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Correct Implementation of Polarization Constants in Wurtzite Materials and Impact on III-Nitrides

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Accurate values for polarization discontinuities between pyroelectric materials are critical for understanding and designing the electronic properties of heterostructures. For wurtzite materials, the zincblende structure has been used in the literature as a reference to determine the effective spontaneous polarization constants. We show that, because the zincblende structure has a nonzero formal polarization, this method results in a spurious contribution to the spontaneous polarization differences between materials. In addition, we address the correct choice of "improper" versus "proper" piezoelectric constants. For the technologically important III-nitride materials GaN, AlN, and InN, we determine polarization discontinuities using a consistent reference based on the layered hexagonal structure and the correct choice of piezoelectric constants, and discuss the results in light of available experimental data.

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I. INTRODUCTION

Pyroelectric materials have emerged in a variety of electronic and optoelectronic applications. Because of the symmetry of their crystal structure, these materials exhibit spontaneous (SP) and piezoelectric (PZ) dipole moments [1], which manifest themselves as electric fields in heterostructure layers and sheet charges at interfaces. In the technologically important III-nitrides, which have the wurtzite (WZ) structure (space group $P6_3mc$), polarization differences allow for strong carrier confinement and the formation of a two-dimensional electron gas (2DEG) with high density at AlGaN/GaN interfaces, exploited in high electron mobility transistors (HEMTs). The effect of polarization can also be detrimental, for example, causing the quantum-confined Stark effect in quantum wells of light-emitting diodes (LEDs), which reduces radiative recombination rates and shifts the emission wavelength. For both HEMTs and LEDs, accurate values of the SP and PZ polarization constants are required for a fundamental understanding as well as for device design.

Since experimental determination of the separate SP and PZ contributions to the total polarization is very difficult, calculated values of SP and PZ polarization constants are widely used in simulations. The PZ polarization constants are, in principle, fairly straightforward to explicitly measure or calculate [2]. However, the reported values exhibit a considerable spread [3]. In addition, the difference between so-called "proper" and "improper" PZ constants [2,4] is often overlooked, even though it can give rise to significant quantitative changes in the resulting polarization fields. This difference is one issue that is elucidated in the present paper.

The definition of SP polarization constants is even more subtle, and they are typically not amenable to explicit experimental determination, except in special cases [5]. The calculation of SP polarization requires the choice of a reference structure, which in the case of WZ semiconductors, has invariably been chosen to be zincblende (ZB) [6–8]. In this work, we show that, although ZB as a reference structure is intuitively appealing, the SP polarization constants that result have been misinterpreted, introducing a source of error into the predicted values for bound sheet-charge densities (and polarization fields). We also demonstrate that a proper choice of reference structure can eliminate these problems, and we provide revised values that can be directly inserted into current simulation tools.

While our theoretical considerations are general, we choose the nitride semiconductors because they provide a suitable example to illustrate the derivations and because our findings have a significant impact on this materials system of high (and still increasing) technological importance. In Sec. II, we review the underlying theory. In Sec. III, we address the issues resulting from the choice of zincblende as a reference structure, and we propose a solution. Section IV deals with piezoelectric contributions, specifically the issue of proper versus improper constants. In Sec. V, we show that our findings have important

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consequences for nitride device structures and compare with previous implementations and with experiment. Section VI concludes the paper.

II. CALCULATING POLARIZATION CONSTANTS IN WURTZITE

For WZ films grown in the [0001] direction (i.e., the $+c$ direction), the polarization component P_3 is given by the sum of the SP polarization at the wurtzite material's own lattice parameters, $P_{\rm SP}$, and the z component of the PZ polarization [1]; for material m,

$$P_3^m = P_{\rm SP}^m + (\epsilon_1^m + \epsilon_2^m)e_{31}^m + \epsilon_3^m e_{33}^m, \tag{1}$$

where (in Voigt notation) ϵ_i ($i = 1,2,3$) is the strain in the i direction and e_{3i} are the corresponding piezoelectric constants (specifically, the "improper" ones; see Sec. IV). Henceforth, we drop the subscript "3" from P for simplicity; all unbolded quantities pertaining to wurtzite are assumed to be in the c direction.

The goal of this work is to derive the appropriate SP and PZ constants that allow Eq. (1) to be used in accurately determining polarization differences at interfaces between different WZ materials.

A. Modern theory of polarization

Direct calculation of the polarization constants in Eq. (1) by first-principles electronic-structure methods was enabled by the formulation of a rigorous theory of bulk polarization, known as the modern theory of polarization (MTP) [9,10]. For a given structure λ, the MTP allows calculation of the so-called "formal" polarization [9]:

$$\begin{aligned}\mathbf{P}_{\rm f} &= \mathbf{P}_{\rm ion} + \mathbf{P}_{\rm el}\\ &= \frac{e}{\Omega}\sum_s Z_s^{\rm ion}\mathbf{R}_s^{(\lambda)} + \frac{ief}{8\pi^3}\sum_j^{\rm occ}\int_{\rm BZ} d\mathbf{k}\,\langle u_{j,\mathbf{k}}^{(\lambda)}|\nabla_{\mathbf{k}}|u_{j,\mathbf{k}}^{(\lambda)}\rangle,\end{aligned} \tag{2}$$

where Ω is the cell volume, $Z_s^{\rm ion}$ is the charge of the ion s and $\mathbf{R}_s^{(\lambda)}$ is its position in the λ structure, f is the spin degeneracy of the bands, the sum j runs over occupied bands, and $u_{j,\mathbf{k}}^{(\lambda)}$ are the cell periodic parts of the Bloch wave functions. In Eq. (2), $\mathbf{P}_{\rm el}$ is the Berry phase taken over the valence-band manifold [9,10]. The formal polarization is defined only modulo the "quantum of polarization" $e\mathbf{R}/\Omega$, where $\mathbf{R}$ is any lattice constant and e is the electron charge [9,10].

