

# Exact-exchange based quasiparticle energy calculations for the band gap, effective masses and deformation potentials of ScN

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The band gaps, longitudinal and transverse effective masses, and deformation potentials of ScN in the rock-salt structure have been calculated employing  $G_0W_0$ -quasiparticle calculations using exact-exchange Kohn-Sham density functional theory one-particle wavefunctions and energies as input. Our quasiparticle gaps support recent experimental observations that ScN has a much lower indirect band gap than previously thought. The results are analyzed in terms of the influence of different approximations for exchange and correlation taken in the computational approach on the electronic structure of ScN.

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## I. INTRODUCTION

Scandium nitride (ScN) is emerging as a versatile material for promising technological applications. As part of the transition metal nitride family it initially generated interest for potential applications as wear resistant and optical coatings due to its mechanical strength, high melting point of  $2600^\circ\text{C}$ <sup>1</sup>, and high hardness ( $H = 21\text{ GPa}$ ) with respect to load deformations<sup>2</sup>. ScN crystallizes in the rock-salt phase with a lattice parameter of  $4.50\text{ \AA}$ <sup>3</sup>. The octahedral bonding arrangement provides a much more favorable environment for the incorporation of transition metal atoms like Mn or Cr than the tetrahedrally coordinated III-V semiconductors, which have up until now been popular candidates for spintronic materials. Successful incorporation of Mn into ScN has been demonstrated<sup>4</sup> and *ab initio* calculations predict Mn-doped ScN to be a dilute ferromagnetic semiconductor<sup>5</sup>. Moreover, ScN has a lattice mismatch of less than 2% to cubic gallium nitride (GaN). This makes ScN structurally compatible with the group-IIIA nitrides<sup>6,7,8,9,10,11,12,13</sup> – an important technological material class, in particular for applications in optoelectronic devices. Alloying ScN with GaN<sup>9,10,11,12</sup> might provide a viable alternative to InGaN alloys for use in light emitting devices or solar cells. In addition multifunctional devices are conceivable if the strong electromechanical response predicted for hexagonal ScN<sup>14</sup> can be utilized.

The electronic band structure of ScN – a key quantity for the design of optoelectronic devices – has been difficult to access both experimentally and theoretically. Early experiments were hampered by various complications in growing films with well defined crystalline orientation, stoichiometry, low background carrier concentration, and surface roughness. For a detailed discussion

we refer to e.g. Ref. 15. Recent advances in growth techniques have led to a systematic improvement of the material's quality<sup>16</sup>. Employing optical spectroscopy and photoemission, Gall *et al.*<sup>15</sup> concluded that ScN is a semiconductor with an indirect  $\Gamma - X$  band gap ( $E_g^{\Gamma-X}$ ) of  $1.3\pm 0.3\text{ eV}$ . The sizable error bar of  $0.3\text{ eV}$  has been mainly attributed to the large background carrier concentration of  $\sim 5\times 10^{20}\text{ cm}^{-3}$  causing an apparent increase of the band gap due to the Burnstein-Moss shift<sup>17</sup>. Reducing the electron carrier concentration to  $4.8\times 10^{18}\text{ cm}^{-3}$  and combining tunneling spectroscopy and optical absorption measurements, Al-Britthen *et al.*<sup>18</sup> were able to reduce the error bar and found a value for  $E_g^{\Gamma-X}$  of  $0.9\pm 0.1\text{ eV}$ .

Early Kohn-Sham density functional theory (KS-DFT) calculations employing the local-density (LDA) or  $X\alpha$  approximations predicted ScN to be a semimetal with a small negative band gap between  $-0.01$  and  $-0.21\text{ eV}$ <sup>19,20,21</sup>. In order to overcome the well known underestimation of the LDA band gap, more advanced exact-exchange (OEPx(cLDA))<sup>15</sup> and screened exchange<sup>22</sup> calculations have been performed, and showed that ScN is a semiconductor with an indirect  $\Gamma$  to  $X$  band gap, in accord with experimental evidence<sup>15,18</sup>. However, the calculated band gap of  $1.60\text{ eV}$  found in both studies is significantly larger than the most recent experimental value of  $0.9\pm 0.1\text{ eV}$ <sup>18</sup>.

In order to shed light on this discrepancy we have performed quasiparticle energy calculations in Hedin's  $GW$  approximation<sup>23</sup>, which is a well established technique to calculate accurate band structure energies and currently the choice for computing quasiparticle band structures of solids<sup>24,25,26</sup>. The quasiparticle calculations predict ScN in the rock-salt phase to have an indirect band gap between the  $\Gamma$  and  $X$  point of  $0.99\pm 0.15\text{ eV}$ , strongly sup-

porting recent experimental findings. In addition we have also determined the direct band gaps and other electronic structure parameters relevant for device simulations: the volume deformation potentials of the main band gaps and the longitudinal and transverse effective masses of the conduction band at the  $X$  point. The effective mass has previously been calculated at the level of the LDA<sup>27</sup>, but to the best of our knowledge only one experimental study has reported a conduction band effective mass for ScN (between 0.1 and 0.2  $m_0$ )<sup>28</sup> so far. For the deformation potentials no experimental or theoretical data is available, yet.

