Accurate calculation of polarization-related quantities in semiconductors

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We demonstrate that polarization-related quantities in semiconductors can be predicted accurately from first-principles calculations using the appropriate approach to the problem, the Berry-phase polarization theory. For III-V nitrides, our test case, we find polarizations, polarization differences between nitride pairs, and piezoelectric constants quite close to their previously established values. Refined data are nevertheless provided for all the relevant quantities.

The importance of spontaneous and piezoelectric polarization in nitride semiconductors is by now widely recognized, and numerous reports of observations and practical exploitations of polarization effects in optoelectronic and electronic nitride nanostructure devices have appeared.[1] Many experiments have been rather successfully interpreted using recently calculated *ab initio* values of the spontaneous polarization and the piezoelectric constants.[2]

Doubts have recently been raised about the accuracy of computed spontaneous polarization values in nitride semiconductors. A recent study[3] based on a supercell method[4] reported values of the spontaneous polarization of AlN, GaN, and InN that differ widely (by ∼50-100%) from those of our recent calculations.[2] Our results were obtained within density-functional theory using numerical methods based on the modern theory of polarization and the Berry-phase concept,[5] so they are expected to be highly reliable. Indeed, they have been used successfully in the experimental[1] and modeling[6] literature. It is therefore appropriate to reexamine the accuracy of the polarization calculations, to dissipate doubts and confusion about which values to use, and to clarify the size of the expected errors. Since the nitrides provide a severe test for polarization calculations, we expect our error estimates to provide a valid upper bound for all semiconductors.

The message of the present paper is fourfold. *First*, we find that it *is* possible to calculate polarizations with the accuracy needed to compare with experiment,[1,6] provided a well-controlled and accurate method is used to calculate the polarization, and that the structure is accurately optimized by state-of-the-art *ab initio* density-functional calculations. The polarization is found to be most sensitive to internal structural parameters (in wurtzite, the parameter u). *Second*, absolute polarization values resulting from the present revision deviate only slightly (∼10%) from the previous values. Moreover, observable quantities, namely polarization *differences* between various compounds, are essentially unchanged with respect to our previous report.[2] *Third*, we report revised values of the piezoelectric constants, again rather close to our previous data; we consider that the present values are more refined and should be preferred in modeling. We accompany the revised piezoconstants by accurately calculated elastic constants, providing a self-consistent set of data to estimate piezoelectric fields in strained nitrides. *Fourth*, we briefly address the possible origin of the discrepancy between the report of Ref. 3 and our results. We suggest that it may be connected with technical shortcomings, especially imperfect convergence of the equilibrium structure, in the superlattice calculation,

We analyze the polarization as obtained using the Berry-phase method[2,5] within two different density-functional theory (DFT) exchange-correlation schemes. Specifically, as do the authors of Ref. 3, we use the VASP package[7] and the pseudopotentials provided therewith. We carry out calculations using both the generalized gradient approximation (GGA) to density-functional theory in the Perdew-Wang PW91 version, and the local-density approximation (LDA) in the Ceperley-Alder-Perdew-Zunger form (used in Ref. 3). Ultrasoft potentials[8] are used (Ga and In d electrons are treated as valence) at a conservative cut-off of 325 eV, and reciprocal-space summation is done on an (888) Monkhorst-Pack mesh.

Our results are as follows. In Tables I, II and III we list the structural parameters a, c/a, and $\epsilon_1 = u - u_{\rm ideal}$, and the spontaneous polarization $P_{\rm sp}$, for the III-V nitrides. To obtain them, we optimize the structure within both the GGA and LDA, then calculate the spontaneous polarization with the Berry-phase technique. In addition, we calculate the polarization for sets of structural parameters reported by others. Specifically, we use the LDA-pseudopotential lattice parameters reported by Bechstedt, Großner, and Furthmüller[3] (BGF), and those calculated with the FLAPW method within the LDA by Wei and Zunger (WZ).[12] The results are labeled 'Present (LDA)', 'Present (GGA)', 'BGF (LDA)', and 'WZ (LDA)' in Tables I to III. Next, in Table IV we give the spontaneous polarization *differences* for some relevant cases. Finally, in Table V we report the piezoelectric constants, dynamical Born charges, spontaneous polarizations, and elastic constants (relevant to the piezofields in strained nitrides layers) as calculated in the GGA approximation, which are proposed as revised values to be used in modeling of experiments involving macroscopic polarization effects.

