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Piezoelectricity of ordered ($Sc_xGa_{1-x}N$) alloys from first principles

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Abstract. First-principles calculations are performed to compute the e_{33} piezoelectric coefficients of GaN, ScN and ($Sc_xGa_{1-x}N$) alloys exhibiting an alternation of *hexagonal* GaN, with *hexagonal* ScN along the *c*-axis. For Sc compositions larger than 50%, each atom has nearly five nearest neighbors (i.e., the ground state exhibits a phase that is five-fold coordinated). On the other hand, Sc-deficient (Sc, Ga) N alloys adopt a ground-state that is four-fold coordinated). The magnitude of e_{33} in the Sc-deficient ideally *ordered* ($Sc_{0.25}Ga_{0.75}N$) is found to be larger than the magnitude of the corresponding e_{33} coefficients resulting from the compositional weighted average over the *hexagonal* (*h*-ScN) and the *wurtzite* (*w*-GaN) parent compounds. On the other hand, the e_{33} coefficients of the Sc-rich ordered ($Sc_{0.75}Ga_{0.25}N$) is found to be *negligibly small.* In addition, e_{33} piezoelectric coefficients in ordered ($Sc_{0.5}Ga_{0.5}N$) exhibit quite large magnitudes, due to the *nonpolar* to *polar* transition occurs at Sc composition $x = 0.5$, and thus can bridge the corresponding coefficients of (Ga, In) N and ferroelectric alloys. The microscopic origins for this huge enhancement in the piezoelectric behavior in Sc-low and Sc-intermediate alloys and the role of each atom are revealed and discussed.

PACS. 71.15.-m Methods of electronic structure calculations – 71.15.Mb Density functional theory, local density approximation, gradient and other corrections – 71.15.Dx Computational methodology (Brillouin zone sampling, iterative diagonalization, pseudopotential construction)

1 Introduction

The III–V nitride semiconductors have attracted much attention in the development of optoelectronic devices and broadly investigated in the last ten years for both fundamental and technological reasons. For instance, the change in the composition of GaInAlN quaternaries or the size of GaN quantum dots results in photoluminescence in the entire visible region of electromagnetic spectrum [1,2]. In contrast to most of the conventional III–V semiconductors that adopt a cubic and nonpolar zinc-blende ground phase, the ground state of most of III-nitride semiconductors (i.e., GaN and InN) is the so-called wurtzite structure that belongs to polar hexagonal symmetry group, and that will be denoted by *w*-GaN and *w*-InN in the following. Consequently, these materials exhibit considerable piezoelectric and dielectric responses when they are subjected to elastic macroscopic stress or strain. In addition, it is well established that another class of materials, called ferroelectrics, was found to demonstrate huge piezoelectricity when subject to a macroscopic stress or strain that is about ten times larger than those of III-nitride semiconductors. It also has been shown that *ferroelectric* materials can undergo a nonpolar to polar temperature dependent phase transition [3]. Such a phase transition is associated with huge piezoelectric coefficients. As a result, the piezoelectric properties of ferroelectrics and those of III–V nitride semiconductors–based materials can be combined together to provide piezoelectric properties of great interest for modern device technology.

Several previous theoretical and experimental studies on ScN focused on the rocksalt phase that this binary compound exhibits in its ground state [4]. A more recent theoretical study has reported the existence of another metastable phase in ScN [5]. Such a phase can be described as a layered hexagonal (nonpolar) phase that is five-fold coordinated, and that will be denoted by *h*-ScN hereafter. It has been predicted that applying a compressive in-plane strain on *h*-ScN can lead to a huge piezoelectric response (see Fig. 1 which shows a schematic representation of *h*-ScN for three different strains [6]), as well as a band gap engineering in the entire visible range.