In the MTP, only *differences* between formal polarizations of appropriate structures, $\lambda = 0$ and $\lambda = 1$, are well defined:

$$\Delta\mathbf{P} = \mathbf{P}_{\rm f}^{(\lambda=1)} - \mathbf{P}_{\rm f}^{(\lambda=0)}. \tag{3}$$

The choice of the "appropriate" structures $\lambda = 0$ and $\lambda = 1$ rests on one of two possible considerations to ensure that physical conclusions can be drawn from their formal polarization differences. First, if the two structures are connected by an adiabatic, gap-preserving deformation path [9,10], then their difference in polarization [$\Delta\mathbf{P}$ in Eq. (3)] is given by the expression

$$\Delta\mathbf{P} = \int_0^1 d\lambda\frac{\partial\mathbf{P}}{\partial\lambda}, \tag{4}$$

and it corresponds to the zero-field adiabatic displacement current. This quantity can, in principle, be determined experimentally. An obvious application is the calculation of piezoelectric constants, which involves polarization differences between structures with slightly different lattice constants and/or internal structural parameters.

B. Interface theorem

The second consideration, as shown by Vanderbilt and King-Smith [11], is that *if* an insulating interface can be constructed between two structures, the difference in formal polarization gives the bound charge $\sigma_{\rm b}$ that builds up at the interface as a result of the continuity of the displacement field over an interface with no free charge:

$$\sigma_{\rm b} = (\mathbf{P}_{\rm f}^{(\lambda=1)} - \mathbf{P}_{\rm f}^{(\lambda=0)})\cdot\hat{\mathbf{n}}. \tag{5}$$

This is often referred to as the "interface theorem." Since there is no adiabatic path necessary between the two structures in this consideration, $\lambda = 0$ and $\lambda = 1$ can be different polymorphs of the same material (such as WZ and ZB structures of GaN) or different materials altogether (such as GaN and AlN); as long as they form an insulating interface, Eq. (5) will give the bound charge accumulation at the interface.

From the interface theorem [Eq. (5)] and Eq. (1), the bound polarization charge at the interface between different III-nitride materials (m and n) is

$$\begin{aligned}\sigma_{\rm b} = {}&[P_{\rm SP}^m + e_{31}^m(\epsilon_1^m + \epsilon_2^m) + e_{33}^m\epsilon_3^m]\\ &- [P_{\rm SP}^n + e_{31}^n(\epsilon_1^n + \epsilon_2^n) + e_{33}^n\epsilon_3^n].\end{aligned} \tag{6}$$

As an example, we take a realistic situation that occurs in heterostructures, assuming that material n is strained coherently to m ($\epsilon_1^m = \epsilon_2^m = \epsilon_3^m = 0$), i.e., under plane stress ($\epsilon_1^n = \epsilon_2^n$, $\epsilon_3^n = -2C_{13}^n/C_{33}^n\epsilon_1^n$, where C_{ij} are the elastic constants). Therefore, we have

$$\begin{aligned}\sigma_{\rm b} &= (P_{\rm SP}^m - P_{\rm SP}^n) - 2\epsilon_1^n(e_{31}^n - e_{33}^n C_{13}^n/C_{33}^n)\\ &= \Delta P_{\rm SP}^{\rm int} - 2\epsilon_1^n(e_{31}^n - e_{33}^n C_{13}^n/C_{33}^n).\end{aligned} \tag{7}$$

Note that $\sigma_{\rm b}$ is the charge density of electrons at an interface for which material n has been grown on top of material m in the $+c$ direction.

III. REFERENCE STRUCTURE FOR SPONTANEOUS POLARIZATION

A. Effective spontaneous polarization constants

We first address the difference in spontaneous polarization in Eq. (7), $\Delta P_{\mathrm{SP}}^{\mathrm{int}}$. Strain effects will be taken into account separately in the PZ part, so that $\Delta P_{\mathrm{SP}}^{\mathrm{int}}$ is simply the difference of formal polarizations of the respective zero-strain structures,

$$\Delta P_{\mathrm{SP}}^{\mathrm{int}} = P_{\mathrm{f}}^{m}|_{\epsilon=0} - P_{\mathrm{f}}^{n}|_{\epsilon=0}. \tag{8}$$

For the purposes of Eq. (1), we would like to define a SP polarization constant that is a property of a single material. Simply taking P_{f}^{m} of Eq. (8) as P_{SP}^{m} is problematic since formal polarization is multivalued, being only well defined modulo a quantum of polarization $e\mathbf{R}/\Omega$. Therefore, in every situation in which Eq. (1) is applied to determine σ_b at an interface, it must be confirmed that formal polarizations of the two materials are taken on the same "branch" of $e\mathbf{R}/\Omega$. A better approach is to take P_{SP}^{m} in Eq. (1) as a so-called "effective" SP polarization, $\mathbf{P}_{\mathrm{eff}}$, defined by Resta and Vanderbilt [12] to be the $\Delta\mathbf{P}$ in Eq. (3) that results as the system is taken from a high-symmetry "reference" structure ($\lambda = 0$) to the structure of interest ($\lambda = 1$):

$$\mathbf{P}_{\mathrm{eff}} = \mathbf{P}_{\mathrm{f}}^{(\lambda=1)} - \mathbf{P}_{\mathrm{f}}^{(\lambda=0)} = \mathbf{P}_{\mathrm{f}} - \mathbf{P}_{\mathrm{f}}^{\mathrm{ref}}. \tag{9}$$

Using $\mathbf{P}_{\mathrm{eff}}$ to define the SP polarization of the material removes the indeterminacy inherent to the formal polarization.

The reference structure is often chosen to be centrosymmetric, but it is important to recognize that the formal polarization of centrosymmetric crystals is not necessarily zero. This is because, as stated above, $\mathbf{P}_{\mathrm{f}}$ is a multivalued vector field, so it is possible for a nonzero formal polarization to be unchanged (modulo $e\mathbf{R}/\Omega$) under the inversion operator. Nevertheless, high symmetry puts restrictions on the possible values of $\mathbf{P}_{\mathrm{f}}^{(\lambda=0)}$ [11].

