concentrational disorder. This can easily be achieved when we drop the constraint that the overall concentration of AC sites \( N_R/N \) per configuration \( i \) should equal the point probability \( x \) and occupy each lattice site independently. In the limit of large \( N \), we will of course have \( \lim_{N \to \infty} \sum_{i=1}^{N} N_{AC}^{i}/N_R^{i} = x \), so that the constraint is fulfilled for sufficiently large ensemble numbers. For most cases, this is closer to experimental reality anyway, as concentration values are commonly averages over macroscopic volumes, e.g. by means of X-ray diffraction [1]. It also allows us to perform calculations for concentration values \( x \) where \( N_R/x \notin \mathbb{N} \).
FIG. 3: (Color online) Direct comparison of the DOS of Cd$_{0.5}$Zn$_{0.5}$Se, calculated in the combination of the VCA (blue), CPA (red) and supercell approach (black) and the EBOM. See text for further details.

III. RESULTS

In this section, we will compare the CPA EBOM and the supercell EBOM to cubic Cd$_x$Zn$_{1-x}$Se, In$_x$Ga$_{1-x}$As and Ga$_x$Al$_{1-x}$N. In addition, we will also add results that are obtained by a pure VCA calculation.

Besides the fact that we have already shown the reliability of the supercell EBOM for cubic Cd$_x$Zn$_{1-x}$Se in comparison with experimental results in [1] (albeit for slightly different material parameters to meet the experimental boundary conditions), this material system is also especially interesting for a quantitative and qualitative analysis of the applicability of the CPA. A closer look at the DOS and the energetic position of the first moments in Fig. 1 reveals that the conduction bands of CdSe and ZnSe neither fulfill the weak scattering nor the split band condition very well, as the energetic range of the overlap is comparable to the difference of the first moments. The In$_x$Ga$_{1-x}$As system under consideration will in contrast be closer to the weak scattering limit. This condition will also apply to the zincblende Ga$_x$Al$_{1-x}$N alloy, which additionally comprises a direct-indirect band gap transition at a certain mixing ratio.

A. Comparison of the overall density of states of Cd$_{0.5}$Zn$_{0.5}$Se

In this section, we will compare the overall DOS of the Cd$_{0.5}$Zn$_{0.5}$Se alloy as calculated with the CPA and the supercell EBOM, using the example of Cd$_{0.5}$Zn$_{0.5}$Se, along with results from the simple VCA. The supercell calculations were performed with 20 microscopically distinct configurations and on cubic supercells with 2048 lattice sites, i.e., 4096 atoms; the numerical parameters for the CPA calculation match those of Fig. 2.

Overall, the alloy DOS of the valence bands is very similar in all three models. This is not very surprising, as the substitutional disorder is restricted to the cations of the material, and the valence bands mainly stem from atomic $p$-orbitals of the Se anions. However, the conduction band DOS accordingly shows different features in the three models.

It is clearly visible that the VCA DOS is an interpolation of the DOS of the pure CdSe and ZnSe material as depicted in Fig. 1, aside from an energetic shift of the bands. No new features arise for the alloy material.

Like in the CPA, the supercell EBOM also gives an alloy DOS of which the structure is more complicated than the DOS of the constituents. The conduction band DOS again splits into a two-subband structure, where the relative spectral weight equals the concentration ratio of the substituents (this also holds for all other values of $x$ with identifiable subband splittings).

Overall, the fact that VCA totally fails to reproduce the additional features of the alloy’s conduction band was to be expected; the one-electron potential which enters the hopping matrix elements is not a self-averaging quantity (in the sense that it can be replaced by its ensemble average for a sufficiently large sample), as opposed to the one-electron Green’s function [2].

B. Comparison of the band gap bowing of Cd$_x$Zn$_{1-x}$Se

We will now extensively examine the accuracy of the CPA approach for properties on a smaller energy scale and use the example of the single-particle band gap for a qualitative as well as quantitative analysis.

