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Article

# Doping of III–V Arsenide and Phosphide Wurtzite Semiconductors

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15 means that it is easier to p-type dope a wurtzite crystal and the charge carrier concentration at a given temperature and doping dose 16 is larger in the wurtzite as well. As for donors, we show that neutral chalcogen impurities have no clear preference for a specific 17 crystal phase, while charged chalcogen impurities favor substitution in the zincblende structure with a transition energy that is 18 smaller when compared to the wurtzite case (thus, charge carriers are more easily thermally excited to the conduction band in the 19 zincblende phase).

# 20 INTRODUCTION

21 Crystal-phase engineering is an emerging field in nanoscience 22 that consists of the design of materials with tailor-made 23 properties by growing *ad hoc* crystal phases. The interest in this 24 field was boosted by the enormous progresses made in recent 25 years in the growth of semiconducting nanowires (NWs)<sup>1,2</sup> 26 and, specifically, by the fact that metastable crystal phases, 27 which in bulk can only be obtained under extreme conditions 28 of temperature and pressure, can be stabilized at room 29 temperature and atmospheric pressure, thanks to a tight 30 control of growth conditions.<sup>3</sup> Many III-V semiconductors, 31 such as arsenides<sup>4-7</sup> and phosphides,<sup>8-11</sup> that in bulk only 32 exhibit the zincblende (ZB) phase, can take the wurtzite (WZ) 33 structure when grown as NWs. Similarly, Si and Ge group-IV 34 semiconductors that in bulk have the 3C cubic-diamond crystal 35 structure can be synthesized in the 2H hexagonal-diamond 36 (*i.e.*, lonsdaleite) polytype.<sup>12-15</sup> The possibility of growing 37 semiconductors in different crystal phases is very appealing, as <sup>38</sup> it might enable novel applications.<sup>16</sup> For instance, ZB GaP has 39 an indirect band gap and thus a limited light emission 40 efficiency, but in WZ GaP NWs, the band gap becomes direct, 41 resulting in a strong photoluminescence.<sup>9</sup> Direct-band gap 42 emission has also been predicted and reported in hexagonal Ge 43 and SiGe alloys,<sup>17,18</sup> materials that have a notoriously poor 44 light emission in the conventional cubic polytype adopted in <sup>45</sup> the bulk. Moreover, in general, different polytypes can present <sup>46</sup> different electronic,  $^{7,19-21}$  optical,  $^{22-26}$  and phononic proper-47 ties.<sup>27-31</sup>

Perhaps, the most ambitious (and exciting) goal of crystal- 48 phase engineering is the design of complex structures by 49 working only (or mostly) with different polytypes of the same 50 material. The conditions that favor the formation of WZ over 51 ZB segments in III-V NWs are well understood<sup>32-34</sup> and can 52 be dynamically tuned during the growth. Therefore, not only 53 isolated *homointerfaces* between the ZB and WZ crystal phase  $_{54}$  of a same material can be obtained<sup>22,35-37</sup> but also periodic  $_{55}$ superlattice structures can be obtained. In these crystal-phase 56 superlattices, different polytypes of the same material—rather 57 than different materials, like in conventional superlattices—are 58 arranged periodically, building a metamaterial with its own 59 unique properties, which can be tuned by controlling the 60 number of periods and their thickness.<sup>38-41</sup> These crystal- 61 phase interfaces present some advantages over the most 62 common heterojunctions between two different materials: (i) 63 they have a very small lattice mismatch and (ii) they have no 64 chemical intermixing. As a result, they are atomically flat and 65 virtually defect-free, which makes them ideal candidates to 66 design materials with tailored electronic<sup>38,42,43</sup> and phononic 67

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68 properties.<sup>44,45</sup> Similar effects have also been reported in the 69 less-common crystal-phase core—multishell NWs.<sup>46,47</sup>

The vast majority of applications that can be envisaged in 70 71 this context rely on impurity doping, which is the primary 72 approach to tune the electrical conductivity of semiconductors. 73 Indeed, the design of electronic devices is based on the 74 juxtaposition of regions with different doping features, for 75 example, in a pn junction, in a bipolar transistor or in a field-76 effect transistor. Therefore, a detailed understanding of doping 77 in different crystal phases is necessary, both from the viewpoint 78 of the fundamental understanding of the underlying physical 79 mechanisms and for the operation of a multitude of 80 applications. Given a material, is it equally easy to dope it in 81 the ZB and WZ phase? Is the dopant activation energy the 82 same or does it differ in different polytypes? The answers to 83 these questions tell us how the solubility and the charge carrier 84 concentration depend on the crystal phase and have thus far 85 reaching consequences for the design and the optimization of 86 any device.

In this paper, we study by means of first-principles electronic 87 88 structure calculations of the doping of GaAs, GaP, and InP in 89 the ZB and WZ crystal phase, considering a few common 90 donor and acceptor impurities and an amphoteric impurity (Si 91 in GaAs), whose doping type—donor or acceptor—depends 92 on the sublattice where the substitution takes place. We 93 consider both the neutral and singly charged impurity, thus 94 allowing us to estimate the transition energy, that is, the 95 shallowness of the dopant electron state, which determines the 96 concentration of extrinsic charge carriers that are excited in the 97 conduction or valence band for a certain doping dose and at a given temperature, and thus the electrical conductivity. We 98 99 carry out our calculations in bulk systems, as a reasonable 100 approximation of NWs with diameters of several tens of nm 101 and where quantum confinement effects are negligible, which 102 are commonly used in emergent electronic devices. We 103 observe, nonetheless, that previous results obtained for Si 104 showed that ultrathin NWs (diameters of ~2 nm) and bulk 105 systems qualitatively exhibit the same behavior regarding the 106 difference between the cubic and hexagonal crystal phase.<sup>4</sup>

# **107 COMPUTATIONAL METHODS**

Electronic Structure Calculations. We perform density 108 109 functional theory (DFT) calculations with the VASP code<sup>4</sup> 110 with the local density approximation (LDA) for the exchange-111 correlation energy functional. We used a plane wave cutoff 112 ranging from 255.2 to 400 eV, depending on the atomic 113 species involved, with the projector augmented-wave meth-114 od,<sup>49,50</sup> including semicore d electrons for Ga and In. At first, 115 we optimized the lattice parameters of the ZB and WZ <sup>116</sup> primitive cells, sampling the Brillouin zone with a  $10 \times 10 \times 10$ 117 and  $10 \times 10 \times 6$  grid of k-points, respectively. Our results are 118 shown in Table 1. Substitutional impurities at both the group-119 III and group-V sublattice were studied in  $5 \times 5 \times 5$  and  $5 \times 5$  $120 \times 3$  supercells of the 2- and 4-atom ZB and WZ primitive cells, 121 with a  $2 \times 2 \times 2$  grid of k-points. The geometry of the doped 122 supercells was optimized with a quasi-Newton algorithm until 123 all the forces on the atoms were lower than 0.01 eV/Å. This 124 computational setup proved to be accurate enough to give 125 converged values of the formation energy, as shown in previous 126 theoretical studies.<sup>51–5</sup>

<sup>127</sup> We also used density functional perturbation theory <sup>128</sup> (DFPT) to compute the macroscopic dielectric tensor, <sup>129</sup> explicitly accounting for local field effects, which is needed

Table 1. Lattice Parameters, Relative Dielectric Constants, and  $G_0W_0$  Band gaps (LDA Values are Indicated in Parenthesis)

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		a (Å)	c (Å)	$\varepsilon_{xx}$	$\mathcal{E}_{zz}$	bandgap (eV)
GaAs	zincblende	5.601		13.75	13.75	1.66 (0.54)
	wurtzite	3.946	6.510	12.80	13.03	1.46 (0.55)
GaP	zincblende	5.381		10.52	10.52	2.17 (1.39)
	wurtzite	3.790	6.254	10.16	10.60	2.28 (1.32)
InP	zincblende	5.821		11.41	11.41	1.42 (0.62)
	wurtzite	4.107	6.748	10.73	10.96	1.49 (0.68)

for the charge correction scheme described below. We used the 130 optimized lattice vectors and atomic positions obtained at the 131 single-particle DFT level. The computational parameters are 132 the same as for the DFT calculations, but we found that greatly 133 increased k-point meshes are needed to obtain converged 134 results. We used a  $36 \times 36 \times 36$  and  $36 \times 36 \times 22$  grid for the 135 ZB and WZ polytypes, respectively. The results are 136 summarized in Table 1.

On top of the previously optimized primitive cells, we 138 performed *single-shot*  $G_0W_0$  calculations, where quasiparticle 139 energies are calculated from a single *GW* iteration, that is, using 140 the screened potential (*W*) as obtained from the DFT (LDA) 141 step. To improve the quality of the results, a large number of 142 real frequency points (200) have been employed for the 143 Hilbert transform of *W* and self-energy,  $\Sigma$ . Similarly, a very 144 large number of empty bands (~200) have been included in 145 the calculations to ensure convergence of the results.