Most commonly, the Greens function  $G_0$  and the screened potential  $W_0$  required in the  $GW$  approach (henceforth denoted  $G_0W_0$ ) are calculated from a set of KS-DFT single particle energies and wave functions  $\{\epsilon_i, \phi_i\}$ . Since  $G_0$  and  $W_0$  are not usually updated by the quasiparticle wave functions and energies  $\{\epsilon_i^{QP}, \phi_i^{QP}\}$  in a self-consistent manner, the quasiparticle energies depend on the approximation used to calculate the input data<sup>25,29,30,31</sup>.

Originally,  $G_0W_0$  calculations were based on LDA data (LDA- $G_0W_0$ ) and were found to accurately predict band gaps of  $sp$ -bonded semiconductors (with a typical error bar of  $\sim 0.1$  eV)<sup>24</sup>. However, complications arise when the LDA- $G_0W_0$  approach is used to calculate the electronic structure of semiconductors with *negative* LDA band gaps<sup>32,33</sup> or when occupied shallow semi-core  $d$  bands are treated as valence in the pseudopotential framework<sup>34,35,36</sup>. For such semiconductors,  $G_0W_0$  calculations based on OEPx(cLDA) data (OEPx(cLDA)- $G_0W_0$ ) have been found to provide a reliable tool to obtain band gaps with an accuracy of 0.1 eV<sup>25,29</sup>.

The key to the improved description in the OEPx(cLDA)- $G_0W_0$  approach can be found in the treatment of exchange. In the exact-exchange KS approach the formal expression for the total energy is the same as in Hartree-Fock. The difference between the two methods lies in the potential felt by the electrons: in Hartree-Fock the exchange potential is non-local, whereas in the exact-exchange KS approach it is local and constructed to be the variationally best local ground state potential to the non-local Hartree-Fock exchange potential<sup>37</sup>. Like Hartree-Fock, the exact-exchange KS approach is therefore free of self-interaction, but since the eigenvalues are solutions to a local potential they are in general closer to (inverse) photoemission data for semiconductors than the Hartree-Fock single particle energies<sup>38,39,40</sup>. The  $GW$  formalism, on the other hand, goes beyond the KS approach and describes the interaction of weakly correlated quasiparticles by means of a non-local, energy dependent self-energy. It takes the form of the non-local exchange potential encountered in the Hartree-Fock approach, which is screened by correlation in the random-phase approximation (RPA). To elucidate the effects of exchange and correlation on the electronic structure of ScN we therefore first analyze the influence of exchange by comparing LDA (GGA) and OEPx(cLDA)

calculations, before turning to the difference between OEPx(cLDA) and  $G_0W_0$ .

The paper is organized as follows. Sec. II describes our computational approach. The results are presented and discussed in Sec. IV. Finally, a summary is given in Sec. IV.

## II. COMPUTATIONAL METHOD

The KS-DFT calculations have been performed with the *ab initio* pseudopotential (PP) plane-wave code SPHingX<sup>41</sup>. A consistent set of norm-conserving scalar-relativistic PPs has been used for each of the exchange-correlation functionals (LDA, GGA and OEPx(cLDA)). The OEPx(cLDA)-PPs have been constructed as described in Ref. 42 and the LDA and GGA ones using the FHI98PP code<sup>43</sup>. All PPs for both Sc and N have been generated according to the Troullier-Martins optimization scheme<sup>44</sup> and have then been transformed into the separable Kleinman-Bylander form<sup>45</sup>. Unlike in the group-III-nitrides GaN and InN the cation  $3s$  and  $3p$  states have moderate binding energies in ScN and the Sc  $3p$  and to a lesser degree also the Sc  $3s$  electrons couple to the upper valence bands as a partial charge density analysis reveals (see Section III A and also Fig. 4 in Ref. 22). For Sc, the entire semicore shell ( $3s$ ,  $3p$  and  $3d$  states) has therefore been treated as valence with an ionic configuration  $[\text{Ne}]3s^23p^63d^1$ . Following Ref. 46, only the  $2s$  and  $2p$  components have been included for N. Adding a  $d$  component for N yields negligible effects on the calculated band structure and total energies of ScN. For Sc, we have chosen a core radius of 1.4, 1.4, and 1.8 bohr for the  $s$ ,  $p$  and  $d$  orbitals, respectively. For N, a common core radius of 1.5 bohr has been adopted. The  $s$  ( $p$ ) component is taken as the local component for Sc (N). Only one projector per angular momentum channel has been used, i.e.  $3p$  and  $3d$  for Sc. We have verified that this procedure does not compromise higher lying states in the same channel by ensuring that the eigenvalues of the  $4s$  and  $4p$  levels in the pseudo-atom reproduce those of the all-electron calculation. These pseudopotentials have been carefully tested (see also below) and are free of ghost states<sup>47</sup>.

For the LDA calculations we have used the Ceperley-Alder<sup>48</sup> exchange-correlation data as parametrized by Perdew and Zunger<sup>49</sup>. The GGA calculations have been performed with the Perdew-Burke-Ernzerhof<sup>50</sup> functional. In the OEPx(cLDA) calculations, the exchange energy and potential have been treated exactly and correlation has been added on the LDA level. Throughout the paper, the combination of exact-exchange and LDA correlation will be referred to as OEPx(cLDA).