While, in principle, effective polarization constants are still *differences* in formal polarization between $\lambda = 1$ and $\lambda = 0$ (reference) structures, in practice they can be used to compare spontaneous polarizations of different materials to obtain ΔP_{SP} if such materials share a reference structure with the same formal polarization. Such a comparison then correctly yields the interface charge density according to the interface theorem of Ref. [11]. In such cases, ΔP_{SP} is just given by the difference in *effective* SP polarization of the materials,

$$\Delta\tilde{P}_{\mathrm{SP}}^{\mathrm{int}} = P_{\mathrm{eff}}^{m} - P_{\mathrm{eff}}^{n}. \tag{10}$$

In the more general case that the reference formal polarizations do not match, the correct change in SP polarization following from Eqs. (8) and (9) is

$$\Delta P_{\mathrm{SP}}^{\mathrm{int}} = \Delta\tilde{P}_{\mathrm{SP}}^{\mathrm{int}} + (P_{\mathrm{f}}^{m,\mathrm{ref}} - P_{\mathrm{f}}^{n,\mathrm{ref}}). \tag{11}$$

Therefore, a correction term of the form

$$\Delta P_{\mathrm{corr}}^{\mathrm{ref}} \equiv P_{\mathrm{f}}^{m,\mathrm{ref}} - P_{\mathrm{f}}^{n,\mathrm{ref}} \tag{12}$$

has to be added to Eq. (10). Unfortunately, this correction term is not typically implemented in device simulation packages (e.g., Ref. [13]) or used in the interpretation of experimental data (e.g., Ref. [14], which is considered a standard reference in the field).

When the PZ terms are included as well, the total interface charge given by Eq. (7) becomes

$$\sigma_{\mathrm{b}} = \Delta\tilde{P}_{\mathrm{SP}}^{\mathrm{int}} + \Delta P_{\mathrm{corr}}^{\mathrm{ref}} - 2\epsilon_1^n(e_{31}^n - e_{33}^n C_{13}^n/C_{33}^n). \tag{13}$$

Equation (13) is a central result of the present work.

B. Correction term for the effective spontaneous polarization with the zincblende reference structure

As mentioned before, previous studies [6–8] have exclusively used ZB (space group $F\bar{4}3m$) as a reference structure for calculating the SP polarization of the WZ. This structure is not centrosymmetric, although it has sufficient symmetry to preclude any SP polarization [1]. The fact that an insulating (111) interface can be constructed between the WZ and ZB polytypes [8] makes it an appropriate reference structure. In fact, experimental measurements have deduced the relative polarization between the WZ and ZB phases of GaN [5], which were found to be consistent with the theoretical values in Refs. [6–8].

However, there is a subtlety with using ZB as a reference structure: It has a nonzero formal polarization in the [111] direction, $P_{\mathrm{f}}^{\mathrm{ZB}}$ (modulo $e\mathbf{R}/\Omega$). Again, this is consistent with the symmetry considerations because P_{f} is a multivalued vector quantity and can be nonzero while still remaining unchanged (modulo $e\mathbf{R}/\Omega$) under the $F\bar{4}3m$ symmetry operations. These symmetry operations dictate the possible values of $P_{\mathrm{f}}^{\mathrm{ZB}}$, and therefore the resulting value depends only on the lattice constant, not on the chemical species of the atoms [11] (see Sec. S1 of Ref. [15] for more details on the formal polarization of ZB). The ZB reference structures for the reported effective SP polarization values for the III-nitrides were those with lattice constants equal to the in-plane lattice constant of the corresponding wurtzite material [6–8] (as confirmed by our calculations), so $P_{\mathrm{f}}^{\mathrm{ZB}}$ will be *different* for GaN, AlN, and InN, and does not simply constitute a constant shift of $P_{\mathrm{f}}^{\mathrm{WZ}}$ for all the materials. Therefore, for the effective SP polarization constants with the ZB reference to be implemented in Eq. (7) to determine the polarization difference between different WZ materials, the correction term of Eq. (12) is required, as in Eq. (13).

Consider the example of the interface charge between InN and GaN. Although, as mentioned above, the formal polarization of zincblende does not necessarily vanish, the symmetry of the structure severely limits the possible values. Specifically, there are two possible values of the formal polarization in the [111] direction that are consistent with the symmetry: Either P_f vanishes, or it is equal to $e\sqrt{3}/2a_n^2$ (both modulo $e\sqrt{2}a_n/\Omega_n$), where a_n is the WZ in-plane lattice constant of material n and Ω_n is the volume of the ZB primitive cell (see Ref. [11] or Sec. S1 of Ref. [15]). For the III-nitrides, it is the latter, giving a correction term for GaN/InN:

$$\begin{aligned}\Delta P_\mathrm{corr}^{(\mathrm{ZB\,ref})} &= P_\mathrm{f}^{\mathrm{GaN,ZB}} - P_\mathrm{f}^{\mathrm{InN,ZB}} \\ &= \frac{e\sqrt{3}}{2}\left(\frac{1}{(a_\mathrm{GaN})^2} - \frac{1}{(a_\mathrm{InN})^2}\right) \\ &= 0.28\ \mathrm{C/m^2}. \end{aligned} \tag{14}$$

When considering the SP polarization differences between WZ nitrides, this represents a significant correction. In fact, as we show in Sec. III C, the correction is an order of magnitude larger than the effective polarizations when they are calculated with the zincblende reference [6,7]. As we see later in Sec. V E, this error is substantially reduced in practice by an approximate error cancellation that occurs in connection with the treatment of the PZ response.

There is nothing intrinsically wrong with the using ZB as the reference structure for defining WZ effective SP polarization; however, if these values are to be used to obtain polarization differences between different WZ materials, the $\Delta P_\mathrm{corr}^\mathrm{ref}$ term [Eq. (12), or Eq. (14) for the example of GaN/InN] must be explicitly included in expressions such as Eq. (11) or Eq. (13). To our knowledge, however, this has not been properly implemented in the numerous previous evaluations of SP polarization for nitride interfaces, and it would require changes in the software for the many simulation tools that include modeling of polarization fields in heterostructures.