In general, to the material scientist and industry, the challenge is to discover or "design" materials which can be "multifunctional", i.e. combine the desirable properties of multiple materials into one [6], which means that

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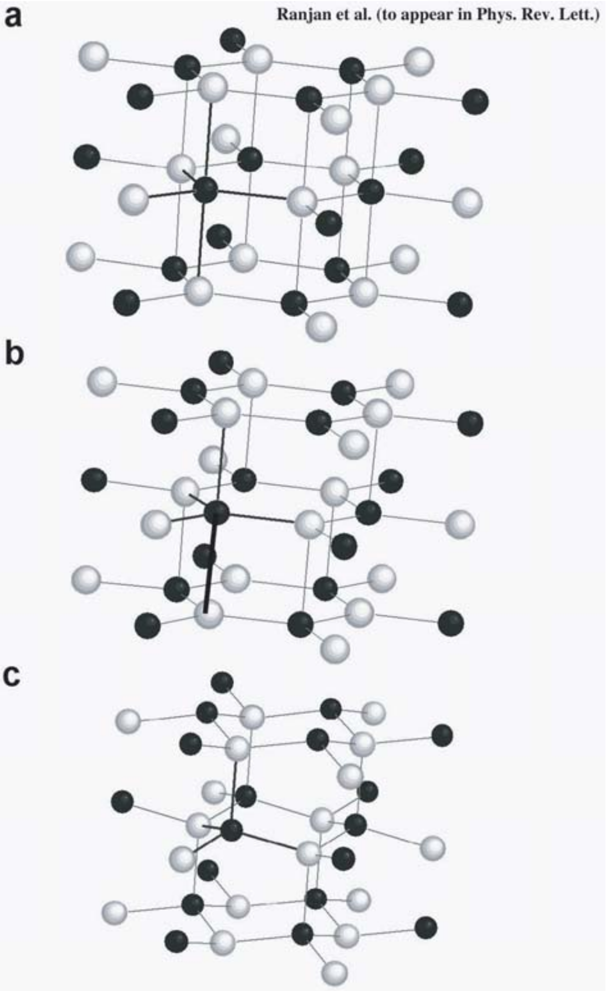

Fig. 1. Schematic representation of hexagonal ScN for three different strains, corresponding to a compression of the in-plane lattice constant with respect to its equilibrium value. The black spheres denote N atoms, while the Sc atoms are represented by white spheres. The bold lines join a given N atom to its nearest Sc neighbors. Panel (a) shows the equilibrium unstrained hexagonal ScN (compressive strain, $\eta = 0$), which adopts a non-polar and nearly fivefold coordinated structure denoted by h-ScN. Panel (b) displays the phase corresponding to a compressive strain of 3.4%, for which a phase transition from a non-polar to a polar structure is predicted to occur. Panel (c) represents the phase corresponding to $\eta = 6.4\%$ and for which the number of atomic nearest neighbors becomes nearly 4 rather than 5 (i.e., four-fold coordinated): the N atoms, all, move further down and, as a result, the bond between N atoms and Sc atoms located in the (0001) plane above them breaks.

certain ScN-based materials combine the benefits of semiconductors and piezoelectrics. Furthermore, it has been shown that alloying hexagonal ScN (h-ScN) with either wurtzite GaN (w-GaN) or wurtzite InN (w-InN) to yield *disordered* ($Sc_{1-x}Ga_x$)N and ($Sc_{1-x}In_x$)N alloys, that exhibit certain optical and piezoelectric properties [5], can bridge the corresponding properties of (Ga, In)N ternaries and the ferroelectric alloys. This is due to the large difference in the structural properties between the metastable layered hexagonal (nonpolar) phase (i.e., h-ScN), which is five-fold coordinated [5], and the wurtzite ground state of both w-GaN and w-InN, that is associated with the polar $P6_3mc(C_{6v})$ point group and which is four-fold coordinated. The existence of the metastable phase h-ScN and the experimental growth of (Sc, Ga) N alloys has been recently achieved [7]. C. Constantin et al. have reported the following results: The alloy formation in ScGaN on (0001) sapphire substrates is explored using rf molecular beam epitaxy over the Sc fraction range $x = 0$–100%. Optical and structural analysis show separate regimes of growth, namely (I) wurtzite-like but having local lattice distortions in the vicinity of the ScGa substitutions for small x ($x \leq 0.17$); (II) a transitional regime for intermediate x; and (III) cubic, rocksalt-like for large x ($x \geq 0.54$). In regimes I and III, the direct optical transition decreases approximately linearly with increasing x but with an offset over region II. Importantly, it is found that for regime I, an anisotropic lattice expansion occurs with increasing x in which a increases much more than c. These observations support the prediction of Farrer and Bellaiche [5] of a metastable layered hexagonal phase of ScN, denoted by h-ScN. In addition, Little and Kordesch reported the growth ScGaN by sputtering [8]. All these findings have motivated us to get more insight into the detailed structural and piezoelectric dependence on composition of these important alloys.