The  $G_0W_0$  calculations have been performed employing the  $GW$  space-time approach<sup>51</sup>, in the `gwst` implementation<sup>52,53,54</sup>. The Kohn-Sham eigenvalues and wavefunctions ( $\epsilon_i$  and  $\phi_i$ ) in either OEPx(cLDA) or LDA are used as input to construct  $G_0$  and  $W_0$ . Head and

Approach	$a_0$ (Å)	$B_0$ (GPa)	$B'_0$
Present work			
PP-PW(LDA)	4.455	221	4.27
PP-PW(GGA)	4.533	196	4.36
Other theoretical calculations			
FP-LAPW(LDA) <sup>22</sup>	4.42	235	
FP-LAPW(LDA) <sup>71</sup>	4.44	220	
FP-LAPW(GGA) <sup>22</sup>	4.50	201	
FP-LAPW(GGA) <sup>71</sup>	4.54	201	3.31
Experiment <sup>2</sup>	4.501	182±40	

TABLE I: Structural parameters of ScN: lattice constant ( $a_0$ ), bulk modulus ( $B_0$ ) and its derivative ( $B'_0$ ) calculated in our pseudopotential, plane-wave (PP-PW) approach compared to previous results obtained with the all-electron full-potential linearised augmented plane-wave approach (FP-LAPW) and experiment.

wings of the dielectric matrix (which converge slowly with respect to the  $\mathbf{k}$ -mesh) have been calculated using a fine  $10 \times 10 \times 10$  Monkhorst-Pack (MP) mesh<sup>55</sup>. We find that using an offset of  $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$  yields faster convergence with respect to the number of  $k$ -points, because the  $k$ -point set then contains fewer high-symmetry points. Contributions arising from the non-local part of the pseudopotential are fully taken into account<sup>54</sup>. A regular  $4 \times 4 \times 4$  MP mesh centered on the  $\Gamma$ -point then proves to be sufficient for the full  $G_0W_0$  calculations.

Brillouin zone integrations in the DFT calculations have been performed on a  $4 \times 4 \times 4$  MP mesh. In all calculations an energy cutoff of 80 Ryd is used for the plane wave expansion of the wavefunctions. For the independent particle polarizability  $\chi_0$ , which enters in the calculation of the OEPx(cLDA) potential (see e.g. Ref. 39), an energy cutoff of 55 Ryd gives converged results. Conduction band states up to the same energy cutoff have been included in the calculation of the electronic Green's function in the OEPx(cLDA) as well as in the  $GW$  calculations. These parameters yield converged KS and quasiparticle energies to within 0.05 eV.

We have tested the reliability of our pseudopotential calculations against all-electron calculations in the full potential linearized augmented plane wave (FP-LAPW) approach, where available. For ground state calculations on the level of LDA and GGA we find good agreement for the structural properties, as Table I illustrates. LDA slightly underestimates the lattice constant of ScN compared to experiment<sup>2</sup> by approximately 1%, whereas GGA results in a slight overestimation.

The issue of performing self-consistent  $GW$  calculations is still a matter of debate<sup>56,57,58,59,60</sup>. Unlike in DFT, a self-consistent solution of the full set of equations for the self-energy in many-body perturbation theory would go beyond the  $GW$  approximation and successively introduce higher order electron-electron interactions with every iteration step. Solving the  $GW$  equations self-consistently is therefore inconsistent if no higher order

Approach	$E_g^{\Gamma-\Gamma}$	$E_g^{\Gamma-X}$	$E_g^{X-X}$
Present work			
OEPx(cLDA)- $G_0W_0$	3.51	0.84	1.98
LDA- $G_0W_0$	3.71	1.14	2.06
$[G_0W_0]_{\text{average}}$	3.62	0.99	2.02
OEPx(cLDA)	4.53	1.70	2.59
GGA	2.43	-0.03	0.87
LDA	2.34	-0.15	0.75
Other theoretical work			
OEPx(cLDA) <sup>15</sup>	4.70	1.60	2.90
sX <sup>22</sup>		1.58	2.41
Experiment			
Ref. 15	~3.8	1.30	2.40
Ref. 18		0.9±0.1	2.15

TABLE II: Calculated and experimental band gaps ( $E_g$ ) of ScN (in eV). sX denotes previous screened exchange calculations and  $[G_0W_0]_{\text{average}}$  the arithmetic average between the OEPx(cLDA)- $G_0W_0$  and LDA- $G_0W_0$  results (see text).

electron-electron interactions are included. It was first observed for the homogeneous electron gas<sup>61</sup> that the spectral features broaden with increasing number of iterations in the self-consistency cycle. Similarly, for closed shell atoms the good agreement with experiment for the ionization energy after the first iteration is lost upon iterating the equations to self-consistency<sup>58</sup>. Imposing self-consistency in an approximate fashion<sup>36,60,62,63</sup> is not unique and different methods yield different results. Since the issue of self-consistency within  $GW$  is still discussed controversially, we refrain from any self-consistent treatment and remain with the zeroth order in the self-energy ( $G_0W_0$ ). We argue (see Section III A) that in the case of ScN the error bar resulting from this approximation is only of the order of 0.15 eV.