C. $P6_3/mmc$ hexagonal layered structure as an alternative reference

In order to avoid extensive changes in the simulation software, and to enhance physical insight, we advocate another approach, namely, to determine effective SP polarization constants with respect to a reference structure for which the formal polarization is explicitly zero (so that $\Delta P_\mathrm{SP}^\mathrm{int} = \Delta\tilde{P}_\mathrm{SP}^\mathrm{int}$). A straightforward choice for this reference structure is the layered hexagonal (H) structure (space group $P6_3/mmc$), as was used for hexagonal $P6_3mc$ ABC materials [16]. This structure is centrosymmetric, and we show below with explicit first-principles calculations that it remains insulating and its formal polarization vanishes. The layered hexagonal structure can be obtained by an adiabatic (gap-preserving) increase of the internal structural u parameter from $u \approx 0.37$–0.38 of the WZ structure to $u = 0.5$. All that is required to avoid correction terms like Eq. (14) is to replace the effective SP polarization constants currently used in the field (the ones referenced to ZB [6,7]) with those referenced to the H reference structure. We have explicitly verified that this leads to expressions that are identical to those that would be obtained for the ZB reference, provided the second term in Eq. (11) or Eq. (13) is included.

The first-principles calculations of P_f for the H, WZ, and ZB structures of the III-nitrides were performed using density functional theory with the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [17] as implemented in the VASP code [18]. Hartree-Fock mixing parameters of 31% for AlN and GaN, and 25% for InN were used to correctly describe the band gaps and structural parameters of each material. Conventional functionals based on the local density approximation (LDA) or generalized gradient approximation (GGA) predict InN to be a metal, precluding the calculation of the polarization constants if the Γ point is included in the k-point mesh (which is required in Vasp). Projector augmented wave potentials (PAW) [19], with the In and Ga d electrons frozen in the core, were used. All calculations were performed on bulk primitive cells, with a $6\times6\times8$ Monkhorst-Pack [20] k-point mesh to sample the Brillouin zone, and a large energy cutoff of 600 eV for the plane-wave basis set, chosen to ensure convergence of the internal structural parameter u. The calculated lattice parameters and band gaps, listed in Sec. S2 of Ref. [15], show good agreement with experimental data.

We have calculated the electronic structure for structures with increasing u, ranging from $u \approx 0.37$ to $u = 0.5$ (Fig. 1), and confirmed that this path between WZ and

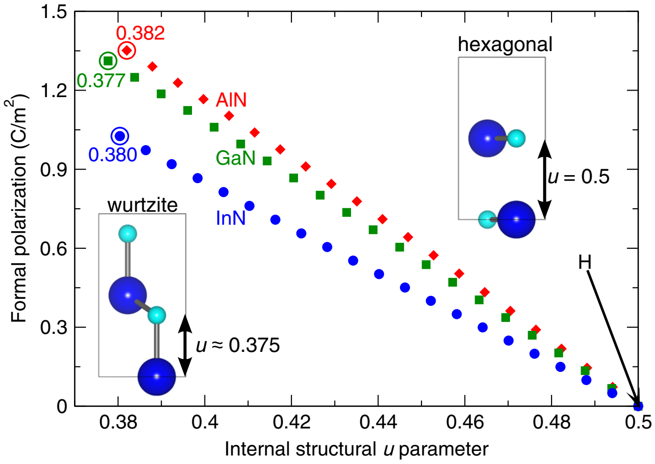

FIG. 1. Formal polarization of InN, GaN, and AlN for structures as a function of the internal structural parameter u, varying between fully relaxed WZ (circled symbols, labeled with the relaxed u value) and H ($u = 0.5$), as shown schematically by ball and stick models, where smaller balls represent N atoms and larger ones represent the cations. All other lattice parameters were fixed at their relaxed WZ values.

H is gap preserving. These calculations also show that the formal polarization of the H structure is zero (modulo $e\mathbf{R}/\Omega$) for the III-nitrides (Fig. 1). We remind the reader that this was not guaranteed since $\mathbf{P}_\mathrm{f}$ can be nonzero and still consistent with inversion symmetry, if the inversion operator changes $\mathbf{P}_\mathrm{f}$ by a multiple of $e\mathbf{R}/\Omega$. We have therefore verified that the hexagonal phase is a reference structure for which there is no spurious term in Eq. (11).

In addition, by correcting for any discontinuities (in the amount of a multiple of $e\mathbf{R}/\Omega$) that may occur in the calculations of formal polarizations along the path between WZ and H, we have ensured that we are comparing formal polarizations of WZ GaN, AlN, and InN on the same branch of $e\mathbf{R}/\Omega$ [12].

The calculated spontaneous polarization coefficients for the WZ structure using either H or ZB as a reference are given in Table I. The results obtained by Bernardini *et al.* [6,7] are listed for comparison. The GGA functional used in that work provides results that are very close to those we obtained with HSE; the discrepancy is the largest for InN, which is probably related to the fact, mentioned above, that GGA predicts InN to be a metal. Table I also shows, however, that the choice of reference structure makes a significant difference. The magnitudes of the coefficients are much larger, and their signs are different when H is used as the reference. We observe that it is not just the absolute values but also the relative differences between the calculated polarization constants of the three materials that differ from the previously reported values [6,7].

The difference in sign of $P_\mathrm{eff}^{(\mathrm{H\,ref})}$ compared to $P_\mathrm{eff}^{(\mathrm{ZB\,ref})}$ demonstrates that the conventional wisdom that the SP polarization in WZ points in the $-c$ direction is misleading. The formal polarization of WZ has no definite sign as this would depend on the chosen branch. The effective SP depends on the polarization difference, and therefore, the sign will depend on the sign and magnitude of the formal polarization of the reference structure.

Even though the values reported in Table I for $P_\mathrm{eff}^{(\mathrm{H\,ref})}$ and $P_\mathrm{eff}^{(\mathrm{ZB\,ref})}$ clearly differ in sign, absolute magnitude, and relative differences between materials, we show in Sec. V that the final predictions based on both formulations are actually rather similar because of the way the PZ contributions have been included in the previous work (cf. Sec. IV).

TABLE I. Effective spontaneous polarization constants in units of C/m^2 of WZ GaN, AlN, and InN calculated using either the hexagonal (H, space group $P6_3/mmc$) or ZB (space group $F\bar{4}3m$) reference structures. The lattice constant of the ZB structure is chosen to match the in-plane lattice constant of the WZ structure for the same material. Results from previous calculations [7] that used the ZB reference are listed for comparison.