Handling of Computational Cells with Net Charge. 147 Plane-wave DFT codes, but also localized basis set codes with 148 a Poisson solver based on reciprocal space, assume that the 149 system extends *ad infinitum* with the periodicity set at the 150 input for the computational cell. For charge-neutral systems, 151 this use of periodic boundary conditions (PBCs) is of course 152 well justified in bulk 3D systems, and in lower dimensionalities, 153 it poses no special difficulties, provided that a thick-enough 154 vacuum buffer is added to prevent the interaction between the 155 (spurious) system replicas. 156

The situation is, however, different when addressing systems 157 with isolated net charges, such as the case with an ionized 158 dopant of interest to us here. The long-range Coulomb 159 interaction between the PBC-induced charge replicas will 160 introduce a spurious contribution to the total energy that must 161 be corrected for. Several correction schemes have been 162 proposed<sup>55-58</sup> (see also ref 59 and references therein), often 163 involving the computation of the Madelung energy for some 164 geometric arrangement of point charges in a compensating 165 background.<sup>60,61</sup> In this work, we use a variant of the Makov- 166 Pavne scheme<sup>56</sup> that some of us extended to the case of the 167 arbitrary shape of the computational cell and tensor value of 168 the dielectric constant,  $^{62}$  which is necessary for the hexagonal  $_{169}$  cells in the WZ case. This type of correction was shown to  $_{170}$ accelerate convergence in the case of NWs,<sup>63</sup> and thus, it is 171 also expected to do it here. 172

The elements of the dielectric tensor that we have used for 173 our Madelung correction have been obtained from a DFPT 174 calculation as detailed above. We do not consider it necessary 175 to correct these dielectric tensor entries with their 176 experimental counterparts, given that the interaction between 177 the point charge replicas will be screened according to our 178 used theory level, that is, LDA. 179

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180 Formation Energy. The formation energy is the central 181 quantity in defect analysis and it tells us how likely it is to 182 observe a defect in a crystal matrix,<sup>59</sup> either in the case of 183 intrinsic imperfections of the crystal lattice or-the case 184 addressed here-when it comes to an impurity added on 185 purpose to alter in a controlled way the property of a material. 186 The knowledge of the formation energy of a defect delivers 187 some important information concerning the impurity equili-188 brium concentrations,<sup>64-66</sup> the solubilities,<sup>67,68</sup> or the 189 diffusivities.<sup>69,70</sup> Additionally, by comparing the formation 190 energy of a neutral and singly charged defect, one can obtain 191 the transition energy, a quantity of paramount importance in 192 semiconductor physics that tells us which is the energy needed 193 to thermally excite carriers from the dopant state to the 194 conduction or valence band. The formation energy, as 195 introduced by Zhang and Northrup,<sup>64</sup> is written as follows

$$E_{\rm form} = E_{\rm tot}^{\rm D} - \sum_{i} n_{i}\mu_{i} + q(\mu_{\rm e} + E_{\rm V})$$
196 (1)

197 where  $E_{\text{tot}}^{\text{D}}$  is the total energy of the system including the defect, 198 the sum runs over all the chemical species present, and  $n_i$  and 199  $\mu_i$  are the number of atoms and chemical potential of species *i*, 200 respectively. *q* is the charge state of the defect and  $\mu_e$  is the 201 chemical potential of the electron, which is referred to as  $E_{\text{V}}$ , 202 the highest occupied eigenvalues of the pristine system. 203 Therefore,  $\mu_e$  varies from 0—at the top of the valence 204 band—to  $E_{\text{gap}}$ —at the bottom of the conduction band—thus 205 spanning the whole range of doping conditions.

In the case of a compound semiconductor like the ones 207 studied in this work, eq 1 is conveniently reformulated as<sup>65</sup>

$$E_{\text{form}} = E_{\text{D}}^{\text{tot}} - \frac{1}{2}(n_{\text{Ga}} + n_{\text{As}})\mu_{\text{GaAs}}^{\text{bulk}} - \frac{1}{2}(n_{\text{Ga}} - n_{\text{As}})$$
$$(\mu_{\text{Ga}}^{\text{bulk}} - \mu_{\text{As}}^{\text{bulk}} + \Delta\mu) +$$
$$q(\mu_{\text{e}} + E_{\text{V}}) - n_{\text{X}}\mu_{\text{X}}$$
(2)

208

209 which, for simplicity, is written for the case of GaAs with a 210 generic impurity X. The chemical potentials  $\mu_{Ga}^{bulk}$ ,  $\mu_{As}^{bulk}$ , and 211  $\mu_{\text{GaAs}}^{\text{bulk}}$  refer to the bulk compound of Ga, As, and GaAs. We 212 computed  $\mu_{\text{Ga}}^{\text{bulk}}$  and  $\mu_{\text{As}}^{\text{bulk}}$  as the energy per atom of Ga and As 213 in the orthorhombic and trigonal phase, respectively; for  $\mu_{GaAs}^{bulk}$ 214 we considered the ZB or WZ crystal phase, depending on the 215 case being addressed. Note that  $\mu_{\mathrm{Ga}}$  and  $\mu_{\mathrm{As}}$  are the chemical 216 potential of Ga and As in GaAs, respectively, and that 217 computing their value is not straightforward. However, one can 218 observe that the chemical potential of bulk GaAs is  $\mu_{\text{GaAs}}^{\text{bulk}}$  = 219  $\mu_{\text{Ga}}^{\text{bulk}} + \mu_{\text{As}}^{\text{bulk}} - \Delta H_{\text{fr}}$  where  $\Delta H_{\text{fr}}$  is the heat of formation of 220 GaAs. Now,  $E_{\text{form}}$  is a function of the bulk chemical potential of 221 Ga and As and of the parameter  $\Delta \mu$  that accounts for the 222 difference between the chemical potentials of Ga and As in 223 GaAs and in their respective bulk state. The reformulation of 224  $E_{\text{form}}$  in eq 2 has the advantage of expressing it in terms of well-225 defined quantities (the bulk chemical potentials) and of the 226 parameter

$$\Delta \mu = (\mu_{Ga} - \mu_{As}) - (\mu_{Ga}^{\text{bulk}} - \mu_{As}^{\text{bulk}})$$
(3)

228 which accounts for the macroscopic stoichiometry conditions 229 of the material.  $\Delta \mu$  can vary between  $-\Delta H_{\bar{p}}$  the limit that 230 corresponds to the As-rich conditions, and  $\Delta H_{\bar{p}}$  for the Ga-231 rich material, conditions fixed by the inequalities  $\mu_{Ga} \leq \mu_{Ga}^{bulk}$  252

and  $\mu_{As} \leq \mu_{As}^{bulk}$ . This formalism is also applied to the case of 232 GaP and InP, where we considered the cubic phase for bulk P 233 and the trigonal phase for bulk In to define  $\mu_{P}^{bulk}$  and  $\mu_{In}^{bulk}$ , 234 respectively.

In the case of the chemical potential of the dopant,  $\mu_X$  (X = 236 Si, C, Zn, S, and Te), we have taken the energy of the isolated 237 atom, assuming that the impurity is incorporated into the 238 crystal from the gas phase. This choice, although sound, is an 239 approximation, because the chemical reservoir where the 240 impurity comes from is not necessarily the one of a 241 monoatomic gas. A different choice would result in a different 242 value of the formation energy (see, e.g., ref 71 for a discussion 243 of the case of H in SiC). Notice, however, that whenever we 244 compare the formation energy of a given impurity in the ZB or 245 WZ crystal phase,  $\mu_X$  cancels out and thus, the conclusions do 246 not depend on its exact value, as already shown in refs 53, 54. 247 The same happens when comparing the formation energy of a 248 dopant in the neutral and singly charged state, which 249 determines the transition energy (neither the transition energy 250 depends on  $\mu_{\rm X}$ ). 251

#### RESULTS AND DISCUSSION

**Stability and Band gap of the Pristine Bulk Systems.** <sup>253</sup> Before discussing impurity doping, it is instructive to revise the <sup>254</sup> theory that explains why a given semiconductor adopts one <sup>255</sup> crystal structure or the other, as it will then be important to <sup>256</sup> understand the stability of dopants as well. The simplest way to <sup>257</sup> understand the difference between the ZB and WZ crystal <sup>258</sup> phases is by looking at the stacking sequence along the [111] <sup>259</sup> cubic axis, which is equivalent to the [0001] axis of the WZ. As <sup>260</sup> it is easy to see in Figure 1a,b, in the ZB crystal structure, the <sup>261</sup> fi



Figure 1. Side view of (a) ZB and (b) WZ lattice structure where the ABCABC vs ABABAB stacking along the cubic [111] axis can be appreciated. (c) Staggered and (d) eclipsed dihedral conformation of the ZB and WZ crystal phases.