### III. RESULTS AND DISCUSSION

#### A. Electronic band structure

The quasiparticle band structure of ScN is calculated employing both the OEPx(cLDA)- $G_0W_0$  and LDA- $G_0W_0$  approach. To understand the effect of the starting point on the  $G_0W_0$  calculations we first analyze the KS band structure using three levels of approximations for the XC potential (OEPx(cLDA), GGA and LDA). For a meaningful comparison between the results of these calculations among themselves and with experiment, these electronic structure calculations have been performed at the experimental equilibrium volume. As an example, we show in Fig. 1 the electronic band structures of ScN in LDA, OEPx(cLDA) and OEPx(cLDA)- $G_0W_0$ . Table II summarizes the calculated band gaps ( $E_g^{\Gamma-X}$ ,  $E_g^{X-X}$  and  $E_g^{\Gamma-\Gamma}$ ), previous OEPx(cLDA)<sup>15</sup> and screened exchange<sup>22</sup> results and experimental data<sup>15,18</sup>. For the following discussion we consider only the latest

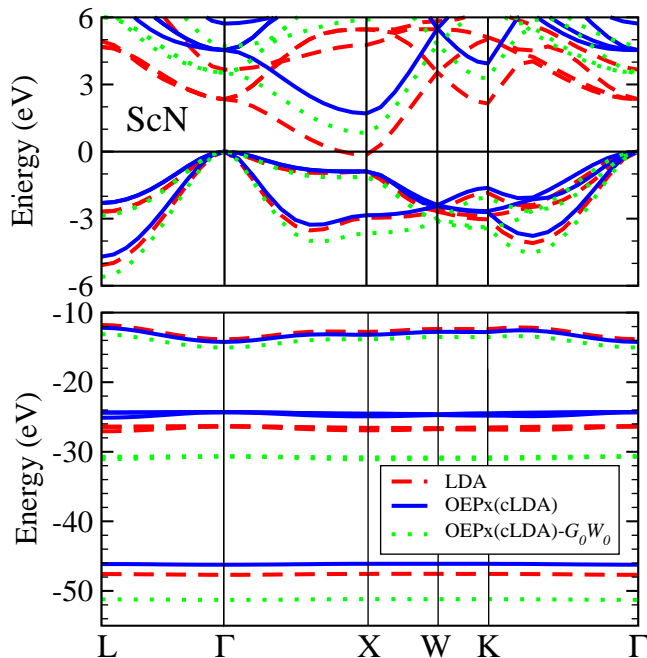


FIG. 1: Electronic band structure of rock-salt ScN in LDA, OEPx(cLDA) and OEPx(cLDA)- $G_0W_0$ . The top panel shows the upper valence and lower conduction bands, aligned at the top of the valence band. The bands in the lower panel have mainly N  $2s$  (around -13 eV), Sc  $3p$  (around -30 eV) and Sc  $3s$  character (around -50 eV).

experimental data of Al-Brithen *et al.* on low background carrier samples<sup>18</sup> as a reference.

In ScN the scandium atom donates its two  $4s$  and single  $3d$  electron to the nitrogen atom. According to the bonding analysis of Harrison and Straub<sup>64</sup>, the five  $d$  states of Sc hybridize with the three valence  $p$  states of the neighboring N atoms in the rock-salt structure of ScN, forming three  $p$ -like bonding, three  $d$ -like anti-bonding  $t_{2g}$  and two  $d$ -like non-bonding  $e_g$  bands. The bonding scheme together with the electron filling of these bands is sketched in Fig. 2. Performing a partial charge density analysis we have confirmed that the upper three valence bands in the DFT calculations correspond to the bonding states and originate mainly from the N  $2p$  states with some admixture of the Sc  $3d$  states, while the lowest conduction bands are the anti-bonding  $t_{2g}$  states with Sc  $3d$  character. The two bands derived from the non-bonding  $e_g$  states are around 1.2 eV higher in energy. This assignment is consistent with the partial density of states analysis of Stampfl *et al.*<sup>22</sup>. The character of the deeper lying bands is given in the caption of Fig. 1.

Focusing first on the band gaps presented in Table II we note that both LDA and GGA underestimate all band gaps by more than 100%. The GGA band gaps are only marginally ( $\sim 0.1$  eV) larger than those of LDA. The reason is a combination of three factors: 1) in direct and inverse photoemission experiments electron addition and removal energies are probed, but the derivative dis-

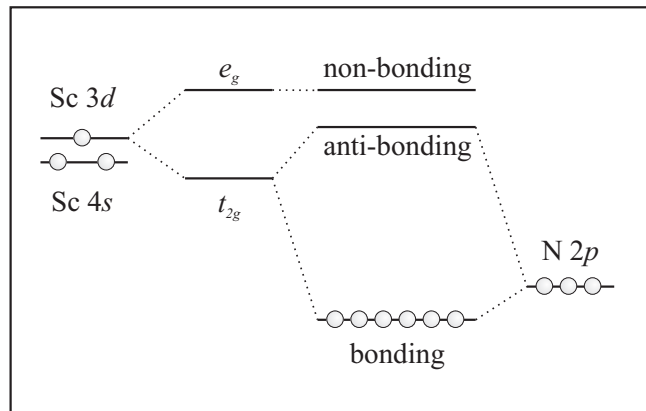


FIG. 2: Schematic diagram of the  $pd$  bonding in rock-salt ScN: the Sc  $3d$  states are split into  $t_{2g}$  and  $e_g$  states by the crystal field. The  $t_{2g}$  states then form bonding and anti-bonding bands with the N  $2p$  states and the  $e_g$  states non-bonding bands that lie higher in energy. The occupation of the relevant states and bands is shown by circles.