Most alloyed bulk semiconductors show a more or less pronounced bowing of the band gap $E_g$ as a function of the concentration $x$. The simplest way to describe...
the deviation from a linear behaviour is the assumption of a parabolic $E_g(x)$ curve and therefore the use of a single, concentration-independent bowing parameter $b$, such that

$$E_g(x) = x E_g^A + (1 - x) E_g^B - x (1 - x) b.$$  \hspace{1cm} (23)

Here, the indices $A$ and $B$ assign the properties of the pure binary materials. In general, the literature values for $b$ show a surprisingly large variety even for apparently comparable experimental conditions (the reader may check comprehensive review articles like \[21\] or \[22\]). For the II-VI bulk alloy Cd$_x$Zn$_{1-x}$Se for example, a broad range of values between $b = 0$ and $b = 1.26$ eV has been reported throughout publications from the last two decades \[17\] \[23\] \[24\] \[25\]. The large disparity on the experimental side can for example result from difficult growth conditions for the mixed systems. On the theoretical side, the inadequate use of too simple approaches like the VCA can lead to wrong results.

In the CPA, the band gap can in principle be read off from the DOS. For numerical reasons, the CPA DOS will not completely fall to zero in the bandgap, as a finite imaginary part $\delta$ of the energy is required. Nevertheless, it is possible to identify the band gap with desired accuracy by increasing the resolution. We used an imaginary part of $\delta = 10^{-4}$ eV and $\# k \approx 10^7$ values in the irreducible BZ. The high BZ resolution has turned out to be crucial to obtain convergence for the results for the band gap. In the Wannier representation, it is furthermore very important to carefully discretize the VCA DOS when using Eq. (16) because the DOS will contain kinks that stem from Van Hove singularities [critical points where $\text{grad}_k E_n(k) = 0$]. The usage of TB models that give a reliable band structure throughout the whole BZ (in contrast to dispersions from effective mass or $k \cdot p$ models) will additionally lead to sharp peaks at some of these critical points, as the slope of non-degenerate bands must also vanish at the BZ boundaries.

Figure 4 shows the conduction band edge region of Cd$_{0.5}$Zn$_{0.5}$Se, calculated in the Wannier CPA. The peak of spectral function of the $k = 0$ quasiparticle obviously coincides with the band edge within the chosen energy resolution of $\Delta z = 5 \times 10^{-3}$ eV. A further analysis (not shown) reveals that the CPA band edge states are mostly $\delta$-like; in case of broadened peaks, the corresponding linewidth is so small that the peak position still allows for a convenient determination of the conduction band edge $E_c$ and the valence band edge $E_v$ with an accuracy of 0.01 eV. Hence, the band gap $E_g(x) = E_c(x) - E_v(x)$ of the alloy can be determined with an accuracy of 0.02 eV.

The corresponding supercell band gap is given by

$$E_g(x) = \min \left\{ E^i_v(x) \right\} - \max \left\{ E^i_v(x) \right\},$$  \hspace{1cm} (24)

where $i$ again numbers the distinct configurations. Note that this definition of the band gap implies

$$E_g(x) \neq \frac{1}{N} \sum_i \left[ E^i_v(x) - E^i_c(x) \right],$$  \hspace{1cm} (25)

i.e., the band gap of the disordered alloy is different from the configurational average over the energy gaps for fixed realizations $i$.

The resulting curves for the Cd$_{0.5}$Zn$_{0.5}$Se band gap are depicted in Fig. 5. In order to perform a detailed examination of the influence of the disorder and the applicability of the CPA, we performed two different supercell calculations for the Cd$_x$Zn$_{1-x}$Se alloy system. In order to get rid of finite size effects, we used supercells with $N_{\text{R}} = 4000$ lattice sites and calculated the band edges for $N = 50$ distinct configurations per concentration. The concentration itself is varied in steps of 0.1.