It is also well-known that the compositional dependence of many structural and optical properties of the semiconductor $A_{1-x}B_xC$ alloys is usually well described by a second-order polynomial of the composition x [1,9]. However, the dependence of piezoelectric coefficients in these alloys is not well established. Since, many unusual physical properties of wurtzite solid solutions, such as $Ga_{1-x}In_xN$ are related to piezoelectric coefficients (see Ref. [10] and references therein); it would be very interesting and useful to investigate the dependence of e_{33} piezoelectric coefficients of (Sc, Ga) N alloys on composition.

2 Methodology

The alloys under study in this work are made of binaries (h-ScN and w-GaN) that belong to a hexagonal h_c class with a direct Bravais lattice that has primitive lattice vectors given by:

$$\begin{aligned}
\vec{a}_1 &= a\left(\frac{1}{2}\widehat{x} - \frac{\sqrt{3}}{2}\widehat{y}\right),\\
\vec{a}_2 &= a\left(\frac{1}{2}\widehat{x} + \frac{\sqrt{3}}{2}\widehat{y}\right),\\
\vec{a}_3 &= c\widehat{z},
\end{aligned} \tag{1}$$

where a and c are the in-plane and along the c-axis lattice constants, respectively, and c/a is the axial ratio. The unit vectors along the Cartesian axes are denoted by $\widehat{x}$, $\widehat{y}$ and $\widehat{z}$. There are four atoms per unit cell: two cations located

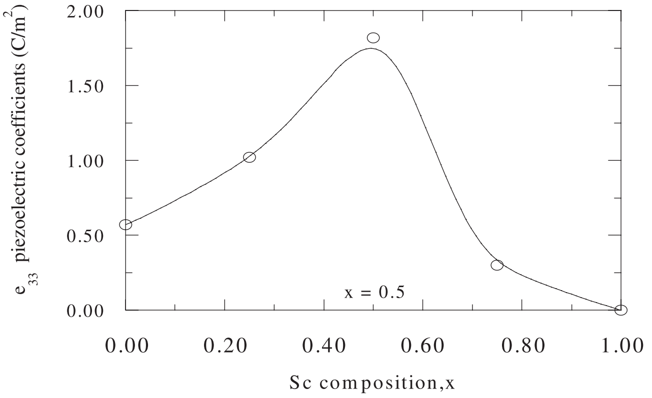

Fig. 2. Shows the e_{33} piezoelectric coefficients as a function of Sc. composition. As Sc composition increases, e_{33} coefficients increase. At intermediate composition, $x = 0.5$, a huge increase of the coefficients occurs associated with an isostructural phase transition from a wurtzite-derived to a hexagonal-derived phase.

at $\vec{r}_1$ and $\vec{r}_2$, and two anions positioned ideally at $\vec{r}_3$ and $\vec{r}_4$, with

$$\begin{aligned}
\vec{r}_1 &= 0,\\
\vec{r}_2 &= \frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3,\\
\vec{r}_3 &= u\vec{a}_3,\\
\vec{r}_4 &= \frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \left(\frac{1}{2} + u\right)\vec{a}_3,
\end{aligned} \tag{2}$$