III–V bilayers are stacked one on top of the other according to 262 an ABCABC stacking motif, while in the WZ one, they follow 263 an ABABAB stacking sequence. When III-arsenides or III- 264 phosphides form, the starting point is always the AB stacking, 265 as the sequence of two bilayers of the same type, for example, 266 AA, is energetically unfavorable. When the next layer grows, it 267 can take the A or C position and thus the ZB or WZ symmetry. 268 In other words, the two polytype structures differ only in the 269 eclipsed (WZ) or staggered (ZB) dihedral conformation that 270 in turn affects the 1,4 atomic interactions (see in Figure 1c,d). 271

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272 Under such conditions, the preference for one of the two 273 crystal phases is the result of a competition between covalent <sup>274</sup> and ionic contributions.<sup>72,73</sup> For compounds following the 275 octet rule,  $A^{N}B^{8-N}$ , the WZ structure is favored when the ionic 276 component is strong. The limiting case is constituted by group-277 IV semiconductors, that is, Si, Ge, and diamond, where the 278 bond is fully covalent and that accordingly adopt the cubic 279 structure. Then, in III-V semiconductors, the larger the ionic contribution is, the less the ZB phase will be favored over the 280 WZ one, until the latter becomes the ground state as in GaN. 281 Our results agree well with this picture, as we found that the 282 283 preference for the ZB structure according to our calculations is 284 21.9 meV for GaAs, 17.4 meV for GaP, and 10.6 meV for InP 285 per unit formula (f.u.), which follows a prediction based on the 286 electronegativity differences between the anion and cation 287 according to the Pauling scale, a crude measure of the ionicity 288 of the bond: 0.37 for GaAs, 0.38 for GaP, and 0.41 in InP. 289 Therefore, the larger the electronegativity difference is, the 290 more ionic is the bond and the less favored is the ZB crystal phase. A more refined definition of the ionicity of a bond is the 291 292 so-called atomic asymmetry parameter (AAS) between a pair 293 of atoms,<sup>74,75</sup> which is known to work well in crystals of the 294 A<sup>N</sup>B<sup>8-N</sup> type. The AAS values for GaAs, GaP, and InP are 295 0.316, 0.371, and 0.506, respectively, which are also in good 296 agreement with the abovementioned energy preferences. Other 297 criteria to estimate the ionic character of the chemical bond are 298 of course possible; see, for example, the ionicity scale based on 299 the centers of maximally localized Wannier functions of Abu-300 Farsakh and Qteish.<sup>76</sup>

One of the reasons of interest in crystal-phase engineering is 301 302 the tunability of the electronic properties. Therefore, another 303 issue that we addressed and briefly discuss before moving to 304 the case of extrinsic doping is the dependence of the electronic 305 band gap on the crystal phase. As it is well known, DFT in its 306 local and semilocal approximation of the exchange-correlation 307 energy severely underestimates the band gap. Therefore, we have performed quasiparticle  $G_0W_0$  calculations that allow 308 309 bypassing this limitation. The results are reported in Table 1. The electronic properties of bulk ZB GaAs have been 310 311 investigated from first principles since decades in view of the 312 microelectronic-oriented applications of the material<sup>77–80</sup> and 313 theoretically assessing the band gap of GaAs main polymorphs 314 remains controversial, as a definitive conclusion is still missing 315 (see ref 16 for a detailed discussion). Furthermore, although 316 on one side, there is a large availability of experimental data 317 about ZB GaAs (see, e.g., refs 81, 82), the scarcity of experimental data about WZ GaAs samples, mostly derived by 318 319 NW structures, makes the comparison with experimental data 320 for this polymorph a quite cumbersome task because of the expected overestimation of the gap due to quantum confine-321 ment effects. Indeed, there are experimental reports for the 322 band gap of WZ-GaAs NWs to be either larger or smaller than 323 the one of ZB-GaAs NWs by few tens of meV.<sup>16</sup> 324

A good description and comparison between DFT- and *GW*calculated electronic properties of the two polymorphs of GaAs have been provided by Zanolli *et al.*:<sup>83</sup> their LDA-calculated value for WZ GaAs is 50 meV larger than the ZB-calculated one, in good agreement with our findings (the absolute values differ because Zanolli *et al.* used a different, custom-made pseudopotential<sup>84</sup>) and with those of Yeh *et al.*<sup>78</sup> On the other hand, the *GW* values they obtained are 1.133 eV (ZB) and 333 1.351 eV (WZ), while at the quasiparticle level, we found the band gap of ZB GaAs to be larger than that of WZ GaAs (see 334 Table 1). 335

A similar problem can be encountered in the case of InP and 336 GaP. Because the WZ bulk phase of these compounds is not 337 stable under normal conditions, all the experimental data 338 concerning its band gap are derived from indirect measure- 339 ments on NWs (in which instead the WZ phase can be 340 stabilized). The theoretical and experimental literature 341 addressing this issue is less extensive when compared to that 342 on GaAs. The band gap of WZ InP has been experimentally 343 reported to be slightly larger than that of ZB InP (see for 344 instance refs 85, 86), in agreement with our results (see Table 345 1) and other theoretical calculations.<sup>87</sup> On the other hand, a 346 limited number of experiments have been performed to 347 investigate the band gap of WZ GaP,<sup>9,26</sup> which is expected to 348 be around 2.19 eV. This value is not far from what we 349 calculated (2.28 eV) and other ab initio quasiparticle 350 calculations. 351

**Impurity Doping: Stability and Transition Energies.** 352 *General Considerations.* Band theory of semiconductors relies 353 on a perfect duality between n- and p-type doping, where 354 electrons and holes are thermally excited from the impurity 355 state to the conduction and valence band. Microscopically, 356 however, this duality breaks down because chemical bonds are 357 formed by electrons only. Therefore, the case of donors, where 358 the four bonds of a tetrahedral semiconductor can be satisfied 359 and there is an additional, loosely bound electron, is different 360 from the case of acceptors, where the substitutional impurity 361 only has three electrons to form bonds. 362

In the ZB phase, all atoms occupy the center of a perfect 363 tetrahedron with all four first neighbor distances equal ( $T_d$  364 symmetry). This local symmetry is maintained in the case of 365 doping with deformations consisting of the sole uniform 366 contraction or expansion of the bond length. In the WZ phase, 367 each atom has three equidistant first neighbors, while the 368 fourth neighbor, along the c direction, is usually more far apart 369  $(C_{3\nu}$  symmetry). The WZ structure has thus more structural 370 freedom to adjust to perturbations induced by impurities 371 because the variations in the bonding can be tuned by the fact 372 that there are two different types of bonds. Therefore, when an 373 acceptor is introduced in the lattice, it will try to form three 374 bonds, something that is favored in the WZ structure where 375 three of the bonds can become stronger and one weaker, the 376 final outcome being the stabilization of the lattice. This does 377 not happen in the ZB lattice. Thus, introducing electron 378 deficiency in the pristine III-V solids provides a bias for the 379 WZ structure. 380

Another way of tuning the WZ–ZB stability is by altering 381 the ionic component of the bonding. In III–V solids, the bond 382 is always partly ionic and one partner is electron-rich, whereas 383 the other is electron-poor. Adding electrons or holes has 384 different effects: adding electrons increases the electronic 385 asymmetry and thus the ionic contribution, whereas adding 386 holes decreases the electronic asymmetry and thus the ionic 387 contribution. According to the discussion in the previous 388 section, an increased ionicity favors the WZ lattice, while more 389 covalent bonds favor the ZB. Therefore, adding (removing) 390 electrons is expected to stabilize the WZ (ZB) crystal phase. 391

Acceptors. We now move to the discussion of the main 392 results of our study and start with impurities that provide p- 393 type doping. We computed the formation energies of five 394 different systems doped with an acceptor:  $C_{As}$ @GaAs,  $Si_{As}$ @ 395 GaAs,  $Zn_{Ga}$ @GaAs,  $Zn_{Ga}$ 

397 notation CAS@GaAs stands for a C atom substituting an As 398 atom in a GaAs lattice (and likewise for the other cases). In all 399 the cases, we considered the neutral charge state and the -1400 charge state, which is expected to be the more stable charge 401 state when the Fermi level lies above the dopant level. These 402 are all textbook cases of acceptors, where an atom of the lattice 403 is substituted by an impurity from the group of the periodic 404 table immediately to its left. Impurities from group-IV can, in 405 principle, be both donors and acceptors, depending on the 406 sublattice chosen for the substitution.<sup>89</sup> This is the case of Si@ 407 GaAs, which acts as an acceptor when it substitutes an As atom 408 and as a donor when it substitutes a Ga atom. C could behave 409 similarly, but substitution at the As sublattice is much more 410 stable than substitution at the Ga sublattice (we found a difference of 0.27 and 0.37 eV in ZB and WZ GaAs, 411 412 respectively), so the latter in practice never occurs. We recall 413 that we carried out our calculations in bulk systems, as an 414 approximation of realistic, large-diameter NWs. For a study of 415 extrinsic defects in GaAs NWs, the interested reader can see, 416 for example, the studies of Galicka et al.<sup>90</sup> and Diao et al.;<sup>91</sup> 417 intrinsic defects in GaAs and their relation with polytypism 418 have been explored by Du et al.<sup>92</sup>

419 The results of the formation energy as a function of the 420 chemical potential of the electron for GaAs are shown in 421 Figure 2. As it can be seen, all the three acceptors have some



**Figure 2.** Formation energies as a function of the chemical potential of the electron of Si, C, and Zn in ZB (continuous line) and WZ (dashed line) GaAs. The side panels show zoomed-in views of  $Si_{As}$  (top) and  $Si_{Ga}$  (bottom).