The left subfigure contains results from the supercell EBOM exactly as described in Sec. II D, thus including the full disorder in the site-diagonal and the hopping matrix elements on the microscopic scale. The supercell results in the right subfigure have been obtained under the artificial restriction to site-diagonal disorder. This means that only the site-diagonal matrix elements differ throughout the cell and with each configuration, while the hopping matrix elements for each concentration were substituted by their VCA values. Both the supercell approach and the CPA then use the same level of mean-field approximation for the hopping matrix elements. As each of supercell bowing curve requires the partial diagonalization of $9 \times 50 = 450$ Hamiltonian matrices (the $x = 0$ and $x = 1$ values are input material parameters), we additionally neglected the spin-orbit coupling for this comparison. Besides an increase in computation time by a factor $2^{3} = 8$, the memory consumption is lowered, as all matrix entries are then real numbers. We also added the pure VCA results to both figures—as the tight-binding matrix is diagonal at $k = 0$, we are left with a linear $E_g(x)$ curve, which is at least able to indicate the deviation of the other results from a linear interpolation.
We will first turn to the full disorder case on the left. Overall, the bowing obtained in the CPA is clearly larger than the corresponding supercell result. When the Wannier representation is used, the bowing curve is slightly closer to the supercell case than in the sp$^3$ basis. This was to be expected, as the overall shapes and bandwidths of the pure CdSe and ZnSe bands are very much alike (see again Fig. 1). Nevertheless, the CPA (as well as the VCA) fails to satisfactorily reproduce the supercell band gaps over the whole concentration range. We can even identify a slight “overbowing”, where the CPA band gap of the alloy dips beneath the value for pure CdSe for the Cd-rich concentrations. This effect is ultimately a consequence of the usage of the concentration-dependent VCA average for the non-diagonal part of the Hamilton. Consequently, it does not occur in standard textbook examples, where the same hopping values for the constituents are used and one is left with a concentration-independent bandwidth.

A look at the right subfigure, where the supercell results with diagonal disorder are given along with the sp$^3$ CPA curve, clearly reveals the importance of the non-diagonal part (as the supercell potential lacks translational invariance, our supercell TB model can only be used in the sp$^3$ basis, so that the Wannier CPA results are also not given again here). We easily notice that the CPA and supercell results now coincide very well. Consequently, we can state that the CPA can in principle simulate the influence of the disorder in the site-diagonal elements on the band gap and the deviations stem from the mean-field treatment for the hopping. If we enforce the constraint $N_{\text{el}}^i/N_R = x$ for single concentration values and thus eliminate the small influence of concentrational disorder (see Sec. III) on the supercell results, the discrepancy is even smaller (not shown).

For the sake of completeness, we depict the Wannier CPA and supercell results including spin-orbit interaction in Fig. 6 (the sp$^3$ CPA results will be omitted from now on). We also added errorbars that account for the reading accuracy and finite size effects. The difference in the first moments of the CdSe and ZnSe conduction bands turns out to be slightly smaller when the spin is included. Obviously, the bowing is reduced and the deviation between the Wannier CPA and supercell results decreases further. Still, only the $x \geq 0.9$ results overlap within the error range. The best possible second-order fit to the $E_g(x)$ curve yields a bowing parameter of $b = (0.71 \pm 0.09)$ eV for the supercell results and $b = (1.0 \pm 0.1)$ eV for the curve as calculated with the Wannier CPA (note that the bowing values in [1] were...
calculated for slightly differing band gap values in the pure case). It should be emphasized that the error range for the bowing values can only account for the influence of the reading accuracy and finite size effects, as well as for the deviation from a parabolic behaviour (this is always to be expected for differing lattice constants, see [20]). The disparities that can arise from the uncertainty in the input parameters for the pure materials (band gaps, effective masses, valence band offsets) from different sources in the literature cannot reliably be estimated at reasonable expense, so that the error range is certainly underestimated.

C. Band gap bowing of In$_x$Ga$_{1-x}$As

As a second example for the calculation of the band gap bowing, we apply the methods to the zincblende bulk alloy In$_x$Ga$_{1-x}$As. The band structures, DOS and corresponding first moments of InAs and GaAs are given in Fig. [8]. A valence band offset of $\Delta E_{vb} = 0.85$ eV [27] has already been incorporated. This value has been obtained by the relative energetic position to transition-metal impurities and is in agreement with experimental data from measurements on Au Schottky barriers [28].

For this parameter set of InAs and GaAs the first moments of the conduction band are closer together than in the case of CdSe and ZnSe, going along with a larger overlap of the bands. Hence, we are closer to the weak scattering condition and therefore expect better results for the concentration-dependent band gap from the (Wannier) CPA. Again using $N = 50$ configurations and $N_R = 4000$ lattice sites for the supercells and also the same numerical parameters for the Wannier CPA, we obtain the bowing curve depicted in Fig. [8].