continuity of the exchange-correlation potential with respect to changes in the particle number is not taken into account in KS-DFT single-particle energy calculations<sup>65</sup> 2) LDA and GGA are approximate exchange-correlation functionals, which 3) suffer from inherent self-interaction effects. The OEPx(cLDA) formalism also does not fulfill criterion 2), but it is self-interaction free. This leads to a significant opening of the Kohn-Sham band gaps compared to those of LDA and GGA<sup>38,39,40</sup> as is evident from Table II. Although the OEPx(cLDA) formalism exhibits a derivative discontinuity<sup>66,67</sup> and therefore fulfills criterion 1) this is of no benefit in KS-DFT single-particle energy calculations. When the excitation energies are calculated by computing total energy differences in OEPx(cLDA) between the  $N$  and the  $N\pm 1$  electron system (frequently denoted  $\Delta$  self-consistent field ( $\Delta$ SCF) approach), the derivative discontinuity is taken into account properly<sup>66</sup>. In KS-DFT, however, the excitation energies are approximated by Kohn-Sham eigenvalue differences of the  $N$ -electron system alone. The derivative discontinuity does hence not enter the calculation and all states experience the same exchange-correlation potential.

Having established that the removal of the self-interaction in the OEPx(cLDA)-KS approach is the distinguishing feature compared to KS-LDA or KS-GGA calculations we will now illustrate how this leads to an opening of the band gap in ScN. For this it is illuminating to start from the eigenvalues of the isolated Sc and N atoms, depicted in Fig. 3. The removal of the self-interaction in OEPx(cLDA) leads to a downward shift of all atomic states. Since the electrons in the 2nd shell of the nitrogen atom are more localized than the electrons populating the 3rd and 4th shell in scandium the self-interaction correction to the N  $2p$  state is much larger than that of the Sc  $3d$  state. Inspection of the differ-

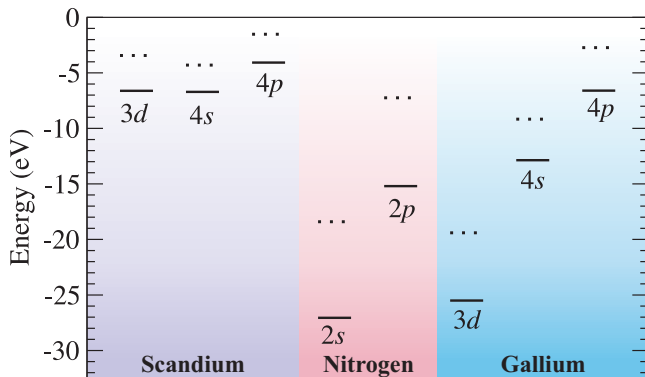


FIG. 3: Eigenvalue spectrum of the isolated Sc atom compared to N and Ga. Dotted lines show the levels in the LDA and solid lines in OEPx(cLDA).

ence between the exchange potential in OEPx(cLDA) ( $v_x^{\text{OEPx(cLDA)}}$ ) and LDA ( $v_x^{\text{LDA}}$ ) shown in Fig. 4(a) reveals that the large relative shift of the atomic N  $2p$  state also translates to the solid. Fig. 4(a) illustrates that  $v_x^{\text{OEPx(cLDA)}}$  is significantly higher than  $v_x^{\text{LDA}}$  in the Sc regions and lower around the N atoms. This difference in  $v_x$  leads to a significant charge density redistribution [shown in Fig. 4(b)]. The charge transfer from the Sc to the N regions gives rise to an increase in the bond ionicity, which, in turn, leads to an opening of the band gap — consistent with our OEPx(cLDA) band structure calculations.

In the II-VI compounds and group-III-nitrides this mechanism is also responsible for an opening of the band gap in OEPx(cLDA) compared to LDA, but it is complemented by a contribution arising from the coupling between the anion semicore  $d$  electrons and the  $2p$  electrons of nitrogen. Taking GaN as example again the Ga  $3d$  electrons of gallium are energetically lower than the  $2p$  electrons of nitrogen, while in Scandium the Sc  $3d$  lie above the N  $2p$  states (cf Fig. 3). Not the anion  $3d$ , like in ScN, but the Ga  $4s$  electrons thus form the lower conduction bands with the nitrogen  $2p$  states. Since the OEPx(cLDA) shift of the N  $2p$  states is larger than that of the Ga  $4s$  states the bond ionicity and hence the band gap increase just like in ScN. In addition the Ga  $3d$  electrons localize stronger in GaN when the self-interaction is removed in the OEPx(cLDA) approach<sup>25</sup>. As a result the  $pd$  repulsion reduces and the valence bands are lowered in energy leading to a further opening of the band gap<sup>68</sup>.