422 features in common: (i) the neutral impurity is always more 423 stable in the WZ lattice, for all values of  $\mu_e$  (see dashed lines in 424 Figure 2); (ii) the increased stability is similar in all the cases; 425 and (iii) the transition energy is (slightly) smaller in the WZ 426 and the impurity state is *shallower* (see the zoomed view for 427 Si<sub>As</sub>@GaAs). Simply put, it is easier to p-type dope GaAs in the 428 WZ phase and these dopants will be easier to activate.

Following the arguments given above, we now attempt to an end to the observed behavior. A very important factor to an understanding the role of the impurity is the mismatch between the impurity and the host lattice. The four and Ga–As bond lengths in pristine WZ GaAs are 2.422 ( $\times$ 3) and and an end 2.433 Å. Let us consider the case of Si<sub>As</sub>@GaAs (the full list of bond lengths is given in the Supporting Information). The Si- 435 As bond lengths around the impurity are 2.348  $(\times 3)$  and 2.353 436 Å, that is, they are all shorter because Si is smaller than As. The 437 four distances associated with the four nearest neighbor Ga 438 atoms are 2.440-2.430 (×3) and 2.348-2.353 Å. This means 439 that the structural perturbation of the impurity is almost 440 limited to the second coordination sphere of the impurity. 441 However, more important to notice is the fact that the three 442 bonds for every nearest neighbor of the impurity connecting 443 with the rest of the GaAs lattice are longer than in the pristine. 444 In other words, the stabilizing effect due to the four bonds of 445 the Si impurity is at least partially compensated by the 446 destabilization of the 12 Ga-As bonds of the second 447 coordination sphere. Of course, this effect occurs even more 448 intensely for the case of CAs@GaAs. A different situation 449 occurs for Zn<sub>Ga</sub>@GaAs. In that case, the Zn-As distances are 450 2.395 ( $\times$ 3) and 2.397 Å, which are shorter than the initial ones 451 but not as much as for Si. However, now, the distances 452 connecting the four nearest neighbors with the rest of the 453 GaAs lattice are all around 2.390-2.400 Å, that is, they are all 454 shorter than the initial ones. Clearly, the better match between 455 the impurity and the host lattice allows a weaker but better 456 balanced distortion of the lattice, which avoids the above- 457 mentioned destabilization of 12 bonds and transforms it into 458 stabilization.

For all neutral acceptor impurities studied (Table 2), we find 460 t2 that whatever the mismatch is, the WZ structure is clearly 461

Table 2. Difference in the Neutral and Charged Impurity Formation Energy,  $\Delta E_{\text{form}}$ , between the ZB and WZ Structures (a Positive Value Indicates That the WZ Is More Stable) for the Series of Acceptor Impurities Studied<sup>*a*</sup>

		GaAs		GaP	InP
	Si <sub>As</sub>	C <sub>As</sub>	Zn <sub>Ga</sub>	Znp	Znp
$\Delta E_{\rm form}^{0}$	187	248	197	94	33
$\Delta E_{\rm form}^{-1}$	201	265	210	119	39
$\Delta E(0/-)$	14	17	13	25	6

<sup>*a*</sup>All energies are given in meV/f.u. We also report the difference in transition energies,  $\Delta E(0/-)$ , between the ZB and WZ structures (a positive value indicates that the impurity state in WZ is shallower).

preferred. This is the consequence of two features, both 462 already anticipated in the discussion in the previous section: 463 (i) acceptor impurities generate electron deficiency in the 464 already electron-deficient sites of the lattice and (ii) as far as 465 the impurity is smaller or similar in size to the original host 466 atom, the induced structural perturbation is more easily 467 accommodated within the WZ lattice because of the larger 468 structural freedom degrees allowing a 3 + 1-type coordination. 469 As shown in Table 2, this preference is even increased for the 470 charged impurities. Thus, the transition energies for acceptor 471 impurities are always smaller (i.e., the impurity level is closer to 472 the valence band,  $\Delta E(0/-)$ , in Table 2) in the WZ structure. If 473 we consider impurities in the GaAs lattice, it is clear that the 474 increase in the preference when the impurity is charged is an 475 almost constant value (the only exception is singly charged Si 476 that does not favor any crystal phase). By analyzing the Bader 477 charges before and after the charging, we could conclude that 478 there is barely any change at the impurity and four nearest 479 neighbor sites, thus suggesting that the hole resulting from the 480 acceptor impurity must be very delocalized in the lattice. 481 Because adding an electron increases the charge asymmetry, 482

483 the WZ should be further stabilized over the ZB because of the 484 charging, although the effect is only modest for acceptor 485 impurities. Consequently, our calculations suggest that smaller 486 transition energies will be associated with larger stabilizations 487 of the WZ structure for the neutral impurity.

All these considerations are straightforwardly extended to 489 the case of  $Zn_{Ga}$ @GaP and  $Zn_{In}$ @InP, whose formation 490 energies are shown in Figures 3 and 4, and thus confirm the 491 generality of the trends discussed.



Figure 3. Formation energies as a function of the chemical potential of the electron of Te, S, and Zn in ZB (continuous line) and WZ (dashed line) GaP. The side panels show zoomed-in views of  $Zn_{Ga}$  (top) and Te<sub>p</sub> (bottom).



Figure 4. Formation energies as a function of the chemical potential of the electron of Te and Zn in ZB (continuous line) and WZ (dashed line) InP. The side panels show zoomed-in views of  $Zn_{\rm in}$  (top) and Te<sub>p</sub> (bottom).

492 **Donors.** We considered four different systems doped with a 493 donor:  $Si_{Ga}$ @GaAs,  $S_P$ @GaP,  $Te_P$ @GaP, and  $Te_P$ @InP. In all 494 these cases, an atom of the lattice is substituted by an impurity 495 from the group of the periodic table immediately to its right. 496 We studied each impurity in the neutral and +1 charge state, 497 which is expected to be the more stable charge state when the Fermi level lies below the dopant level. As mentioned above, Si 498 is an amphoteric dopant, so although  $Si_{As}$ @GaAs is an 499 acceptor, here, we study  $Si_{Ga}$ @GaAs that acts as a donor. 500

The results of the formation energy as a function of the 501 chemical potential of the electron for the three compounds 502 investigated are shown in Figures 2-4. Also, in this case, it is 503 possible to highlight some common features: (i) neutral 504 chalcogen impurities, S and Te, show no clear preference for 505 the ZB or WZ crystal phase; (ii) charged chalcogen impurities 506 favor substitution in the ZB structure; and (iii) the transition 507 energy is smaller in the ZB, that is, the impurity state is 508 shallower (see the zoomed-in view of Si<sub>Ga</sub>@GaAs, Te<sub>P</sub>@GaP, 509 and Tep@InP in the side panels). Therefore, at variance with 510 the case of acceptors, donor impurities are more easily 511 activated in the ZB crystal phase, while their solubility is 512 larger in ZB structures when the impurities are in the +1 513 charge state. We note that occasionally, the transition energy 514 falls within the conduction band, this being a known 515 shortcoming of using LDA to account for the exchange- 516 correlation energy and thus of the underestimation of the band 517 gap. We have indeed computed much more accurate band gaps 518 from  $G_0W_0$  calculations, but treating the doped supercells at 519 the same level of the theory is beyond the current 520 computational capabilities and, obviously, single-particle and 521 many-body results cannot be mixed together. Therefore, the 522 conclusions directly related to transition energies obtained 523 from DFT-LDA calculations can only be taken to be 524 semiquantitative,<sup>59</sup> and approaches that suggest to ignore the 525 calculated band edges and reference charge transition levels to 526 marker levels<sup>93</sup> or to the average electrostatic potential<sup>94–96</sup> 527 have been proposed. We recall once again, however, that our 528 main goal is understanding the difference between doping with 529 a certain impurity the ZB and WZ crystal phase of a given 530 semiconductor and not to quantitatively estimate the transition 531 energies. Hence, we argue that all the conclusions based on 532 such comparisons are robust and the physical insight they 533 provide is reliable. 534