the equilibrium structural parameters a, c/a and the dimensionless internal parameter u determine the location of the atoms inside the unit cell and are thus needed to characterize the structural properties of these binary hexagonal parent compounds and the derived (Sc, Ga)N alloys. Considering the parent compounds of the current investigated alloys, it is well established that GaN exhibits wurtzite structure as its ground state, while in the ScN binary, a given Sc (N) atom forms short bonds $d_{nn1} = 2.11$ Å with three N (Sc) atoms belonging to the same basal plane but forms longer bonds $d_{nn2} = 2.21$ Å with two other N (Sc) atoms being in the c-planes below and above it, respectively. This is exactly the same structure described and depicted in Figure 2 of reference [5]. The existence of this metastable phase in ScN has been recently supported experimentally [7]. Moreover, the unit cells for the (Sc, Ga) N ordered *ternary alloys* in the present study are formed by stacking layers along the [0001] direction. For instance, the $Sc_{0.5}Ga_{0.5}N$ structure is formed by alternating equal layers of Sc and Ga along (0001) (i.e., along $\vec{a}_3$), leading to a 4-atom cell, while the $Sc_{0.25}Ga_{0.75}N$ or $Sc_{0.75}Ga_{0.25}N$ are formed by stacking one layer of ScN followed by three layers of GaN, or three layers of ScN followed by one layer of GaN along $\vec{a}_3$, respectively, to yield an 8-atom cell. It is worth noting that this specific atomic ordering exhibited by the (Sc, Ga) N alloys presented in this study is exactly the same as the one adopted by (Ga, In) N alloys depicted in Figure 1 of reference [11]. Note that these ordered structures can be thought of as exhibiting two different kinds of u parameter (see Eq. (2)): the first kind are the ones connecting the Ga and N atoms that are nearest neighbors along the c-axis — for which the average over all Ga atoms is referred to as $\langle u_{\mathrm{GaN}} \rangle$ — and the other kind are the ones binding the Sc and its closest N atoms along the $\vec{a}_3$ — for which the average over all Sc atoms is denoted by $\langle u_{\mathrm{ScN}} \rangle$ (see Tab. 1).

Computationally, we perform total-energy calculations using the first-principles density functional theory (DFT) within the local-density approximation (LDA) [12] calculations on h-ScN, w-GaN, and ordered ($Sc_{1-x}Ga_x$) N systems using Vanderbilt ultrasoft-pseudopotential scheme [13]. The valence states for Sc, Ga, and N are taken as $3s^23p^63d^14s^2$, $3d^{10}4s^24p^1$, and $2s^22p^3$, respectively. The plane-wave cutoff was chosen to be 25 Ry. We use the Ceperley-Alder exchange and correlation [14] as parameterized by Perdew and Zunger [15]. We also use a $6 \times 6 \times 4$ (respectively, $6 \times 6 \times 2$) Monkhorst-Pack [16] k-point grid for the first Brillouin-zone integration of four (respectively, eight) atoms per unit cell. All the structural parameters are fully relaxed in each structure by minimizing the total-energy and following the Hellman-Feynman forces (these latter being smaller than 0.045 meV/Å at convergence). The unit cells of all structures presented in this work were enlarged in plane and found to exhibit the same structural parameters. The electronic structure code used for the calculations of structural parameters is based on total energy minimization and is called CUSP code.

In this paper, we first report an accurate value for e_{33} piezoelectric coefficients in *ordered* ($Sc_{1-x}Ga_x$) N for different compositions ranging from $x = 0$ to $x = 1$. Second, we reveal the microscopic origins of the piezoelectric behavior in these ordered systems, in addition to the role of different kinds of atoms (i.e., Sc, Ga and N atoms), on the piezoelectric response of such technologically important materials.