¿From Tables I to III, it is evident that the Berry-phase results are quite homogeneous despite the methodological differences of the various methods and DFT parameterizations (the main exception, GaN in the Bechstedt structure, is discussed below). As pointed out below, they differ considerably from the values calculated[3] in the supercell approach. The major source of these deviations are inaccuracies in the determination of the internal parameter u. In the ideal wurtzite structure, u=$u_{\rm ideal}$=0.375 in units of c/a. Here we compare different calculations through the parameter $\epsilon_1 = u - u_{\rm ideal}$, expressed in units of $10^{-3}\,c/a$. It can be noticed from the Tables that polarization is very sensitive to ϵ_1, though relatively insensitive to other structural parameters, as also noted previously.[4,13] For GaN, the ϵ_1 value of Ref. 3 deviates significantly from the others, and indeed we calculate a corresponding Berry-phase $P_{\rm sp}$ which is more than a factor of two larger than all the others. The polarization of $-0.074\,{\rm C/m}^2$ obtained in the superlattice calculations[3] is also too large by a factor 2. This suggests that the origin of the discrepancy for GaN is the overestimation of the ϵ_1 parameter (ϵ_1=6.5) in Ref. 3. Since the same group reported[14] ϵ_1=1.5 for GaN (in good agreement with other entries in our Table and with experiment) using the same code and pseudopotentials, but a much finer k-point summation mesh, the deviation is possibly due to k-space summation.

For AlN, the largest discrepancy (between the values for the GGA and LDA–Bechstedt structures) is $13\,{\rm mC/m}^2$, i.e., a difference of $\sim$1.0 in ϵ_1. Indeed, the GGA structure is closer to experiment, and it should be more reliable. In any event, the superlattice value of $-0.120\,{\rm C/m}^2$ is about 20-25 ${\rm mC/m}^2$, or 25%, larger than all the Berry-phase values. For InN, ϵ_1 is quite homogeneous throughout, and indeed so are the polarizations, all within 5%. The superlattice polarization is $-0.050\,{\rm C/m}^2$, also in the vicinity of the Berry-phase values.

¿From the data in Tables I, III, and II, it appears that the Berry-phase polarization values are quite stable and largely independent of exchange-correlation scheme, once the structure (mostly, the ϵ_1 parameter) is determined correctly. The polarizations previously determined[2] for AlN, GaN, and InN were −0.081, −0.029, −0.032; the present GGA values are 11%, 9% and 23% larger. We also remark that the GGA values obtained in this paper produce polarization differences between nitride pairs that compare quite well with those in current use.[2] Table IV reports the comparison.

We recalculated the dynamical charges and piezoelectric constants of the nitrides in the GGA approximation to verify our earlier results. The present values are fairly close to our previously reported ones (Table II of Ref. 2). The data listed in Table V are proposed as updated reference values. Our values compare well with recent experiments[15] for AlN, slightly less favorably for GaN. One source of uncertainty is that the set of elastic constants used in Ref. 15 to translate the measured stress-piezoelectric d tensor into the strain-piezoelectric e tensor, may or may not be consistent with our present approximations. This issue can be solved by a direct prediction of the full d tensor from calculations of polarization vs stress, which we will be presenting in a forthcoming work.

We also evaluated within the GGA the subset of elastic constants needed in the determination of strain in epitaxial nitride layers, which bears on their built-in piezoelectric fields. Our values are somewhat smaller than the LDA values reported e.g. by Wright,[16] as is not unexpected given the smaller equilibrium volume in LDA compared to GGA. The rather scattered experimental data (collected in Ref. 16) do not allow to express a preference for either of the two approaches in this respect.

It has recently been shown[17] that the proper piezoelectric response is related to a current flow across a sample in response to polarization. This response corresponds to a set of so-called *proper* piezoelectric constants. These differ from the polarization derivatives with respect to strain (the *improper* constants) by a quantity proportional to the spontaneous polarization, hence of order 10%. The piezoelectric constants just reported in Table V are the improper constants.[17] These constants are those to be used in the interpretation or modeling of experiments involving depolarizing fields and polarization-induced interface charges.[18] On the other hand, in view of their definition,[17] the proper constants are those to be compared with experiments based on measurements of *current* across piezoelectric samples and with values calculated from linear-response theory.[19] The proper constants as calculated within the GGA are reported in Table VI. Only the e_{31}'s are affected, while the e_{33}'s are unchanged.

Going back to the accuracy of calculated polarizations, it is appropriate to note that the theoretical results are relatively stable in other systems also. For BeO (note that Ref. 3 misquotes Refs. 2 and 4 about this material), a longitudinal polarization $P_{\rm L}$= $-15\,{\rm mC/m}^2$ is reported[4] for a length-optimized clamped-ion wurtzite half cell. This corresponds to a transverse $P_{\rm T}$ = ε_∞ $P_{\rm L}$= $-48\,{\rm mC/m}^2$, in excellent agreement with our Berry-phase value[2] of $-50\,{\rm mC/m}^2$. Also, the transverse spontaneous polarization of ZnO was found to be $-57\,{\rm mC/m}^2$ using pseudopotentials[2] and $-50\,{\rm mC/m}^2$ using FLAPW.[13] Again, the accuracy depends most critically on the internal parameters. A similar but more stringent test for GaN/AlN strained superlattices[18] showed that the calculated interface charge agrees to within less than $1\,{\rm mC/m}^2$ with that predicted from bulk transverse polarizations and dielectric constants.[20]