The donors that we studied belong to two different 535 categories. When P is substituted by S or Te neutral impurities, 536 a structural perturbation different from that discussed above 537 takes place. Both atoms are strongly electronegative and 538 although they act as donors toward the lattice by generating an 539 extra electron, they also gain electron density. For instance, the 540 calculated Bader charges for Sp@GaP and Tep@GaP are 6.85 541 and 6.38 e<sup>-</sup>, respectively, in the WZ structure and 6.83 and 542 6.42 e<sup>-</sup> in the ZB structure (for comparison, the Bader charge 543 of P in the pristine GaP lattice amounts to 5.70 e<sup>-</sup> in the ZB 544 and 5.72 e<sup>-</sup> in the WZ; remember that because of the inclusion 545 of 3d electrons in the valence of the Ga atom, the total charge 546 for each Ga-P pair is 18 e<sup>-</sup>). In fact, this electronic gain 547 mostly originates from the polarization of the bonds between 548 the very electronegative chalcogen atom and the weakly 549 electronegative Ga atom. The important structural observation 550 is that in contrast with acceptors, the bonds between the 551 chalcogen and the four nearest neighbors become clearly 552 longer than in the pristine crystal. For instance, the Ga-P 553 bonds in WZ GaP are 2.327 (×3) and 2.338 Å. The X–Ga (X 554 = S and Te) bond lengths around the impurity in  $X_P @GaP$  are 555 as long as 2.407 (×3) and 2.413 Å for X = S and 2.610 (×3) 556 and 2.617 Å for X = Te. The anionic chalcogen atoms, with 557 their high electron density, strongly push the four nearest 558 neighbor atoms, compressing the lattice around the second 559 coordination sphere of the impurity. Under such circum- 560

561 stances, the additional structural degree of freedom of the WZ 562 structure becomes considerably less effective and the very 563 isotropic nature of the ZB structure becomes comparable or 564 even slightly preferred. Only for the more expanded lattice of 565 InP, the WZ structure is again slightly favored (see Table 3).

Table 3. Difference in the Neutral and Charged Impurity Formation Energy,  $\Delta E_{\text{form}}$ , between the ZB and WZ Structures (a Positive Value Indicates That the WZ Is More Stable) for the Series of Donor Impurities Studied<sup>a</sup>

	GaAs	GaP		InP
	Si <sub>Ga</sub>	Sp	Tep	Tep
$\Delta E_{ m form}{}^0$	152	-7	-39	20
$\Delta E_{\rm form}^{+1}$	-8	-130	-122	-117
$\Delta E(+/0)$	160	123	83	137

<sup>*a*</sup>All energies are given in meV/f.u. We also report the difference in transition energies,  $\Delta E(+/0)$ , between the ZB and WZ structures (a positive value indicates that the impurity state in ZB is shallower).

In contrast, because of the structural mismatch, Si<sub>Ga</sub>@GaAs 567 behaves in the same way described above for the case where Si 568 was acting as an acceptor; the only difference is that the short 569 distances with the four nearest neighbors are now a bit longer 570 (*i.e.*, 2.372 (×3) and 2.382 Å for Si<sub>Ga</sub> compared with 2.348 571 (×3) and 2.353 Å for Si<sub>As</sub> in GaAs WZ). Thus, according to 572 our calculations, Si in GaAs has a preference for WZ 573 irrespective of acting as a donor or an acceptor. In fact, the 574 calculated energy differences are comparable (187 meV/f.u. for 575 Si<sub>As</sub> and 152 meV/f.u. for Si<sub>Ga</sub>). This result emphasizes the key 576 role of the mismatch in enforcing the WZ–ZB preference.

Note that among the different impurities studied, charging the impurity always favors the ZB structure even when the impurity is smaller than the host atom replaced (Table 3). This contribution is relatively large and finally determines the preference of all donor impurities studied for the ZB structure. Be believe the origin of this result is that, as noted above, removing the electron provided by the neutral impurity electrons the ionicity of the lattice and consequently, the ZB structure is favored. According to our calculations, for donors for donors will increase with the size of the impurity and/or decreasing the cell constants of the pristine lattice.

As a final remark, we observe that our computed transition 90 energies, indicating that donor states are shallower in the ZB 91 crystal phase, agree well with the predictions of the hydrogenic 92 model of substitutional impurities within effective mass theory 93 (EMT). Within this simple model, the substitutional impurity 94 form four bonds with the nearest neighbors, with negligible 95 relaxation effects and charge transfer, leaving one unpaired 96 electron whose energy is approximately given by

$$E_n \sim -\mathrm{Ry}\frac{m^*}{\varepsilon^2 n^2} \tag{4}$$

597

598 where  $m^*$  is the effective mass in units of the electron mass, n599 is the main quantum number,  $\varepsilon$  is the (relative) static dielectric 600 constant, and Ry is the Rydberg constant. This is the quantum 601 mechanical solution of the hydrogen atom except for the fact 602 that it contains parameters of the bulk host crystal, such as  $m^*$ 603 and  $\varepsilon$ .  $E_n$  is the energy of the unpaired electron relative to the 604 conduction band minimum, so large values of  $\varepsilon$  and small 605 values of  $m^*$  both contribute to make the impurity shallower, 628

that is,  $E_n$  small. If we look at the computed values of the static 606 dielectric constant collected in Table 1, we see that for GaAs, 607 GaP, and InP, when going from the ZB to the WZ, it decreases 608 (with a reduction, *i.e.*, slightly more pronounced for the *zz* 609 component of the tensor). As for the electron effective mass, it 610 has been shown experimentally that it is heavier in the WZ 611 than in the ZB,  $^{36,37,97,98}$  a trend corroborated by our 612 calculations. Therefore, both these effects tend to make the 613 impurity state deeper in the WZ, in agreement with the 614 computed transition energies. EMT also provides an estimate 615 for the effective Bohr radius of the ground state, which is 616

$$a_{\rm B} \sim (\varepsilon/m^*) a_0 \tag{5}_{617}$$

where  $a_0 \sim 0.577$  Å is the Bohr radius of the isolated hydrogen 618 atom. The effective Bohr radius gives a useful indication of the 619 distance over which the dopant wavefunction extends. This 620 value ranges from 0.5 to 11 nm, indicating that the 621 wavefunction can be considerably delocalized and that the 622 donor electron loosely binds to the dopant atom. This 623 observation agrees with the computed Bader charges of the 624 donors that barely change when the system goes from neutral 625 to charged, that is, the additional charge effectively spreads all 626 over the atoms of the supercell. 627

We have presented first-principles density functional calcu- 629 lations of impurity doping in GaAs, GaP, and InP, comparing 630 their stability and transition energies when dopants are 631 introduced in the ZB or in the WZ. The cubic ZB crystal 632 structure is the common crystal phase of bulk arsenides and 633 phosphides, but doping of the WZ is becoming increasingly 634 important because this crystal phase can be stabilized even at 635 room temperature and atmospheric pressure when these 636 semiconductors are grown as NWs. Our results highlight a 637 general trend where acceptors favor substitution in WZ 638 crystals, where they have a shallower electronic state, allowing 639 an easier excitation of charge carriers for band transport. The 640 situation is reversed for donors, which feature a shallower 641 impurity state and higher solubilities in the ZB. These 642 observations are rationalized in terms of the local distortion 643 and electronic charge reorganization upon doping. In 644 particular, we show that (i) the reduced symmetry of the 645 WZ is better suited to accommodate the local relaxation of 646 acceptors, which favors a three-fold coordination and (ii) ionic 647 bonds favor the WZ lattice, while more covalent bonds favor 648 the ZB and the ionic character of the bond can be increased 649 (decreased) by adding electrons (holes). These results are 650 important for the design and optimization of electronic devices 651 based on semiconducting NWs in the growing field of crystal- 652 phase engineering. 653

ASSOCIATED CONTENT	654			
Supporting Information	655			
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First-neighbor distances of the pristine crystal, of the	658			
impurity, and of the four first neighbors (PDF)	659			
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#### 690 Notes

691 The authors declare no competing financial interest.

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## 712 **REFERENCES**

- 713 (1) Wang, N.; Cai, Y.; Zhang, R. Q. Growth of nanowires. *Mater. Sci.* 714 *Eng.*, R **2008**, *60*, 1–51.
- 715 (2) Schmidt, V.; Wittemann, J. V.; Senz, S.; Gösele, U. Silicon 716 Nanowires: A Review on Aspects of their Growth and their Electrical 717 Properties. *Adv. Mater.* **2009**, *21*, 2681–2702.
- 718 (3) Caroff, P.; Bolinsson, J.; Johansson, J. Crystal Phases in III–V 719 Nanowires: From Random Toward Engineered Polytypism. *IEEE J.* 720 Sel. Top. Quantum Electron. **2011**, *17*, 829–846.
- 721 (4) Koguchi, M.; Kakibayashi, H.; Yazawa, M.; Hiruma, K.; 722 Katsuyama, T. Crystal Structure Change of GaAs and InAs Whiskers

from Zinc-Blende to Wurtzite Type. Jpn. J. Appl. Phys., Part 1 1992, 723 31, 2061. 724 (5) Persson, A. I.; Larsson, M. W.; Stenström, S.; Ohlsson, B. J.; 725

Samuelson, L.; Wallenberg, L. R. Solid-phase diffusion mechanism for 726 GaAs nanowire growth. *Nat. Mater.* **2004**, *3*, 677–681. 727