	$P_\mathrm{eff}^{(\mathrm{H\,ref})}$	$P_\mathrm{eff}^{(\mathrm{ZB\,ref})}$	$P_\mathrm{eff}^{(\mathrm{ZB\,ref})}$, previously reported[a]
GaN	1.312	−0.035	−0.034
AlN	1.351	−0.090	−0.090
InN	1.026	−0.053	−0.042

[a] From Ref. [7].

IV. IMPROPER VERSUS PROPER PIEZOELECTRIC CONSTANTS

We now address the specifics of the PZ terms in Eqs. (7) and (13). A complication that must be addressed is the choice between improper and proper e_{31} (e_{33} has no such complication) [2,4].

As we have done above, we consider a thin layer of a WZ material grown in the c direction. If the layer is strained perpendicular to the c direction, the total bound charge on the $+c$ and $-c$ surfaces will change as a result of the polarization current, or redistribution of charge, in the layer. If metallic contacts on the $+c$ and $-c$ surfaces are short-circuited when the strain occurs, the current flow can be measured directly and will give the proper PZ constant, denoted e_{31}^prop [2,4].

If the $+c$ and $-c$ faces are in open-circuit boundary conditions, the layer will have a field across it due to the SP polarization, which will be modified by the strain via two mechanisms. The first is the same as in the proper case, as the strain will cause a flow of polarization current. But in addition, since the field depends on the charge *density*, the change in the area of the c plane as a result of ϵ_1 will dilute or concentrate the "pre-strain" bound charge. For small strains, the latter is given by the zero-strain formal polarization [2,4]. Taking both of these mechanisms into account gives the improper PZ constant, e_{31}^imp.

In the case of, e.g., Eq. (13), the PZ constants correspond to the improper case since their role in the equation is to take into account the change in formal polarization of material n with strain, so that σ_b corresponds to the bound charge at the coherent interface with the in-plane lattice constant of material m. The change in formal polarization with strain is an alternative definition of the improper PZ constants [4].

From Refs. [2] and [4], the improper PZ constant $e_{31}^{n,\mathrm{imp}}$ is related to the proper constant by

$$e_{31}^{n,\mathrm{imp}} = e_{31}^{n,\mathrm{prop}} - P_\mathrm{f}^n|_{\epsilon=0}, \tag{15}$$

where $P_\mathrm{f}^n|_{\epsilon=0}$ is the zero-strain formal polarization of material n. There is no change to the e_{33} PZ constant. The proper PZ constant is a well-defined bulk quantity, as it is related to the polarization current; however, the improper PZ constant is branch dependent [4]. Here, also, defining polarization with respect to the H reference proves useful. Since the formal polarization of the H structure vanishes (Fig. 1), $P_\mathrm{eff}^{n,(\mathrm{H\,ref})} = P_\mathrm{f}^{n,\mathrm{WZ}}|_{\epsilon=0}$; this also ensures that improper PZ constants for the different materials are taken on the same branch, in the same way as this is confirmed for the SP polarization constants. Therefore, consistent use of the H reference structure allows us to write Eq. (7) as

$$\sigma_{\mathrm{b}} = \Delta\tilde{P}_{\mathrm{SP}}^{\mathrm{int},(\mathrm{H\,ref})} - 2\epsilon_1^n\left(e_{31}^{n,\mathrm{prop}} - P_{\mathrm{eff}}^{n,(\mathrm{H\,ref})} - e_{33}^{n,\mathrm{prop}}C_{13}^n/C_{33}^n\right), \qquad (16)$$

where $P_{\mathrm{eff}}^{n,(\mathrm{H\,ref})}$ can be taken from Table I.

Calculated proper PZ constants are given in the "proper" column of Table II. Since the HSE hybrid functional was used (and therefore density functional perturbation theory was not implemented), finite differences were used to calculate the derivatives with strain, following the procedure outlined in Eqs. (4)–(6) in Ref. [6]. Specifically, improper PZ constants were calculated and converted to proper constants by adding $P_{\mathrm{f}}^n|_{\epsilon=0}$ [see Eq. (15)] as determined in the calculation. This removes any dependence on the branch choice used in finite-difference calculations [4]. We then convert *back* to improper constants using $P_{\mathrm{eff}}^{n,(\mathrm{H\,ref})}$ as discussed above, in order to ensure that the constants are reported for the same branch for each material ("improper" column in Table II).

The WZ structure does have another nonzero piezoelectric constant e_{15}, which couples a shear deformation in a plane perpendicular to the c plane (ϵ_{13} or ϵ_{31}) to the polarization in the c plane. In this case, there are two improper PZ constants since a correction must be included in the case of ϵ_{13} but not for ϵ_{31} [4]. These elements do not enter in the situation we consider in this work (plane stress conditions with the c plane as the growth plane) but may be important for growth on nonpolar or semipolar planes [21].

It is important to comment on the PZ constants reported in the literature [3]. When PZ polarization constants have been implemented in simulations (e.g., Refs. [3,13,14]), it has never been specified *which* PZ constants are used for WZ III-nitrides. However, by comparing our calculations of proper and improper PZ constants ("Proper" and "Improper" columns of Table II) with the reported PZ constants in the literature ("Previously reported" of Table II), we have found that the reported constants are more likely to be the proper PZ constants.

TABLE II. Calculated piezoelectric polarization constants in units of $\mathrm{C/m^2}$ compared with reported values from the literature.

		Proper	Improper	Previously reported[a]
GaN	e_{31}	−0.551	−1.863	−0.22 to −0.55
	e_{33}	1.020	1.020	0.43 to 1.12
AlN	e_{31}	−0.676	−2.027	−0.38 to −0.81
	e_{33}	1.569	1.569	1.29 to 1.94
InN	e_{31}	−0.604	−1.63	−0.23 to −0.59
	e_{33}	1.238	1.238	0.39 to 1.09

[a] From Ref. [3] and references therein.

From an experimental perspective, most of the experimental techniques have measured *total* polarization and then deduced the PZ constants in the nitrides using the SP constants from, e.g., Ref. [6] using Eq. (1). As we show in Sec. V, observation of the effects of total polarization can be misleading with regards to the differentiation between proper and improper PZ constants because of the error cancellation from the use of the ZB reference in defining the SP polarization (discussed in Sec. III B).