The piezoelectric coefficients are calculated as:

$$e_{ij} = \frac{1}{2\pi\Omega} \sum_{\alpha} R_{\alpha,i} \frac{d}{d\eta_j} (\Omega \vec{G}_\alpha . \vec{P}), \tag{3}$$

where $\vec{P}$ is the spontaneous polarization which is computed as a Berry phase of the Bloch states [17] and Ω is the volume of the unit cell which, in terms of the lattice constants a and c, is given by $\sqrt{3}/2a^2c$, $\alpha = 1, 2, 3$ runs over the three real-space lattice vectors $\vec{R}_\alpha$ and reciprocal lattice vectors $\vec{G}_\alpha$ and η_j is the macroscopic strain. Equation (3) leads to the calculation of the "proper" piezoelectric coefficients [17,18]. It is also evaluated by finite differences between two states: first that of the ground state, and then for a η_j macroscopic strain of 1.5% relative to the ground state. The internal atomic coordinates of all atoms in the unit cell are reoptimized after the strain is applied. A small value of macroscopic strain (i.e., 1.5%) was chosen to ensure a linear piezoelectric regime where equation (3) can be evaluated by finite differences involving the ground state. The numerical code used to perform the calculation of piezoelectric coefficients is based on Berry

Table 1. Comparison between the LDA-predicted properties of the *h*-ScN, *w*-GaN, and the (Sc, Ga) N ordered alloys (see text). a, c/a, and u are the in-plane lattice constant, axial ratio, and dimensionless internal parameter, respectively.

Property	*h*-ScN	*w*-GaN	$\mathrm{Sc_{0.25}Ga_{0.75}N}$	$\mathrm{Sc_{0..5}Ga_{0.5}N}$	$\mathrm{Sc_{0.75}Ga_{0.25}N}$
a Å	3.660	3.162	3.220	3.33	3.54
c/a	1.207	1.631	1.618	1.553	1.220
$\langle u_{\mathrm{GaN}} \rangle$		0.376	0.370	0.375	0.486
$\langle u_{\mathrm{ScN}} \rangle$	0.500		0.405	0.410	0.500

Table 2. Piezoelectric coefficients (in C/m^2) of *w*-GaN, *h*-ScN, and the ordered ($\mathrm{Sc}_x\mathrm{Ga}_{1-x}\mathrm{N}$) alloys. Values in parentheses are those refer to e_{33}^{av} which are computed from the linear average over *w*-GaN and *h*-ScN piezoelectric coefficients.

Piezoelectric coefficients	*h*-ScN	*w*-GaN	$\mathrm{Sc_{0.25}Ga_{0.75}N}$	$\mathrm{Sc_{0..5}Ga_{0.5}N}$	$\mathrm{Sc_{0.75}Ga_{0.25}N}$
e_{33}	0	+0.57	+1.02(0.43)	+1.82(0.29)	+0.30 (0.14)
$e_{33,c}$	0	–0.84	–0.95	–0.90	0
$e_{33,int}$	0	+1.41	+1.97	+2.72	+0.30

phase approach within the framework of the modern theory of polarization.

3 Results

3.1 Structural properties

Our local-density approximation (LDA) calculations predicted that GaN in its equilibrium hexagonal ground-state has the in-plane lattice constant $a = 3.162$ Å (=5.975 Bohr), the axial ratio $c/a = 1.631$, and the internal dimensionless parameter $u = 0.376$ as shown in Table 1. This specific combination of lattice parameters leads to what is so-called wurtzite phase, which is associated with the polar $\mathrm{P6_3}mc(\mathrm{C_{6v}})$ point group, and which is 4-fold coordinated. Our results agree well with previous theoretical findings [6,10,11]. Recent experimental measurements for the axial ratio of *w*-GaN found it to be 1.635 [7], which in a good agreement with our predicted value. The value of the internal parameter u was also found to be in excellent agreement with the recent available data (see Refs. [6,10,11] and references therein). Our predicted values for the lattice constant of *h*-ScN and the axial ratio c/a are 3.66 Å and 1.207, respectively. Thus a can potentially locally be increased by up to 13.6%, depending on x; at the same time, c would locally decrease in the $\mathrm{Sc}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloys. The value of the internal parameter u for *h*-ScN was found to be 0.5. In other words, u varies within the alloy away from the *w*-GaN value of 0.376. These findings are in excellent agreement with the results of references [5–7]. With such equilibrium lattice parameters, ScN adopts a layered, nearly five — fold coordinated structure that has a nonpolar $P6_3/mmc(D_{6h})$ space group. Furthermore, the lattice constant and axial ratio of the ordered ($\mathrm{Sc}_x\mathrm{Ga}_{1-x}\mathrm{N}$) alloys with compositions ranging between $x = 0.25$ and $x = 0.75$ *approximately* follow Vegard's law as shown in Table 1. Recently, reference [7] has reported the measured c/a values for (Sc, Ga) N alloys with compositions x ranging from 0 to 0.17. The data show decreasing values of c/a for increasing x in good agreement with our predicted trend for the c/a parameter. This experimental data show that the change in c/a over the range $x = 0$ to $x = 0.17$ is –0.040. As shown in Table 1, our data predicts that the change in c/a over the range $x = 0$ to $x = 0.5$ is –0.078. Thus, it would be very interesting, from the experimental point of view, to test the change of c/a over the composition $x > 0.17$. The equilibrium structural parameters (a, c/a and u) for the *h*-ScN and *w*-GaN parent compounds and the different generated ordered (Sc, Ga) N alloys are summarized in Table 1.