(6) Harmand, J. C.; Patriarche, G.; Péré-Laperne, N.; Mérat- 728 Combes, M.-N.; Travers, L.; Glas, F. Analysis of vapor-liquid-solid 729 mechanism in Au-assisted GaAs nanowire growth. *Appl. Phys. Lett.* 730 **2005**, *87*, 203101. 731

(7) Funk, S.; Li, A.; Ercolani, D.; Gemmi, M.; Sorba, L.; Zardo, I. 732
Crystal Phase Induced Bandgap Modifications in AlAs Nanowires 733
Probed by Resonant Raman Spectroscopy. ACS Nano 2013, 7, 1400-734
1407. 735

(8) Mohan, P.; Motohisa, J.; Fukui, T. Controlled growth of highly 736 uniform, axial/radial direction-defined, individually addressable InP 737 nanowire arrays. *Nanotechnology* **2005**, *16*, 2903. 738

(9) Assali, S.; Zardo, I.; Plissard, S.; Kriegner, D.; Verheijen, M. A.; 739 Bauer, G.; Meijerink, A.; Belabbes, A.; Bechstedt, F.; Haverkort, J. E. 740 M.; Bakkers, E. P. A. M. Direct Band Gap Wurtzite Gallium 741 Phosphide Nanowires. *Nano Lett.* **2013**, *13*, 1559–1563. 742

(10) Vu, T. T. T.; Zehender, T.; Verheijen, M. A.; Plissard, S. R.; 743 Immink, G. W. G.; Haverkort, J. E. M.; Bakkers, E. P. A. M. High 744 optical quality single crystal phase wurtzite and zincblende InP 745 nanowires. *Nanotechnology* **2013**, *24*, 115705. 746

(11) Lehmann, S.; Wallentin, J.; MÅrtensson, E. K.; Ek, M.; 747
Deppert, K.; Dick, K. A.; Borgström, M. T. Simultaneous Growth of 748
Pure Wurtzite and Zinc Blende Nanowires. *Nano Lett.* 2019, *19*, 749
2723–2730. 750

(12) Vincent, L.; Patriarche, G.; Hallais, G.; Renard, C.; Gardès, C.; 751 Troadec, D.; Bouchier, D. Novel Heterostructured Ge Nanowires 752 Based on Polytype Transformation. *Nano Lett.* **2014**, *14*, 4828–4836. 753

(13) Hauge, H. I. T.; Verheijen, M. A.; Conesa-Boj, S.; Etzelstorfer, 754
T.; Watzinger, M.; Kriegner, D.; Zardo, I.; Fasolato, C.; Capitani, F.; 755
Postorino, P.; Kölling, S.; Li, A.; Assali, S.; Stangl, J.; Bakkers, E. P. A. 756
M. Hexagonal Silicon Realized. *Nano Lett.* 2015, 15, 5855–5860. 757

(14) Hauge, H. I. T.; Conesa-Boj, S.; Verheijen, M. A.; Koelling, S.; 758
Bakkers, E. P. A. M. Single-Crystalline Hexagonal Silicon-Germanium. 759
Nano Lett. 2017, 17, 85–90. 760

(15) Vincent, L.; Djomani, D.; Fakfakh, M.; Renard, C.; Belier, B.; 761 Bouchier, D.; Patriarche, G. Shear-driven phase transformation in 762 silicon nanowires. *Nanotechnology* **2018**, *29*, 125601. 763

(16) Tizei, L. H. G.; Amato, M. Electronic structure and optical 764 properties of semiconductor nanowires polytypes. *Eur. Phys. J. B* 765 **2020**, 93, 16. 766

(17) Cartoixà, X.; Palummo, M.; Hauge, H. I. T.; Bakkers, E. P. A. 767
M.; Rurali, R. Optical Emission in Hexagonal SiGe Nanowires. *Nano* 768 *Lett.* 2017, 17, 4753–4758. 769

(18) Fadaly, E. M. T.; Dijkstra, A.; Suckert, J. R.; Ziss, D.; van 770 Tilburg, M. A. J.; Mao, C.; Ren, Y.; van Lange, V. T.; Korzun, K.; 771 Kölling, S.; et al. Direct-bandgap emission from hexagonal Ge and 772 SiGe alloys. *Nature* **2020**, 580, 205–209. 773

(19) Zardo, I.; Yazji, S.; Hörmann, N.; Hertenberger, S.; Funk, S.; 774 Mangialardo, S.; Morkötter, S.; Koblmüller, G.; Postorino, P.; 775 Abstreiter, G. E1(A) Electronic Band Gap in Wurtzite InAs 776 Nanowires Studied by Resonant Raman Scattering. *Nano Lett.* 777 **2013**, *13*, 3011–3016. 778

(20) De Luca, M.; Polimeni, A. Electronic properties of wurtzite- 779 phase InP nanowires determined by optical and magneto-optical 780 spectroscopy. *Appl. Phys. Rev.* **2017**, *4*, 041102. 781

(21) Senichev, A.; Corfdir, P.; Brandt, O.; Ramsteiner, M.; Breuer, 782 S.; Schilling, J.; Geelhaar, L.; Werner, P. Electronic properties of 783 wurtzite GaAs: A correlated structural, optical, and theoretical analysis 784 of the same polytypic GaAs nanowire. *Nano Res.* **2018**, *11*, 4708–785 4721. 786

(22) Spirkoska, D.; Arbiol, J.; Gustafsson, A.; Conesa-Boj, S.; Glas, 787 F.; Zardo, I.; Heigoldt, M.; Gass, M. H.; Bleloch, A. L.; Estrade, S.; 788 et al. Structural and optical properties of high quality zinc-blende/ 789 wurtzite GaAs nanowire heterostructures. *Phys. Rev. B: Condens.* 790 *Matter Mater. Phys.* **2009**, 80, 245325. 791 792 (23) Heiss, M.; Conesa-Boj, S.; Ren, J.; Tseng, H.-H.; Gali, A.; 793 Rudolph, A.; Uccelli, E.; Peiró, F.; Morante, J. R.; Schuh, D.; Reiger, 794 E.; Kaxiras, E.; Arbiol, J.; Fontcuberta i Morral, A. Direct correlation 795 of crystal structure and optical properties in wurtzite/zinc-blende 796 GaAs nanowire heterostructures. *Phys. Rev. B: Condens. Matter Mater.* 797 *Phys.* **2011**, *83*, 045303.

798 (24) De Luca, M.; Zilli, A.; Fonseka, H. A.; Mokkapati, S.; 799 Miriametro, A.; Tan, H. H.; Smith, L. M.; Jagadish, C.; Capizzi, M.; 800 Polimeni, A. Polarized Light Absorption in Wurtzite InP Nanowire 801 Ensembles. *Nano Lett.* **2015**, *15*, 998–1005.

802 (25) Zilli, A.; De Luca, M.; Tedeschi, D.; Fonseka, H. A.; 803 Miriametro, A.; Tan, H. H.; Jagadish, C.; Capizzi, M.; Polimeni, A. 804 Temperature Dependence of Interband Transitions in Wurtzite InP 805 Nanowires. *ACS Nano* **2015**, *9*, 4277–4287.

806 (26) Assali, S.; Greil, J.; Zardo, I.; Belabbes, A.; de Moor, M. W. A.;
807 Koelling, S.; Koenraad, P. M.; Bechstedt, F.; Bakkers, E. P. A. M.;
808 Haverkort, J. E. M. Optical study of the band structure of wurtzite
809 GaP nanowires. J. Appl. Phys. 2016, 120, 044304.

810 (27) Zardo, I.; Conesa-Boj, S.; Peiro, F.; Morante, J. R.; Arbiol, J.; 811 Uccelli, E.; Abstreiter, G.; Fontcuberta i Morral, A. Raman 812 spectroscopy of wurtzite and zinc-blende GaAs nanowires: Polar-813 ization dependence, selection rules, and strain effects. *Phys. Rev. B:* 814 *Condens. Matter Mater. Phys.* **2009**, *80*, 245324.

(28) Raya-Moreno, M.; Aramberri, H.; Seijas-Bellido, J. A.; Cartoixà,
816 X.; Rurali, R. Thermal conductivity of hexagonal Si and hexagonal Si
817 nanowires from first-principles. *Appl. Phys. Lett.* 2017, *111*, 032107.

(29) Raya-Moreno, M.; Rurali, R.; Cartoixà, X. Thermal conductivity
for III-V and II-VI semiconductor wurtzite and zinc-blende polytypes:
The role of anharmonicity and phase space. *Phys. Rev. Mater.* 2019, *3*,
084607.

822 (30) Fasolato, C.; De Luca, M.; Djomani, D.; Vincent, L.; Renard, 823 C.; Di Iorio, G.; Paillard, V.; Amato, M.; Rurali, R.; Zardo, I. 824 Crystalline, Phononic, and Electronic Properties of Heterostructured 825 Polytypic Ge Nanowires by Raman Spectroscopy. *Nano Lett.* **2018**, 826 *18*, 7075–7084.