There have been direct measurements of the PZ constants, either by probing the electromechanical coupling constants via surface acoustic waves [22,23] or by using interferometry to determine the strain caused by the application of a voltage [24–27]. Both of these techniques measure the *proper* constants since neither is sensitive to the change in surface charge density resulting from the deformation. These reported values indeed agree well with our calculated values for the proper PZ constants, both in sign and in magnitude.

In previous work [7], $P_{\mathrm{eff}}^{n,(\mathrm{ZB\,ref})}$ was used instead of $P_{\mathrm{f}}^n|_{\epsilon=0}$ in Eq. (15) to convert improper to proper e_{31} PZ constants (cf. Tables VI and V of Ref. [7]). Because of the nonvanishing formal polarization of the ZB reference structure, $P_{\mathrm{eff}}^{n,(\mathrm{ZB\,ref})} \neq P_{\mathrm{f}}^{n,\mathrm{WZ}}|_{\epsilon=0}$; instead, we see from the discussion resulting in Eq. (14) that Eq. (15) can be expressed as

$$e_{31}^{n,\mathrm{imp}} = e_{31}^{n,\mathrm{prop}} - \left(P_{\mathrm{eff}}^{n,(\mathrm{ZB\,ref})} + \frac{e\sqrt{3}}{2a_n^2}\right), \qquad (17)$$

where a_n is the equilibrium, in-plane lattice constant of the WZ material n. To our knowledge, the inclusion of the last term in Eq. (17) has not been discussed in the literature. Because of the small magnitude of $P_{\mathrm{eff}}^{n,(\mathrm{ZB\,ref})}$, neglecting the last term in Eq. (17) led to the conclusion in Ref. [7] that the difference between the proper and improper PZ constants is small, seemingly rendering the distinction of no consequence. Instead, because of the large magnitude of $P_{\mathrm{eff}}^{n,(\mathrm{H\,ref})}$ [and $e\sqrt{3}/2a_n^2$ in Eq. (17)], the distinction between proper and improper PZ constants is actually very significant.

V. COMPARISON WITH REPORTED EXPERIMENTAL RESULTS

A. Correct expressions for total polarization for wurtzite materials

Before discussing specific quantitative results for nitride semiconductors, we briefly summarize the main points of the previous sections and rigorously express the polarization of a given WZ material [Eq. (1)]. Spontaneous polarization constants must be defined with respect to a reference structure, and this choice of reference structure must be taken into account when evaluating polarization discontinuities at interfaces. We determined a correction term [Eq. (12)] that is necessary when effective SP polarization constants are used to determine the SP polarization difference between materials at an interface. This correction term is significant when the ZB reference structure is used [e.g., Eq. (14)] but is zero for the H reference. Using H as a reference is therefore more straightforward and is the approach we advocate, with the SP constants $P_{\mathrm{eff}}^{(\mathrm{H\,ref})}$ listed in Table II.

In addition, the improper PZ constants should be used to determine interface bound charge and fields in heterostructure layers. These can be obtained from the proper constant e_{31}^{prop} by subtracting $P_{\mathrm{eff}}^{(\mathrm{H\,ref})}$ (Table II). Therefore, in the notation of this paper, Eq. (1) is written rigorously as

$$P = P_{\mathrm{eff}}^{(\mathrm{H\,ref})} + (\epsilon_1 + \epsilon_2)(e_{31}^{\mathrm{prop}} - P_{\mathrm{eff}}^{(\mathrm{H\,ref})}) + \epsilon_3 e_{33}^{\mathrm{prop}}. \qquad (18)$$

B. Calculation of sheet charges for III-nitrides

Because of the important impact of polarization on device performance and design, a plethora of experimental studies have been aimed at determining the effects of polarization at GaN/InGaN and GaN/AlGaN heterostructures. We have plotted these reported results in Fig. 2, expressed as the magnitude of polarization bound charge at the interface, as a function of alloy content (a full list of references is provided in Sec. S3 of Ref. [15]).

For GaN grown in the $+c$ direction with the InGaN (AlGaN) grown on top, the sign of the bound charge at the interface will be negative (positive) [28].

In Fig. 2, the black dashed curves correspond to the current practice in the field: Sheet charges are predicted based on (i) SP constants referenced to the ZB structure ($P_{\mathrm{eff}}^{(\mathrm{ZB\,ref})}$ in Table I) and Eq. (13) *without* the correction term $\Delta P_{\mathrm{corr}}^{(\mathrm{ZB\,ref})}$, and (ii) proper PZ constants (“Proper” column in Table II). Quantities for alloys were obtained using linear interpolation. For an explicit expression in terms of alloy content, see Eq. (3) in Sec. S4 of Ref. [15]. Elastic constants were taken from Ref. [29].

The red solid line in Fig. 2 corresponds to the implementation recommended in this work, i.e., using the H reference structure and the improper PZ constants, as in Eqs. (16) and (18) [and Eq. (5) in Sec. S4 of Ref. [15]].

In view of the arguments given above, it may seem surprising that the dashed black and solid red curves agree as well as they do; we return to this point in Sec. V E.

C. InGaN/GaN interfaces

For the InGaN/GaN system, most experimental studies have applied optical techniques to determine the polarization fields in GaN/InGaN/GaN quantum wells (QWs). This field can be probed by varying the QW width [30] or external bias [31] and measuring the change in the optical properties of the QW (labeled “optical” in Fig. 2).