3.2 Piezoelectric properties

The results for e_{33} piezoelectric coefficients in *w*-GaN, *h*-ScN and the ordered ($\mathrm{Sc}_x\mathrm{Ga}_{1-x}\mathrm{N}$) alloys are those averaged over the tensile and compressive ±1.5% strains as shown in Table 2. The compositionally weighted average between the e_{33} values in *w*-GaN and *h*-ScN, that will be denoted by e_{33}^{av} in the following discussion, is also given in the same table.

The most important feature implied in Table 2 is that the magnitude of e_{33} coefficients in the ordered ($\mathrm{Sc_{0.25}Ga_{0.75}N}$) alloys is larger than that of the corresponding compositionally weighted average e_{33}^{av}. This upward deviation from linear piezoelectric response with composition is *quite* large and thus indicates that this system has anomalous piezoelectric behavior. The most striking feature of Table 2 and Figure 2 is the *huge* magnitude of e_{33} piezoelectric coefficients in $\mathrm{Sc_{0..5}Ga_{0.5}N}$ system as compared with that in Sc-deficient or Sc-rich (Sc, Ga) N alloys. As a result, this system has a piezoelectric coefficient that is larger than those of (Ga, In) N alloys and a little less than the corresponding coefficients of some ferroelectric alloys. This clearly shows that the piezoelectric properties of such a system can bridge the piezoelectric properties of (Ga, In) N and ferroelectric alloys. There are two major effects that might be responsible for this huge change in piezoelectricity of (Sc, Ga) N ordered systems with respect to the compositionally weighted average response of the parent compounds. First, the dominant dielectric effect that is indicated by the Born dynamical effective charge of different atoms. Second, an elastic effect that measures the response of different atoms in the unit cell to the macroscopic strain. In order to determine these effects quantitatively, we further decompose the piezoelectric coefficients into what is called "clamped-ion" and internal strain or "intrinsic" contributions [17–20]:

$$e_{ij} = e_{ij,c} + e_{ij,int}. \tag{4}$$

The "clamped-ion" or "homogenous-strain" contribution $e_{ij,c}$ is calculated from equation (3) and evaluated by keeping the internal atomic coordinates frozen at their equilibrium positions. The "intrinsic" part $e_{ij,int}$ measures the contributions to the piezoelectric response coming from the displacements of internal atomic coordinates induced by the macroscopic strain. Table 2 indicates such a decomposition and evidently shows that the main contribution to the huge difference between the e_{33} piezoelectric coefficient of the ordered (Sc, Ga) N systems and the e_{33}^{av} is due to the elastic effect represented by the internal-strain contributions, $e_{33,int}$, due to the fact that the clamped-ion $e_{33,c}$ coefficient of different (Sc, Ga) N alloys is *nearly* the same as that of *w*-GaN. This observation encourages us to further get more insight into the microscopic origin of the piezoelectric response in the ordered (Sc, Ga) N systems. Indeed, the $e_{3j,int}$ coefficient (for which $i = 3$) can further be decomposed into internal atomic contributions [17–20] via:

$$e_{3j,int} = \sum_i e_{3j,int}(k), \tag{5}$$

where k runs over all the atoms in the unit cell, and where

$$e_{3j,int}(k) = \frac{2e}{\sqrt{3}a^2} Z_{33}^*(k) \frac{du_3(k)}{d\eta_j}. \tag{6}$$