Overall, the deviation from a linear behaviour (again indicated by the VCA results) is smaller for In$_x$Ga$_{1-x}$As than for Cd$_x$Zn$_{1-x}$Se. Furthermore, all results from the supercell calculations and the CPA calculations now overlap within the error range, although the CPA still slightly overestimates the bowing behaviour. A second-order fit of the $E_E(x)$ values gives a bowing of $b = (0.39 \pm 0.04)$ eV for the supercell results and $b = (0.49 \pm 0.05)$ eV for the curve as calculated with the Wannier CPA. The fact that the resulting ranges touch but do not overlap is mainly due to the deviation from a parabolic curve. Nevertheless, including the error boundaries both values lie in the range between $b = 0.32$–0.46 eV that is recommended in the literature by Vurgaftman et al. [21]. More recent ab initio calculations within the DFT+LDA (which are known to systematically underestimate the band gap) give a slightly larger bowing in the range of 0.5–0.8 eV [29].

D. Band gap bowing of Ga$_x$Al$_{1-x}$N

As a final example, we will calculate the concentration dependent band gap of the zincblende phase of Ga$_x$Al$_{1-x}$N, which is frequently used as barrier material in optoelectronics [21]. While the wurtzite modification of AlN is the only Al-containing III-V semiconductor with a direct band gap, its zincblende modification is most likely indirect with the conduction band minimum at the X-point and the valence band maximum at the Γ-point [30] (although a direct band gap is sometimes also assumed, see e.g. [31]). As can be seen in Fig. 9, the $sp^3$ EBOM is able to reproduce the indirect band gap of AlN properly, as it is also fitted to the X-point energies. We use a valence band offset of $\Delta E_{vb} = 0.8$ eV [21] [22], the resulting relative positions of the first moments and the large conduction band overlap indicate again a good applicability of the CPA. In contrast to the previous material systems, the spin-orbit coupling is one order of magnitude smaller in the nitride compounds and does not influence the results for the bowing.

The $E_E(x)$ results for Ga$_x$Al$_{1-x}$N are depicted in Fig. [10]. The numerical parameters for the CPA and the supercell calculations were chosen identical to those of the previous sections. In all three models, we can clearly identify a crossover in the bowing between $x = 0.3$ and $x = 0.2$. In this region, the character of the band gap changes from a behaviour which is strongly influenced by the indirect AlN material to a direct band gap behaviour dominated by GaN.

While the CPA results coincide very well with the supercell results for the GaN-dominated side at large $x$, they overestimate the bowing on the Al-rich side. In contrast, the VCA, which shows a piecewise linear behaviour with two different slopes, can reproduce the supercell results for high Al contents quite well, but deviates for $0.7 \geq x \geq 0.3$. It additionally should be noted that the CPA results in the Al-rich part have larger error bars, as the determination of the band gap is afflicted with a larger uncertainty in this range due to a larger broadening of the corresponding spectral functions (not shown).

In [23], Vurgaftman et al. report bowing parameters of $b_T = 0.05$–0.53 eV for the Γ-valley of cubic Ga$_x$Al$_{1-x}$N from theory. By additionally taking several experimental results into account (which obviously render larger bowing parameters), they recommend an approximate value of $b_T \approx 0.7$ eV. By only fitting the Γ-valley bowing, i.e. only taking the values for $x \geq 0.3$ into account, augmented by the AlN energy difference at Γ as boundary value, we obtain bowing parameters of $b_T = (0.37 \pm 0.02)$ eV from the supercell calculations and $b_T = (0.4 \pm 0.1)$ eV from the CPA. Consequently, the CPA and supercell values agree within the error range and our results are in reasonably good agreement with the literature values. More recent results from DFT+LDA calculations [32] yield a value of $b_T \approx 0.5$ eV and predict the crossover at about $x = 0.4$. However, it should be noted that these results suffer from the usual underestimation of band gaps in DFT+LDA. The pure GaN and AlN band gaps in their calculations are obtained as 1.93 eV and 3.23 eV respectively. Consequently, they strongly deviate from our input values of 3.26 eV for GaN and 5.346 eV for AlN.
For the sake of comparison, we summed up the results for the bowing parameters in Tab. I. As already stated, the given error ranges only account for the reading accuracy, finite size effects and non-parabolicity of $E_g(x)$ but cannot reflect the reliability of the input band structure parameters for the pure materials.