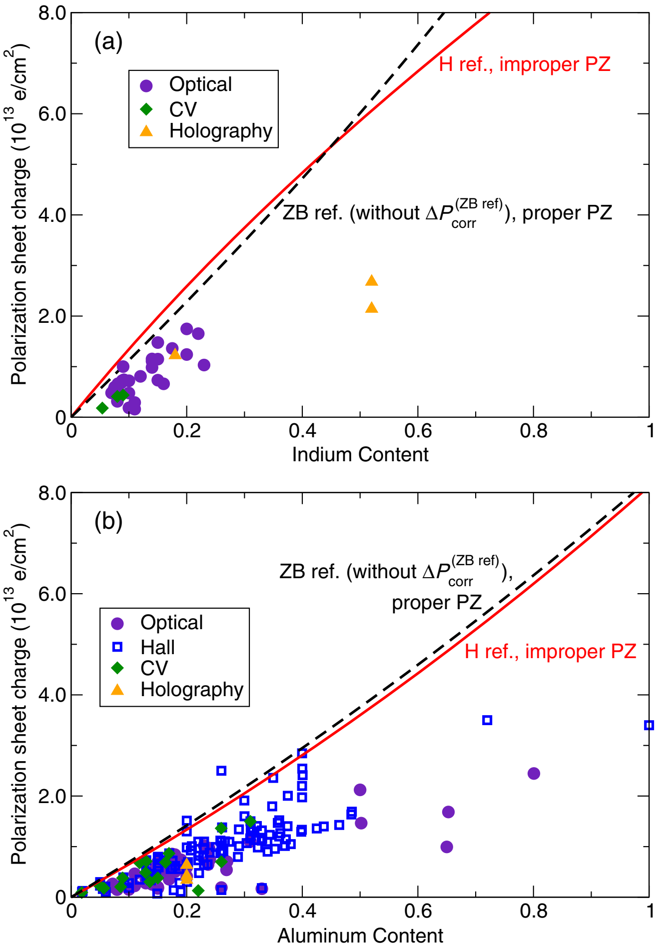

FIG. 2. Absolute values for polarization sheet charges at the (a) InGaN/GaN and (b) AlGaN/GaN interfaces as a function of alloy content predicted from the spontaneous polarization constants calculated using either the ZB reference structure [without a correction term, Eq. (14)] and the proper piezoelectric constants (black dashed curve), or the H reference structure and improper piezoelectric constants (red solid curve). Points are experimental values from the literature (see Sec. S3 of Ref. [15] for references and values).

In addition, there have also been studies using time-resolved PL to measure shifts due to screening of the polarization field by photoexcited or electrically injected carriers [32]. Other studies have been based on capacitance-voltage (CV) profiling of the fields [33], and on electron holography [34], where cross-sectional transmission electron microscopy is conducted on InGaN/GaN heterostructures to determine the depth-resolved electrostatic potential in the growth direction. When fields are reported, we convert to the bound charge for the purposes of Fig. 2(a), assuming GaN/InGaN/GaN quantum wells (with thick barriers such that the electric field in the barriers is presumed to be zero) using a simple parallel-plate capacitor model ($E = \sigma/\varepsilon_0\varepsilon_r$, using a relative dielectric constant for GaN of 10 [35] and for InN of 15 [36] and a linear interpolation for the dielectric constant of InGaN). For specific values of the points in Fig. 2, see Sec. S3 of Ref. [15].

The red curve in Fig. 2(a) is indeed in reasonable agreement with the experimental observations, appearing to be an upper bound of the data. The optical experiments usually rely on Schrödinger-Poisson simulations to determine the field magnitude from the measured optical properties. Uncertainties in input parameters to these models such as well widths, compositions, and composition profiles can result in quantitative differences. It has been shown recently that taking into account the deviations from an ideal QW structure when interpreting experimental observations can account for the apparent discrepancy between the measurements and theoretical prediction of polarization fields [37,38]. Such deviations are expected to be significant for InGaN/GaN because of the large lattice mismatch and the large difference in optimal growth temperatures for GaN and InGaN.

D. AlGaN/GaN interfaces

For the AlGaN/GaN system, there are two basic strategies for experimentally determining polarization effects. The first is to directly measure the polarization field in an AlGaN/GaN/AlGaN (QW) structure with the same methods as used in the InGaN/GaN case [39,40]. For the purposes of Fig. 2(b), we have converted these fields into bound sheet-charge densities in an AlGaN/GaN/AlGaN quantum well (using a relative dielectric constant for GaN of 10 [35]).

The other strategy is to measure the density of the 2DEG at the AlGaN/GaN interface in a HEMT structure (GaN channel, AlGaN barrier); from this, the bound interface charge $\sigma_{\rm b}$ can be derived [41]. The 2DEG density can be determined either by Hall effect [14] or CV [41] measurements.

The significant scatter in the experimental data in Fig. 2(b) may have several origins. There are experimental uncertainties that can influence fields, such as incomplete strain relaxation in buffer layers [42] and differences in background doping [43–45].

As in the case of InGaN/GaN, the predicted sheet charges appear to be an overestimation compared to the experimental observations. In the case of optical measurements, Schrödinger-Poisson modeling is again typically used to interpret the measured properties, and the same uncertainties and systematic errors may arise as discussed in the case of InGaN/GaN [46,47]. For the cases where the compensating 2DEG density is measured, the thickness of the AlGaN layer and Schottky barrier height at the AlGaN surface will determine whether the entire bound charge is compensated, which could be a reason that the observations are slightly lower than predicted theoretically [48]. Also, interface roughness and electron traps due to dislocations and/or surface states have been proposed to explain the reduced 2DEG density [14].

E. Comparison of theoretical implementations

The degree of agreement between results obtained based on the current practice in the field (ZB reference, no correction term, proper PZ) and our revised implementation (H reference, improper PZ constants) merits some discussion. It is clear from Table I that the SP polarization values determined with the H reference structure are very different from those determined with the ZB reference; also, from Table II, the improper and proper e_{31} coefficients are very different. However, the similarity between the red solid and black dashed curves in Fig. 2 demonstrates that these two large corrections cancel when we evaluate Eq. (18). In other words, the correct implementation (H reference, improper PZ constants) results in values that are only slightly different from the current (incorrect) practice in the field (ZB reference, no correction term, proper PZ). We now demonstrate analytically how this accidental agreement comes about.