In equation (6), e is the electronic charge and a is the planar lattice constant. $Z_{33}^*(k)$ is the Born effective charge of atom k which is calculated using Berry-phase approach. The elastic response to the macroscopic strain η_j to the kth atom's internal coordinate along the symmetry c axis is characterized by the $du_3(k)/d\eta_j$.

From Table 2 and Figure 2, it can be also easily observed that the e_{33} piezoelectric coefficient is negligibly small in (Sc, Ga) N alloys, when x is larger than 0.5. This is due to the fact that, for these compositions, the ground-state of the alloy is derived dominantly from the *h*-ScN, which is *a non-polar* phase. On the other hand, when Sc composition becomes smaller than 0.5, the piezoelectric coefficient becomes much larger, since the equilibrium ground-state resembles the wurtzite phase — which is polar in nature. Moreover, Table 2 which shows the decomposition of e_{33} into $e_{33,c}$ and $e_{33,i}$, indicates that $e_{33,c}$ is zero and $e_{33,i} = 0.3$ C/m^2, respectively, when $x = 0.75$. Hence, it is largely the $e_{33,i}$ intrinsic component that determines the value of e_{33} piezo-coefficient in this structure. Furthermore, for Sc composition ranging from $x = 0$ to $x = 0.5$, the $e_{33,c}$ is nearly constant, whereas $e_{33,i}$ increases significantly, as a result, $e_{33,i}$ component is mainly responsible for the trends in e_{33} piezoelectric coefficient with atomic ordering and composition.

Table 3. Piezoelectric coefficients $e_{33,int}$ (k) in C/m^2, dynamical Born effective charge $Z_{33}^*(k)$ in au, and the derivative $du_3(k)/d\eta_3$ of the internal atomic displacements with respect to a macroscopic strain η_3 for the different types of atoms in the primitive cell of *h*-ScN, *w*-GaN, and ordered (Sc, Ga) N alloys. Note that the acoustic sum rules $\sum_k du_3(k)/d\eta_3 = 0$ and $\sum_k Z_{33}(k) = 0$ are conventionally used.

System	Atom	$e_{33,int}(k)$	$Z_{33}^*(k)$	$du_3(k)/d\eta_3$
h-ScN	Sc	≈0	+4.49	≈0
	N	≈0	–4.49	≈0
w-GaN	Ga	+0.350	+2.70	+0.0699
	N	+0.350	–2.70	–0.0699
$Sc_{0.25}Ga_{0.75}$	Sc	+0.26	+3.00	+0.049
	Ga_1	+0.35	+2.96	+0.066
	Ga_2	+0.27	+2.85	+0.053
	Ga_3	+0.15	+2.67	+0.033
	N_1	+0.18	–2.77	–0.038
	N_2	+0.19	–2.84	–0.040
	N_3	+0.28	–2.83	–0.055
	N_4	+0.29	–3.04	–0.057
$Sc_{0..5}Ga_{0.5}N$	Sc	+0.787	+3.25	+0.136
	Ga	+0.569	+2.85	+0.112
	N_1	+0.513	–2.88	–0.100
	N_2	+0.849	–3.22	–0.148
$Sc_{0.75}Ga_{0.25}N$	Sc_1	+0.017	+3.74	+0.0033
	Sc_2	+0.095	+4.11	+0.0168
	Sc_3	+0.017	+3.88	+0.0033
	Ga	+0.022	+4.10	+0.0039
	N_1	+0.103	–3.90	–0.0191
	N_2	+0.014	–4.14	–0.0025
	N_3	+0.028	–3.90	–0.0053
	N_4	+0.0033	–3.80	–0.0004