(31) de Matteis, D.; De Luca, M.; Fadaly, E. M. T.; Verheijen, M. A.;
López-Suárez, M.; Rurali, R.; Bakkers, E. P. A. M.; Zardo, I. Probing
Lattice Dynamics and Electronic Resonances in Hexagonal Ge abd
Si<sub>x</sub>Ge<sub>1-x</sub> Alloys in Nanowires by Raman Spectroscopy. *ACS Nano*2020, *14*, 6845–6856.

(32) Glas, F.; Harmand, J.-C.; Patriarche, G. Why Does Wurtzite
Form in Nanowires of III-V Zinc Blende Semiconductors? *Phys. Rev. Lett.* 2007, 99, 146101.

(33) Dubrovskii, V. G.; Sibirev, N. V.; Harmand, J. C.; Glas, F.
Growth kinetics and crystal structure of semiconductor nanowires. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2008, 78, 235301.

838 (34) Dubrovskii, V. G.; Sibirev, N. V. Growth thermodynamics of 839 nanowires and its application to polytypism of zinc blende III-V 840 nanowires. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, 77, 841 035414.

(35) Zheng, H.; Wang, J.; Huang, J. Y.; Wang, J.; Zhang, Z.; Mao, S.
X. Dynamic Process of Phase Transition from Wurtzite to Zinc
Blende Structure in InAs Nanowires. *Nano Lett.* 2013, *13*, 6023–
6027.

846 (36) Corfdir, P.; Van Hattem, B.; Uccelli, E.; Conesa-Boj, S.; 847 Lefebvre, P.; Fontcuberta i Morral, A.; Phillips, R. T. Three-848 Dimensional Magneto-Photoluminescence as a Probe of the 849 Electronic Properties of Crystal-Phase Quantum Disks in GaAs 850 Nanowires. *Nano Lett.* **2013**, *13*, 5303–5310.

851 (37) Tedeschi, D.; Fonseka, H. A.; Blundo, E.; del Águila, A. G.;
852 Guo, Y.; Tan, H. H.; Christianen, P. C. M.; Jagadish, C.; Polimeni, A.;
853 De Luca, M. Hole and Electron Effective Masses in Single InP
854 Nanowires with a Wurtzite-Zincblende Homojunction. ACS Nano

(38) Caroff, P.; Dick, K. A.; Johansson, J.; Messing, M. E.; Deppert,
K.; Samuelson, L. Controlled polytypic and twin-plane superlattices in
858 III–V nanowires. *Nat. Nanotechnol.* 2009, *4*, 50–55.

855 2020, 14, 11613-11622.

(39) Dick, K. A.; Thelander, C.; Samuelson, L.; Caroff, P. Crystal 859 Phase Engineering in Single InAs Nanowires. *Nano Lett.* **2010**, *10*, 860 3494–3499. 861

(40) Algra, R. E.; Verheijen, M. A.; Borgström, M. T.; Feiner, L.-F.; 862 Immink, G.; van Enckevort, W. J. P.; Vlieg, E.; Bakkers, E. P. A. M. 863 Twinning superlattices in indium phosphide nanowires. *Nature* **2008**, 864 456, 369–372. 865

(41) Burgess, T.; Breuer, S.; Caroff, P.; Wong-Leung, J.; Gao, Q.; 866 Tan, H. H.; Jagadish, C. Twinning Superlattice Formation in GaAs 867 Nanowires. ACS Nano **2013**, 7, 8105–8114. 868

(42) Zhang, L.; Luo, J.-W.; Zunger, A.; Akopian, N.; Zwiller, V.; 869 Harmand, J.-C. Wide InP Nanowires with Wurtzite/Zincblende 870 Superlattice Segments Are Type-II whereas Narrower Nanowires 871 Become Type-I: An Atomistic Pseudopotential Calculation. *Nano* 872 *Lett.* **2010**, *10*, 4055–4060. 873

(43) Amato, M.; Kaewmaraya, T.; Zobelli, A.; Palummo, M.; Rurali, 874 R. Crystal Phase Effects in Si Nanowire Polytypes and Their 875 Homojunctions. *Nano Lett.* **2016**, *16*, 5694–5700. 876

(44) De Luca, M.; Fasolato, C.; Verheijen, M. A.; Ren, Y.; Swinkels, 877
M. Y.; Kölling, S.; Bakkers, E. P. A. M.; Rurali, R.; Cartoixà, X.; Zardo, 878
I. Phonon Engineering in Twinning Superlattice Nanowires. *Nano* 879 *Lett.* 2019, 19, 4702–4711. 880

(45) Carrete, J.; López-Suárez, M.; Raya-Moreno, M.; Bochkarev, A. 881 S.; Royo, M.; Madsen, G. K. H.; Cartoixà, X.; Mingo, N.; Rurali, R. 882 Phonon transport across crystal-phase interfaces and twin boundaries 883 in semiconducting nanowires. *Nanoscale* **2019**, *11*, 16007–16016. 884

(46) Corfdir, P.; Lewis, R. B.; Marquardt, O.; Küpers, H.; Grandal, 885 J.; Dimakis, E.; Trampert, A.; Geelhaar, L.; Brandt, O.; Phillips, R. T. 886 Exciton recombination at crystal-phase quantum rings in GaAs/ 887 In<sub>x</sub>Ga<sub>1-x</sub>As core/multishell nanowires. *Appl. Phys. Lett.* **2016**, *109*, 888 082107. 889

(47) Royo, M.; De Luca, M.; Rurali, R.; Zardo, I. A review on III-V 890 core-multishell nanowires: growth, properties, and applications. *J.* 891 *Phys. D: Appl. Phys.* **201**7, *50*, 143001. 892

(48) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab 893 initio total-energy calculations using a plane-wave basis set. *Phys. Rev.* 894 *B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169. 895

(49) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B*: 896 *Condens. Matter Mater. Phys.* **1994**, 50, 17953. 897

(50) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the 898 projector augmented-wave method. *Phys. Rev. B: Condens. Matter* 899 *Mater. Phys.* **1999**, *59*, 1758. 900

(51) El-Mellouhi, F.; Mousseau, N.; Ordejón, P. Sampling the 901 diffusion paths of a neutral vacancy in silicon with quantum 902 mechanical calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* 903 **2004**, 70, 205202. 904

(52) Sholihun; Ishii, F.; Saito, M. First-principles calculations of 905 multivacancies in germanium. *Jpn. J. Appl. Phys.* **2016**, *55*, 011301. 906 (53) Amato, M.; Ossicini, S.; Canadell, E.; Rurali, R. Preferential 907 Positioning, Stability, and Segregation of Dopants in Hexagonal Si 908 Nanowires. *Nano Lett.* **2019**, *19*, 866–876. 909

(54) Amato, M.; Kaewmaraya, T.; Zobelli, A. Extrinsic Doping in 910 Group IV Hexagonal-Diamond-Type Crystals. J. Phys. Chem. C 2020, 911 124, 17290–17298. 912

(55) Leslie, M.; Gillan, N. J. The energy and elastic dipole tensor of 913 defects in ionic crystals calculated by the supercell method. *J. Phys. C:* 914 *Solid State Phys.* **1985**, *18*, 973–982. 915

(56) Makov, G.; Payne, M. C. Periodic boundary conditions in ab 916 initio calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *51*, 917 4014–4022. 918

(57) Freysoldt, C.; Neugebauer, J.; de Walle, C. G. V. Fully Ab Initio 919 Finite-Size Corrections for Charged-Defect Supercell Calculations. 920 *Phys. Rev. Lett.* **2009**, *102*, 016402. 921

(58) Freysoldt, C.; Neugebauer, J.; Van de Walle, C. G. Electrostatic 922 interactions between charged defects in supercells. *Phys. Status Solidi* 923 *B* **2011**, 248, 1067–1076. 924

(59) Freysoldt, C.; Grabowski, B.; Hickel, T.; Neugebauer, J.; 925 Kresse, G.; Janotti, A.; Van de Walle, C. G. First-principles 926 927 calculations for point defects in solids. *Rev. Mod. Phys.* **2014**, *86*, 253–928 305.

929 (60) Ziman, J. M. Principles of the Theory of Solids, 2nd ed.; 930 Cambridge University Press, 1972; pp 37-41.

931 (61) Ewald, P. P. Die Berechnung optischer und elektrostatischer 932 Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253–287.

933 (62) Rurali, R.; Cartoixà, X. Theory of Defects in One-Dimensional
934 Systems: Application to Al-Catalyzed Si Nanowires. *Nano Lett.* 2009,
935 9, 975–979.

936 (63) Rurali, R.; Palummo, M.; Cartoixà, X. Convergence study of
937 neutral and charged defect formation energies in Si nanowires. *Phys.*938 *Rev. B: Condens. Matter Mater. Phys.* 2010, *81*, 235304.