We now turn to the quasiparticle band structure. In the OEPx(cLDA)- $G_0W_0$  approach the band structure is calculated directly at the experimental lattice constant. However, the *negative* LDA band gap (see Table II) impedes the application of this direct approach in the LDA- $G_0W_0$  formalism with the **gwst** code, since in its current implementation<sup>52,53</sup> a clear separation between conduction and valence bands is required. Therefore, an indirect

approach is adopted. First, LDA- $G_0W_0$  calculations are performed at a lattice constant ( $a_0 = 4.75$  Å) larger than the experimental one, where the fundamental band gap in the LDA is small but positive. We then use the LDA *volume* deformation potentials (see Section III B) to determine the corresponding LDA- $G_0W_0$  band gaps at the equilibrium lattice constant. Using the volume deformation potentials of the LDA instead of the quasiparticle ones is a well justified approximation, as we will show in the next subsection. While this approach is in principle not limited to band gaps, it proves to be too cumbersome for a whole band structure calculation, because for every band structure point the corresponding deformation potential would have to be determined.

The quasiparticle band structure is shown in Fig. 1 and the direct band gaps at the  $\Gamma$  and X-point are presented together with the indirect gap between  $\Gamma$  and X in Table II. It is interesting to note that the LDA- $G_0W_0$  and OEPx(cLDA)- $G_0W_0$  calculations, starting from the two extremes (negative band gap in LDA, 0.8 eV overestimation in OEPx(cLDA)), yield quasiparticle band gaps that agree to within 0.3 eV. Since the LDA-based calculations are close to the limit of metallic screening, whereas the OEPx(cLDA)-based calculations form the opposite extreme of starting from a completely self-interaction free exchange-correlation functional, we expect the results of a self-consistent  $GW$  calculation to fall in the range between the LDA- $G_0W_0$  and OEPx(cLDA)- $G_0W_0$  calculations. From these results we estimate the error bar associated with omitting self-consistency in  $GW$  to be of the order of 0.15 eV for ScN. Taking OEPx(cLDA)- $G_0W_0$  results as lower and those of the LDA- $G_0W_0$  as upper bounds, the arithmetic averages for  $E_g^{\Gamma-X}$ ,  $E_g^{\Gamma-\Gamma}$  and  $E_g^{X-X}$  are 0.99, 3.62 and 2.02 eV, respectively. These are significantly lower than those from OEPx(cLDA) and the more approximate screened exchange calculations, as Tab. II demonstrates. Our quasiparticle gaps clearly support recent experimental findings of an indirect gap of  $0.9 \pm 0.1$  eV<sup>18</sup> and are at the lower bound of earlier measurements on samples with unintentionally high background carrier concentration ( $1.3 \pm 0.3$  eV)<sup>15</sup>.

The fact that LDA- $G_0W_0$  and OEPx(cLDA)- $G_0W_0$  calculations yield very similar quasiparticle band gaps is in disagreement with our previous observation for II-VI compounds and GaN<sup>25</sup>. The difference between ScN and these compounds is that for the latter the cation semicore  $d$  shell is fully filled and the remaining  $s$  and  $p$  electrons in the semicore shell are much lower in energy. Taking GaN as an example the  $3s$  electrons in the Gallium atom are approximately 100 eV and the  $3p$  electrons approximately 60 eV lower than in Scandium. Unlike in ScN the  $3p$  derived bands therefore show no noticeable dispersion in GaN (cf Fig. 1). Resolving these more strongly localized  $3s$  and  $3p$  electrons in GaN with plane-waves will thus require significantly higher plane-wave cutoffs<sup>25</sup> than the 80 Ry used in the present study for ScN. In a pseudopotential framework it would hence make sense to explicitly include the  $d$  electrons of the cations in the II-VI