If we take the difference between our revised implementation (solid red curve in Fig. 2) and the current practice in the field (dashed black curve in Fig. 2) for a given x, we obtain the total error in using the current practice in the field:

$$\Delta P_{\rm error} = x\Delta P_{\rm corr}^{\rm (ZB\,ref)} + 2\epsilon_1(x)P_{\rm eff}^{n,\rm (H\,ref)}(x). \tag{19}$$

A derivation of this expression is given in Sec. S5 of Ref. [15]. For both AlGaN/GaN and InGaN/GaN, the two terms on the right-hand side of Eq. (19) have opposite signs and a tendency to cancel. To understand why, first note that $\epsilon_1(x)$ is approximately linear in x, so that both terms can be regarded as being roughly proportional to $\epsilon_1(x)$. In particular, linearizing Eq. (14) in ϵ_1, we find $x\Delta P_{\rm corr}^{\rm (ZB\,ref)} \simeq -2\epsilon_1(x)P_{\rm f}^{m,\rm ZB}$ [see also Eq. (8) of Ref. [15]]. Thus,

$$\begin{aligned}\Delta P_{\rm error} &\simeq 2\epsilon_1(x)(P_{\rm eff}^{n,\rm (H\,ref)} - P_{\rm f}^{m,\rm ZB})\\ &= 2\epsilon_1(x)(P_{\rm f}^{n,\rm WZ} - P_{\rm f}^{m,\rm ZB})\\ &= 2\epsilon_1(x)[P_{\rm eff}^{n,\rm (ZB\,ref)} + (P_{\rm f}^{n,\rm ZB} - P_{\rm f}^{m,\rm ZB})],\end{aligned} \tag{20}$$

where in the second step we used the fact that the formal polarization of the H structure vanishes. For the III-nitrides, $|\epsilon_1| < 0.1$, and we see from Table I that $|P_{\rm eff}^{n,\rm ZB}| < 0.1\ {\rm C/m^2}$. The second term in the last line of Eq. (20), $P_{\rm f}^{n,\rm ZB} - P_{\rm f}^{m,\rm ZB}$, is related to the difference in in-plane lattice constants between material n and material m (Sec. III B). The largest value it will take for the materials considered in this study is $0.28\ {\rm C/m^2}$ for InN on GaN, as calculated in Eq. (14), and it will be significantly smaller for lower alloy content and for the case of AlGaN on GaN. The error is therefore the product of small factors, and thus small in practice, significantly smaller than the errors in the SP and PZ parts individually.

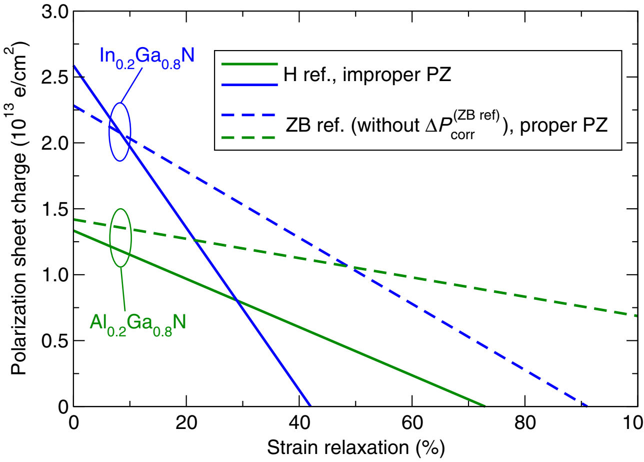

FIG. 3. Absolute values for polarization sheet charges at the $In_{0.2}Ga_{0.8}N/GaN$ (blue) and $Al_{0.2}Ga_{0.8}N/GaN$ (green) interface as a function of percent strain relaxation. Here, 0% relaxation corresponds to perfectly strained layers, and 100% relaxation to an unstrained overlayer at its bulk lattice constant. Solid curves are the correct implementation described in this work (H reference for SP and improper PZ constants); dashed curves are the current practice in the field (ZB reference for SP, without the correction term, and proper PZ constants).

The small magnitude of $P_{eff}^{n,ZB}$ (Table I) demonstrates that $P_f^{WZ} \sim P_f^{ZB}$ in these materials (see Sec. S1 of Ref. [15]). The similarity between P_f^{ZB} and P_f^{WZ} is not unexpected. Although ZB has sufficient symmetry to preclude SP polarization, in the [111] direction the structure only differs from the WZ c direction by the stacking of the cation/anion planes and a small deviation from the ideal WZ u parameter and c/a lattice constants. In WZ materials other than the III-nitrides, such deviations could, in principle, be larger, and in that case, $P_{eff}^{ZB\ ref}$ will be larger, resulting in ΔP_{error} being more significant.

For AlGaN/GaN, the relatively modest difference in lattice constants between AlN and GaN (and therefore modest ϵ_1 values for coherently strained alloy layers), and an almost exact cancellation between $P_f^{GaN,ZB}$ and $P_{eff}^{AlGaN,(H\ ref)}$ means that the difference between implementations is small over the whole composition range (cf. Sec. S5 of Ref. [15]). For InGaN/GaN, the large lattice mismatch of InN and GaN and a less complete cancellation of $P_f^{GaN,ZB}$ and $P_{eff}^{InGaN,(H\ ref)}$ results in a significant deviation at higher In content; this will be important for the prediction of polarization fields in applications such as tunnel field-effect transistors based on thin, high In-content interlayers [49].

The two implementations differ significantly in the *relative* contributions of SP and PZ polarization. An effect of this is illustrated by the case where there is strain relaxation in the alloy layer. In Fig. 3, the predicted polarization bound charges for $In_{0.2}Ga_{0.8}N/GaN$ (blue curves) and $Al_{0.2}Ga_{0.8}N/GaN$ (green curves) are shown as a function of strain relaxation of the layer, modeled by simply scaling ϵ_1. For both InGaN/GaN and AlGaN/GaN, the revised implementation of this work predicts a much faster decrease in bound charge at the interface than the current practice in the field. Of course, strain relaxation is associated with the presence of edge dislocations at the interface, which may themselves influence the interface bound charge; this effect has not been taken into account in either version of the implementation.

VI. CONCLUSIONS

We have derived a rigorously correct implementation of polarization constants in wurtzite materials, focusing on the example of the III-nitrides. Our derivation has demonstrated the impact of the choice of reference structure when calculating spontaneous polarization constants using the modern theory of polarization. Insufficient care in using the values can result in spurious contributions to the polarization discontinuities at heterostructure interfaces. We have provided new values calculated with a consistent hexagonal (rather than zincblende) reference structure. In addition, we have demonstrated the importance of choosing the correct piezoelectric constants (improper) and provided values for these improper constants. These revised values of the spontaneous and piezoelectric constants can be directly used in simulations and to interpret experimental observations. The revised implementation predicts a more rapid decrease of polarization charge with strain relaxation for an alloy layer on GaN.

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