939 (64) Zhang, S.; Northrup, J. Chemical potential dependence of 940 defect formation energies in GaAs: Application to Ga self-diffusion. 941 *Phys. Rev. Lett.* **1991**, *67*, 2339–2342.

942 (65) Northrup, J. E.; Zhang, S. B. Dopant and defect energetics: Si in 943 GaAs. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 47, 6791– 944 6794.

945 (66) Van de Walle, C. G. Energies of various configurations of 946 hydrogen in silicon. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 947 49, 4579–4585.

948 (67) Van de Walle, C. G.; Laks, D. B.; Neumark, G. F.; Pantelides, S. 949 T. First-principles calculations of solubilities and doping limits: Li, Na, 950 and N in ZnSe. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 47, 951 9425–9434.

952 (68) Luo, X.; Zhang, S. B.; Wei, S.-H. Theory of Mn supersaturation 953 in Si and Ge. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 954 033308.

955 (69) Fahey, P. M.; Griffin, P. B.; Plummer, J. D. Point defects and 956 dopant diffusion in silicon. *Rev. Mod. Phys.* **1989**, *61*, 289–384.

957 (70) Stumpf, R.; Scheffler, M. Theory of self-diffusion at and growth 958 of Al(111). *Phys. Rev. Lett.* **1994**, *72*, 254–257.

959 (71) Aradi, B.; Gali, A.; Deák, P.; Lowther, J. E.; Son, N. T.; Janzén,
960 E.; Choyke, W. J. Ab initio density-functional supercell calculations of
961 hydrogen defects in cubic SiC. *Phys. Rev. B: Condens. Matter Mater.*962 *Phys.* 2001, 63, 245202.

963 (72) Yeh, C.-Y.; Lu, Z. W.; Froyen, S.; Zunger, A. Zinc-blende– 964 wurtzite polytypism in semiconductors. *Phys. Rev. B: Condens. Matter* 965 *Mater. Phys.* **1992**, *46*, 10086–10097.

966 (73) Ito, T. Simple Criterion for Wurtzite-Zinc-Blende Polytypism
967 in Semiconductors. Jpn. J. Appl. Phys., Part 1 1998, 37, L1217–L1220.
968 (74) García, A.; Cohen, M. L. First-principles ionicity scales. I.
969 Charge asymmetry in the solid state. Phys. Rev. B: Condens. Matter

970 Mater. Phys. 1993, 47, 4215–4220.
971 (75) García, A.; Cohen, M. L. First-principles ionicity scales. II.
972 Structural coordinates from atomic calculations. Phys. Rev. B: Condens.
973 Matter Mater. Phys. 1993, 47, 4221–4225.

974 (76) Abu-Farsakh, H.; Qteish, A. Ionicity scale based on the centers 975 of maximally localized Wannier functions. *Phys. Rev. B: Condens.* 976 *Matter Mater. Phys.* **2007**, 75, 085201.

977 (77) Wei, S.-H.; Zunger, A. Predicted band-gap pressure coefficients 978 of all diamond and zinc-blende semiconductors: Chemical trends. 979 Phys. Rev. B: Condens. Matter Mater. Phys. **1999**, 60, 5404–5411.

980 (78) Yeh, C.-Y.; Wei, S.-H.; Zunger, A. Relationships between the 981 band gaps of the zinc-blende and wurtzite modifications of 982 semiconductors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 983 50, 2715–2718.

984 (79) Lany, S.; Zunger, A. Assessment of correction methods for the 985 band-gap problem and for finite-size effects in supercell defect 986 calculations: Case studies for ZnO and GaAs. *Phys. Rev. B: Condens.* 987 *Matter Mater. Phys.* **2008**, *78*, 235104.

(80) Giorgi, G.; Schilfgaarde, M.; Korkin, A.; Yamashita, K. On the
989 Chemical Origin of the Gap Bowing in (GaAs)<sub>1-x</sub>Ge<sub>2x</sub> Alloys: A
990 Combined DFT-QSGW Study. *Nanoscale Res. Lett.* 2010, 5, 469–
991 477.

(81) Ley, L.; Pollak, R. A.; McFeely, F. R.; Kowalczyk, S. P.; Shirley,
93 D. A. Total valence-band densities of states of III-V and II-VI
94 compounds from x-ray photoemission spectroscopy. *Phys. Rev. B:*95 Solid State 1974, 9, 600–621.

(82) Lautenschlager, P.; Garriga, M.; Logothetidis, S.; Cardona, M. 996 Interband critical points of GaAs and their temperature dependence. 997 *Phys. Rev. B: Condens. Matter Mater. Phys.* **1987**, *35*, 9174–9189. 998 (83) Zanolli, Z.; Fuchs, F.; Furthmüller, J.; von Barth, U.; Bechstedt, 999

F. Model GW band structure of InAs and GaAs in the wurtzite phase. 1000 *Phys. Rev. B: Condens. Matter Mater. Phys.* 2007, 75, 245121. 1001
(84) Zanolli, Z. Private communication. 1002

(85) Tedeschi, D.; De Luca, M.; del Águila, A. G.; Gao, Q.; 1003 Ambrosio, G.; Capizzi, M.; Tan, H. H.; Christianen, P. C. M.; 1004 Jagadish, C.; Polimeni, A. Value and anisotropy of the electron and 1005 hole mass in pure wurtzite InP nanowires. *Nano Lett.* **2016**, *16*, 6213–1006 6221. 1007

(86) Mishra, A.; Titova, L. V.; Hoang, T. B.; Jackson, H. E.; Smith, 1008 L. M.; Yarrison-Rice, J. M.; Kim, Y.; Joyce, H. J.; Gao, Q.; Tan, H. H.; 1009 Jagadish, C. Polarization and temperature dependence of photo- 1010 luminescence from zincblende and wurtzite InP nanowires. *Appl. Phys.* 1011 *Lett.* **2007**, *91*, 263104. 1012

(87) Belabbes, A.; Panse, C.; Furthmüller, J.; Bechstedt, F. Electronic 1013 bands of III-V semiconductor polytypes and their alignment. *Phys.* 1014 *Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 075208. 1015

(88) Belabbes, A.; Bechstedt, F. Forbidden Band-Edge Excitons of 1016 Wurtzite-GaP: A Theoretical View. *Phys. Status Solidi B* **2019**, 256, 1017 1800238. 1018

(89) Giorgi, G.; Yamashita, K. Amphoteric behavior of Ge in GaAs: 1019 an LDA analysis. *Modell. Simul. Mater. Sci. Eng.* **2011**, *19*, 035001. 1020

(90) Galicka, M.; Buczko, R.; Kacman, P. Segregation of Impurities 1021 in GaAs and InAs Nanowires. J. Phys. Chem. C **2013**, 117, 20361– 1022 20370. 1023

(91) Diao, Y.; Liu, L.; Xia, S. Exploration the p-type doping 1024 mechanism of GaAs nanowires from first-principles study. *Phys. Lett.* 1025 *A* **2019**, 383, 202–209. 1026

(92) Du, Y. A.; Sakong, S.; Kratzer, P. As vacancies, Ga antisites, and 1027 Au impurities in zinc blende and wurtzite GaAs nanowire segments 1028 from first principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, 1029 87, 075308.

(93) Coutinho, J.; Torres, V. J. B.; Jones, R.; Briddon, P. R. Electrical 1031 activity of chalcogen-hydrogen defects in silicon. *Phys. Rev. B:* 1032 *Condens. Matter Mater. Phys.* **2003**, *67*, 035205. 1033

(94) Alkauskas, A.; Broqvist, P.; Pasquarello, A. Defect Energy 1034 Levels in Density Functional Calculations: Alignment and Band Gap 1035 Problem. *Phys. Rev. Lett.* **2008**, *101*, 046405. 1036

(95) Komsa, H.-P.; Broqvist, P.; Pasquarello, A. Alignment of defect 1037 levels and band edges through hybrid functionals: Effect of screening 1038 in the exchange term. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, 1039 *81*, 205118. 1040

(96) Alkauskas, A.; Pasquarello, A. Band-edge problem in the 1041 theoretical determination of defect energy levels: The O vacancy in 1042 ZnO as a benchmark case. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1043 **2011**, *84*, 125206. 1044

(97) Graham, A. M.; Corfdir, P.; Heiss, M.; Conesa-Boj, S.; Uccelli, 1045 E.; Fontcuberta i Morral, A.; Phillips, R. T. Exciton localization 1046 mechanisms in wurtzite/zinc-blende GaAs nanowires. *Phys. Rev. B:* 1047 *Condens. Matter Mater. Phys.* **2013**, *87*, 125304. 1048

(98) De Luca, M.; Rubini, S.; Felici, M.; Meaney, A.; Christianen, P. 1049 C. M.; Martelli, F.; Polimeni, A. Addressing the Fundamental 1050 Electronic Properties of Wurtzite GaAs Nanowires by High-Field 1051 Magneto-Photoluminescence Spectroscopy. *Nano Lett.* **2017**, *17*, 1052 6540–6547. 1053