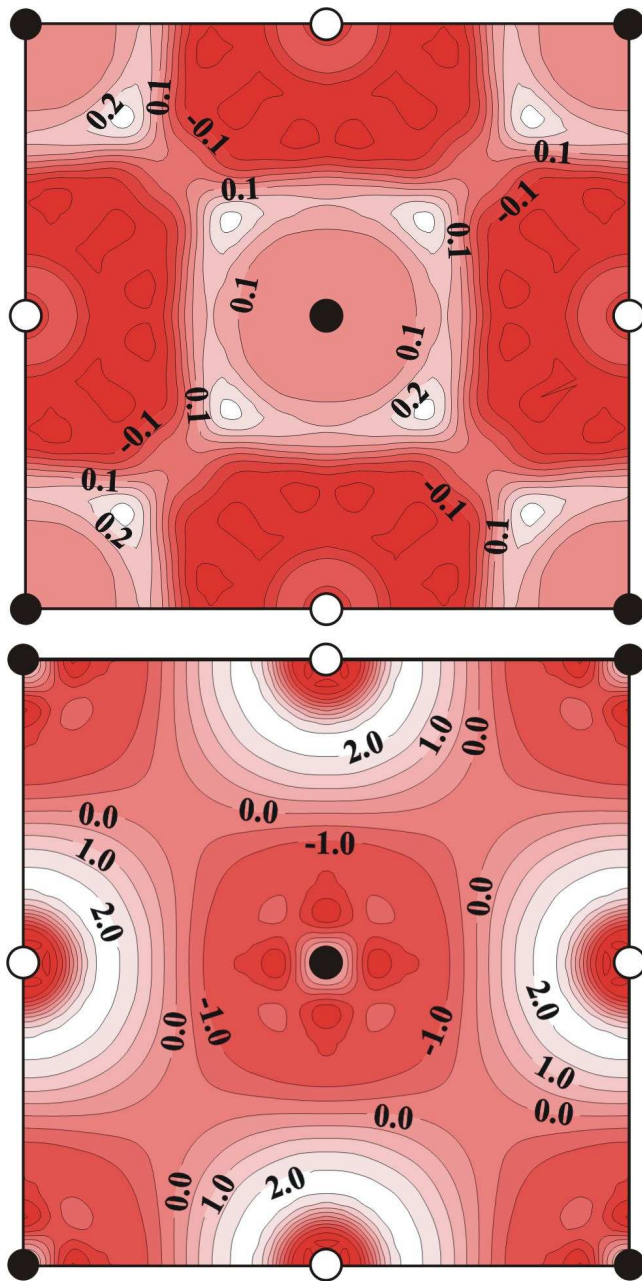


FIG. 4: The difference between (a) the OEPx(cLDA) and LDA exchange potentials (in Hartree) and (b) the electronic charge densities (in electrons/unit cell) of ScN for one of the square faces of the conventional rock-salt unit cell. Black circles denote Sc and white circles N atoms.

compounds and group-III-nitrides as valence electrons, but to freeze the chemically inert semicore  $s$  and  $p$  electrons in the core of the pseudopotential. However, due to the large spatial overlap of the atomic semicore  $s$  and  $p$  with the  $d$  wavefunctions, core-valence exchange is large in these compounds. As a consequence core-valence exchange is treated inconsistently when going from LDA to LDA- $G_0W_0$ , if pseudopotentials are used in this fashion, because the exchange self-energy in the  $GW$  approach

acts on the  $d$  electrons in the solid, but cannot act on the  $s$  and  $p$  electrons in the semicore shell, too. The result is a severe underestimation of the LDA- $G_0W_0$  band gaps and  $d$ -bands that are pushed energetically into the  $p$ -derived valence bands in the II-VI compounds<sup>25,34,35</sup>.

The only way to remedy this problem within LDA- $G_0W_0$  is to free the electrons in question by performing all-electron  $G_0W_0$  calculations<sup>32</sup> or by using pseudopotentials that include the entire shell as valence electrons<sup>34,35,36</sup>, which in the latter case introduces formidably high plane-wave cutoffs. If, on the other hand, OEPx(cLDA) is used for the ground state calculation, then the exchange self-energy already acts on the semicore  $s$  and  $p$  states in the generation of the pseudopotential. Since the exchange self-energy can be linearly decomposed into a core and a valence contribution no non-linear core corrections<sup>69</sup> arise in the Hartree-Fock case and they are expected to be small for OEPx(cLDA) pseudopotentials<sup>39</sup>. We take the fact that the quasiparticle band structure in the OEPx(cLDA)- $G_0W_0$  approach agrees well with (inverse) photoemission data for these materials as indication that when switching from the local potential in OEPx(cLDA) to the non-local self-energy in OEPx(cLDA)- $G_0W_0$  core-valence exchange is treated consistently, as long as OEPx(cLDA) pseudopotentials are used<sup>25</sup>. Since the semicore  $s$  and  $p$  states are less localized in ScN it is computationally feasible to include the entire 3rd shell of Sc as valence in the pseudopotentials (see Section II) and thus to conduct a meaningful comparison between the LDA- $G_0W_0$  and OEPx(cLDA)- $G_0W_0$  calculations, which enables us to assess the error bar with respect to a self-consistent  $GW$  treatment.

It remains to be added that in previous studies, where a significant starting point dependence in LDA- $G_0W_0$  compared to GGA- $G_0W_0$  calculations was noted, this was either due to structural effects<sup>30</sup> or significant differences in the ground state<sup>31</sup> introduced when going from LDA to GGA. Since all calculations in this work were performed at the experimental equilibrium volume the KS band structures in LDA and GGA are very similar (cf. Tab. II) and LDA- $G_0W_0$  and GGA- $G_0W_0$  calculations yield essential the same result.

Finally, Fig. 1 illustrates that the Sc  $3p$  and Sc  $3s$  bands are significantly lowered by the quasiparticle energy calculations. We have argued recently<sup>68</sup> that this lowering can to a large degree be attributed to charge density relaxation effects arising from the removal of an electron from these states. These effects are accounted for in the  $G_0W_0$  approach, but not in DFT Kohn-Sham single-particle energy calculations and are larger for more localized states such as the Sc  $3s$  and  $3p$  bands.

## B. Effective masses and deformation potentials

In this final part we present additional band structure parameters of ScN, namely the transverse ( $m_t^*$ ) and longitudinal ( $m_l^*$ ) conduction band effective masses – at the X

Approach	$m_t^*$	$m_l^*$	$a_v^{\Gamma-\Gamma}$	$a_v^{\Gamma-X}$	$a_v^{X-X}$
OEPx(cLDA)- $G_0W_0$	0.189	1.483	1.54	2.02	2.04
OEPx(cLDA)	0.253	1.450	1.07	2.06	2.21
GGA	0.139	1.625	1.43	1.87	1.92
LDA	0.126	1.570	1.36	1.95	2.03
LDA <sup>27</sup>	0.124	1.441			

TABLE III: Transverse ( $m_t^*$ ) and longitudinal ( $m_l^*$ ) effective masses of the conduction electrons at the X point (in units of  $m_0$ ) and different band gap volume deformation potentials ( $a_v^\alpha$ ) (in eV) for ScN.