IV. CONCLUSION AND OUTLOOK

In this paper, we showed that the electronic properties of substitutional semiconductor alloys with an underlying zincblende structure of the type $A_xB_{1-x}C$ can well be described with empirical TB models. We presented a combined theoretical approach, starting from a multi-band TB model with a realistic dispersion and bandwidth throughout the whole Brillouin zone. The density of states and the band gap of the disordered system can then either be determined by exact diagonalization of a large supercell with a large number $N$ of microscopically distinct configurations, or by combination of the TB model with the coherent potential approximation (CPA) and/or the virtual crystal approximation (VCA).

Using the supercell results for Cd$_x$Zn$_{1-x}$Se as reference, we gave a careful quantitative and qualitative analysis of the scope of validity of the CPA and VCA, especially with regards to the calculation of the concentration dependent band gap $E_g(x)$ of the alloy. While the VCA failed over the whole concentration range, the CPA also turned out to be not accurate enough for the Cd$_x$Zn$_{1-x}$Se system under consideration, although the proper choice of the basis set could significantly reduce the discrepancy.

We then applied our TB model to two further different alloy systems, namely the III-V alloy In$_x$Ga$_{1-x}$As and the III-nitride system Ga$_x$Al$_{1-x}$N. For both systems, the CPA gave good results. In case of In$_x$Ga$_{1-x}$As, the CPA and the supercell calculations yielded bowing parameters in good agreement with literature values from experiments. For Ga$_x$Al$_{1-x}$N the band gap bowing showed a crossover behaviour between $x = 0.3$ and $x = 0.2$, due to the fact that cubic GaN has a direct energy gap at the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Material & Supercells & Wannier CPA & Literature \\
\hline
Cd$_x$Zn$_{1-x}$Se & 0.71 ± 0.09 & 1.0 ± 0.1 & 0–1.26 \\
In$_x$Ga$_{1-x}$As & 0.39 ± 0.04 & 0.49 ± 0.05 & 0.32–0.46 \\
Ga$_x$Al$_{1-x}$N & 0.37 ± 0.02 & 0.4 ± 0.1 & 0.05–0.7 \\
\hline
\end{tabular}
\caption{Summary of the results for the bowing parameter $b$ in eV. In case of Ga$_x$Al$_{1-x}$N, the value solely refers to the bowing of the Γ-valley.}
\end{table}
FIG. 9: (Color online) Band structure (left) and DOS and first moments (right) of zincblende GaN and AlN, calculated in the $sp^3$ EBOM, assuming a valence band offset $\Delta E_{vb} = 0.8$ eV and an indirect band gap for AlN. See appendix for details.

FIG. 10: (Color online) Concentration-dependent band gap $E_g(x)$ of Ga$_x$Al$_{1-x}$N, calculated in the VCA (blue), Wannier CPA (red) and supercell method (black).

BZ center, while the conduction band minimum of cubic AlN is located at $X$. This crossover was reproduced in all three models. The CPA and the supercell calculations were able to reproduce the $\Gamma$-valley bowing in satisfactory agreement with the literature. On the Al-rich side ($x \leq 0.3$), the CPA underestimated the band gap when compared to the supercell approach, while the VCA was in surprisingly good agreement.

For the sake of completeness, it should be emphasized that the computational costs of the CPA are far smaller than in the supercell case. If the number of bands has to be augmented or properties far from the band edges become relevant, the supercell approach can quickly become infeasible, as the calculation time scales with the cube of the dimension of the Hamiltonian matrix.

As the supercell calculations and, under certain conditions outlined in this paper, also the CPA can give good results for the concentration-dependent band gap when combined with the ETBM and especially the EBOM, the application to further material systems (with disorder either in the cations or in the anions) will be an interesting task for the future, ideally alongside actual experimental data. Furthermore, the same calculation scheme can be transferred to alloy systems with underlying wurtzite structure by using a suitable TB Hamiltonian [15] for direct as well as indirect band gap materials.