We briefly note that the structural issues discussed above do not account for all the discrepancies observed with the calculations of Ref. 3. Two possible additional sources of error are related to the presence of large depolarizing electrostatic fields in the supercell (see Fig. 3 of Ref. 3). First, the length of the clamped-ion superlattice was not optimized. In a non-zero field E_z, this has the same effect[20] of an inverse-piezoelectric distortion, leading to a spurious polarization $\delta P_z = -[e_{33}^{(0)}]^2\, E_z/C_{33}$ (with $e_{33}^{(0)}$ the clamped-ion piezoconstant and C_{33} the elastic modulus). However, this is only a small correction (~1 mC/m^2). Second, the field causes a large potential drop over the superlattice, amounting respectively to about 1.4, 3.3 and 6.0 eV in InN, GaN, and AlN (in the wurtzite region; see Fig. 3 of Ref. 3). This drop is larger than the calculated LDA gap of the materials. While there seems to be no evidence for instability,[3] we presume this could be a significant source of error.

In summary we have shown that the polarization of nitride semiconductors can be calculated within the DFT-based first-principles Berry-phase approach in a stable and reproducible manner. Calculated polarizations can therefore be used safely in comparisons with experiment in nitride quantum structures. Given the demanding test case provided by the nitrides, we believe this conclusion applies to any semiconductor whose structure, and in particular whose internal parameters, can be accurately predicted.

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TABLE I. Structure and polarization of GaN. The Berry-phase spontaneous polarization $P_{\rm sp}$ has been calculated for each structure and setting listed. The structures are those obtained in the LDA by Bechstedt, Großner, and Furthmüller[3] (BGF) and by Wei and Zunger[12] (WZ), and by ourselves (Present) in both the LDA and GGA. Lattice constant a in Å, ϵ_1 in $10^{-3} c/a$, and $P_{\rm sp}$ in C/m^2. Ref. 3 reports a supercell-based $P_{\rm sp}$=−0.074 C/m^2 for the BGF (LDA) case.

Structure from	a	c/a	ϵ_1	$P_{\rm sp}$
BGF (LDA)	3.150	1.6310	6.5	−0.080
WZ (LDA)	3.180	1.6259	1.8	−0.032
Present (LDA)	3.131	1.6301	1.6	−0.032
Present (GGA)	3.197	1.6257	1.9	−0.034
Experiment[a]	3.1890	1.6263	2.0	—

[a]Ref. 9

TABLE II. Structure and polarization of AlN. Details as in Table I. Ref. 3 reports a supercell-based $P_{\rm sp}$=−0.120 C/m^2 for the BGF (LDA) case.

Structure from	a	c/a	ϵ_1	$P_{\rm sp}$
LDA (BGF)	3.080	1.6070	7.4	−0.103
LDA (WZ)	3.112	1.6009	6.9	−0.094
LDA (present)	3.070	1.5997	7.1	−0.099
GGA (present)	3.108	1.6033	6.4	−0.090
Experiment[a]	3.1106	1.6008	7.1	—

[a]Ref. 10

TABLE III. Structure and polarization of InN. Details as in Table I. Ref. 3 reports a supercell-based $P_{\rm sp}$=$-0.050\,{\rm C/m^2}$ for the BGF (LDA) case.

Structure from	a	c/a	ϵ_1	$P_{\rm sp}$
LDA (BGF)	3.530	1.6320	5.0	-0.043
LDA (WZ)	3.544	1.6134	4.0	-0.042
LDA (present)	3.509	1.6175	3.6	-0.041
GGA (present)	3.580	1.6180	3.7	-0.042
Experiment[a]	3.538	1.6119	—	—

[a]Ref. 11

TABLE IV. Modulus of the spontaneous-polarization differences (mC/m^2) between binary nitrides. The values of Ref. 2 and Ref. 3 are reported together with the present GGA result.

$\mid \Delta P \mid$	Present (GGA)	Ref. 2	Ref. 3
AlN/GaN	55	52	46
GaN/InN	7	3	24
InN/AlN	48	49	70

TABLE V. Spontaneous polarization (C/m^2), improper piezoelectric constants (C/m^2), dynamical charges, and elastic constants (GPa) for the nitrides as obtained in the GGA approximation.

	$P_{\rm sp}$	e_{33}	e_{31}	Z^*	C_{33}	C_{31}
AlN	-0.090	1.50	-0.53	2.65	377	94
GaN	-0.034	0.62	-0.34	2.76	354	68
InN	-0.042	0.81	-0.41	3.10	205	70

TABLE VI. Proper piezoelectric constants (C/m^2) for the nitrides in the GGA approximation.

	e_{33}	e_{31}
AlN	1.50	-0.62
GaN	0.62	-0.37
InN	0.81	-0.45