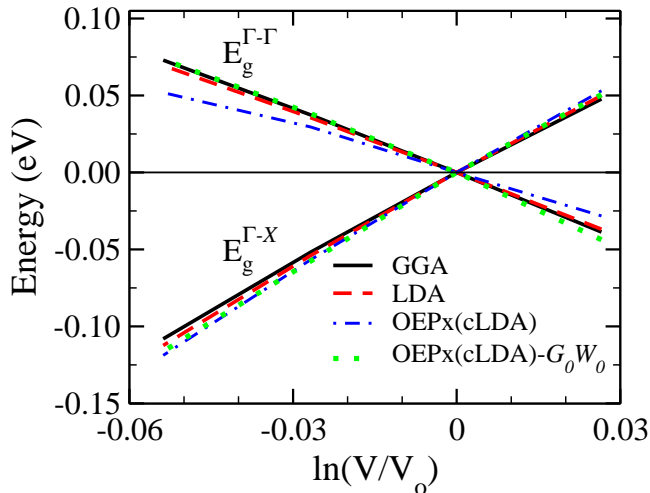


FIG. 5: Variation of the indirect band gap ( $E_g^{\Gamma-X}$ ) and the direct band gap at the  $\Gamma$ -point ( $E_g^{\Gamma-\Gamma}$ ) of ScN with respect to the corresponding band gaps at the experimental equilibrium volume ( $V_0$ ), as a function of  $\ln(V/V_0)$ .

point – and the volume band gap deformation potentials, extracted from our quasiparticle energy calculations. For comparison we will also discuss the corresponding values obtained from LDA, GGA and OEPx(cLDA).

The conduction band effective masses at the X point are calculated by fitting a quadratic function to the corresponding band structure energies along the  $\Delta$  ( $\Gamma$ -X) and Z ( $X$ -W) directions for  $m_t^*$  and  $m_l^*$ , respectively. A small  $k$ -point spacing of 0.01 in units of  $2\pi/a$  yields converged effective masses, which are listed in Table III. Our LDA results are in good agreement with those of Ref. 27. As far as an experimental reference is concerned, we are only aware of one study, where a conduction band effective mass between 0.1 and 0.2  $m_0$  has been reported<sup>28</sup>. Apart from the OEPx(cLDA) results, all our KS-DFT and quasiparticle energy calculations give a transverse effective mass in this range, while the longitudinal effective mass is approximately one order of magnitude larger.

To determine the volume deformation potentials  $a_v^\alpha$ <sup>70</sup> for the band gaps  $E_g^{\Gamma-\Gamma}$ ,  $E_g^{\Gamma-X}$  and  $E_g^{X-X}$ , the rele-

vant band gaps are calculated at four different lattice constants around the experimental equilibrium one. For illustration, we show in Fig. 5 the variation of  $E_g^{\Gamma-\Gamma}$  and  $E_g^{\Gamma-X}$ , with respect to their values at the experimental equilibrium volume, as a function of  $\ln(V/V_0)$ . The corresponding band gaps are then fitted to a quadratic function of  $\ln V$ . The linear deformation potentials obtained in this way are listed in Table III. To the best of our knowledge, no experimental or previous theoretical results are available for the deformation potentials of ScN. Based on our results we conclude that  $a_v^\alpha$  is almost insensitive with respect to the computational approaches considered in this article. The only exception is  $a_v^{\Gamma-\Gamma}$  obtained using the OEPx(cLDA) approach. The fact, that the LDA curves in Fig. 5 are very close to the OEPx(cLDA)- $G_0W_0$  ones, *a posteriori* justifies the use of the LDA volume deformation potential for the indirect calculation of the LDA- $G_0W_0$  band gaps.

#### IV. CONCLUSIONS

Pseudopotential  $G_0W_0$  calculations based on Kohn-Sham density-functional theory calculations in both the LDA and OEPx(cLDA) have been performed for the electronic structure of ScN in the thermodynamically stable rock-salt phase. To analyze the effects of exchange and correlation the atomic and electronic structure has been studied within DFT for several levels of approximations for the exchange-correlation functional (LDA, GGA and OEPx(cLDA)). In agreement with previous calculations for ScN, our LDA (OEPx(cLDA)) band gaps are underestimated (overestimated) by about 100%. Despite this large difference, OEPx(cLDA)- $G_0W_0$  and LDA- $G_0W_0$  calculations for the quasiparticle band structure agree to within 0.3 eV. Our quasiparticle gap of  $0.99 \pm 0.15$  eV supports the recent observation that ScN has a much lower indirect band gap than previously thought. The main advantage of the OEPx(cLDA)- $G_0W_0$  approach lies in the fact that it facilitates a direct calculation of the electronic structure of ScN at the experimental equilibrium volume, whereas for the LDA- $G_0W_0$  calculation an indirect approach has to be taken due to the negative LDA band gap.

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