Our supercell approach is also applicable to disordered low-dimensional structures, as shown in [1],[16]. Therefore, in principle also disordered nanowires or superlattices can be investigated. As the CPA is exact only in the limit of infinite dimensions, it may turn out that the CPA + EBOM is less reliable when applied to low-dimensional systems, so that suitable extensions of the CPA must be used.
Appendix

The following tables give the material parameters used throughout this paper, including the sources from the literature.

The band structures in the $sp^3$ EBOM can be fitted to the conventional lattice constant $a$, the spin-orbit splitting $\Delta_{so}$, the effective conduction band mass $m_c$, the Luttinger parameters $\gamma_1, \gamma_2, \gamma_3$, and to a set of energies at the $\Gamma$-point and the $X$-point (denoted by the usual single group notation), where the energy gap $E_g$ is given as $\Gamma_1 - \Gamma_1$ in case of a direct band gap. Additionally, a valence band offset $\Delta E_{vb}$ is incorporated in order to account for the relative energetic position of the two constituents.

These parameters are uniquely connected to the non-vanishing TB matrix elements from Eq. (1) of the present paper by the equations (7)–(17), (33) and (45)–(53) of Ref. [3].

Appendix A: Material parameters CdSe and ZnSe

| Parameter | CdSe | ZnSe |
|-----------|------|------|
| $a$ (Å)   | 6.078 | 5.668 | 33 |
| $\Delta_{so}$ (eV) | 0.41 | 0.43 | 33 |
| $m_c$ (m$_0$) | 0.12 | 0.147 | 31 |
| $\Gamma_1 - \Gamma_{15}$ (eV) | 1.76 | 2.82 | 35 |
| $X_1^c$ (eV) | 2.94 | 4.41 | 36 |
| $X_5^y$ (eV) | -1.98 | -2.08 | 36 |
| $X_3^y$ (eV) | -4.28 | -5.03 | 36 |
| $\gamma_1$ | 3.33 | 2.45 | 34 |
| $\gamma_2$ | 1.11 | 0.61 | 31 |
| $\gamma_3$ | 1.45 | 1.11 | 31 |
| $\Delta E_{vb}$ (eV) | 0.22 | 0 | 33 |

Appendix B: Material parameters InAs and GaAs

| Parameter | InAs | GaAs |
|-----------|------|------|
| $a$ (Å) | 6.058 | 5.653 | 34 |
| $\Delta_{so}$ (eV) | 0.39 | 0.34 | 31 |
| $m_c$ (m$_0$) | 0.022 | 0.067 | 21 |
| $\Gamma_1 - \Gamma_1$ (eV) | 0.417 | 1.519 | 21 |
| $X_1^c$ (eV) | 2.28 | 2.18 | 38 |
| $X_5^y$ (eV) | -2.42 | -2.8 | 38 |
| $X_3^y$ (eV) | -6.64 | -6.7 | 38 |
| $\gamma_1$ | 20.0 | 6.98 | 21 |
| $\gamma_2$ | 8.5 | 2.06 | 21 |
| $\gamma_3$ | 9.2 | 2.93 | 21 |
| $\Delta E_{vb}$ (eV) | 0.85 | 0 | 27 |

Appendix C: Material parameters GaN and AlN

| Parameter | GaN | AlN |
|-----------|-----|-----|
| $a$ (Å) | 4.50 | 4.38 | 34 |
| $\Delta_{so}$ (eV) | 0.017 | 0.019 | 31 |
| $m_c$ (m$_0$) | 0.15 | 0.25 | 31 |
| $\Gamma_1 - \Gamma_{15}$ (eV) | 3.26 | 5.84 | 30 |
| $X_1^c$ (eV) | 4.43 | 5.346 | 30 |
| $X_5^y$ (eV) | -2.46 | -2.315 | 30 |
| $X_3^y$ (eV) | -6.30 | -5.388 | 30 |
| $\gamma_1$ | 2.67 | 1.92 | 31 |
| $\gamma_2$ | 0.75 | 0.47 | 31 |
| $\gamma_3$ | 1.10 | 0.8 | 31 |
| $\Delta E_{vb}$ (eV) | 0.8 | 0 | 33 |

*This parameter has been adjusted by hand, as the origin-inal value of $\gamma_3=0.85$ used in [31] leads to an erroneous curvature in the $\Gamma-K$ direction.*

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