Table 3 shows several interesting features about the deviation of the piezoelectricity behavior of ordered (Sc, Ga) N alloys from the compositionally weighted average of the piezoelectric coefficients of the *h*-ScN and *w*-GaN parent compounds. It also demonstrates that the atoms mostly responsible for the tremendous increase of e_{33} in the $Sc_{0.5}Ga_{0.5}N$ ordered system with respect to e_{33}^{av} are the Scandium and the nitrogen atom designated by N_2 in Table 3, since they exhibit the largest values among all other atoms for $e_{33,int}(k)$. Evidently, Table 3 further indicates that Sc and N_2 atoms have a Born effective charge of relatively large magnitude in comparison to the corresponding values for Ga and N_1 atoms. As a result of these findings, this increase in e_{33} coefficients is thus due to an elastic effect, as evidenced by the large values of $du_3(\mathrm{Sc})/d\eta_3$ and $du_3(\mathrm{N}_2)/d\eta_3$, and a dielectric effect associated with the Sc and N_2 atoms (see the striking large $Z_{33}^*(\mathrm{Sc})$ and $Z_{33}^*(\mathrm{N}_2)$ values). Interestingly, Sc atom has a vanishing $du_3(\mathrm{Sc})/d\eta_3$ in the parent *h*-ScN compound. In this regard, one can easily note that the cation mostly responsible for the large increase of the magnitude of e_{33} in $Sc_{0.5}Ga_{0.5}N$ is Sc which moves away from N_2 when the macroscopic strain η_3 is applied. Furthermore, a deep insight into the interpretation of the results in Table 3, one concludes that the large e_{33} values for $Sc_{0.25}Ga_{0.75}N$ ordered alloy comes from the elastic effect of all atoms in the unit cell (see the striking large magnitude of $e_{33,int}(k)$ for Sc, Ga_1, Ga_2, N_3 and N_4 atoms in the unit cell in comparison to the corresponding values of Sc, Ga, and N atoms in the parent compounds). On the other hand, the dielectric effects due to all atoms (see the $Z^*_{33}(k)$ values for all atoms of the unit cell in comparison to the corresponding values of $Z^*_{33}(k)$ for these atoms in the parent compounds), *approximately* contribute equally to the $e_{33,int}(k)$ (and hence, to e_{33} coefficients). In addition, Tables 1–3 and Figure 2 indicate that manipulating the Sc composition x in hexagonal ($Sc_xGa_{1-x}N$) alloys results in the following anomalous effects: (1) a continuous evolution of the axial ratio c/a from ≅1.2 0 to ≅1.63 and the dimensionless internal parameter u from 0.376 to 0.500; (2) an *isostructural* phase transition from a wurtzite-derived to a hexagonal –derived phase when applying a macroscopic strain occurs at a composition close to $x = 0.5$ resulting in an *enhancement* of the piezoelectric behavior in this alloy; (3) a considerable change in the cationic-dynamical Born effective charge in the ordered ($Sc_xGa_{1-x}N$) alloys which is due to the fact that Sc is a transition atom, unlike Ga atom.

4 Conclusion

In conclusion, first-principles calculations were performed to investigate the piezoelectric properties of *ordered* ($Sc_xGa_{1-x}N$) alloys. It was found that the enhancement of the piezoelectric coefficients of these alloys with respect to the compositionally-weighted average of the corresponding coefficients of the *h*-ScN and *w*-GaN parent compounds comes mainly from the elastic and dielectric effects of different atoms in the unit cell. It has also been found that playing with the Sc composition in these alloys lead to structural and optical anomalies. The ($Sc_xGa_{1-x}N$) alloys with low and intermediate Sc composition have large piezoelectric coefficients since the Sc-deficient alloys adopt a ground state that is *polar* and *nearly* four fold coordinated. On the other hand, the corresponding e_{33}piezoelectric coefficients of Sc-rich ($Sc_xGa_{1-x}N$) alloys solid solution are *extremely small* which indicates that they belong to a *non polar* phase in which each atom has five nearest neighbors. As a result, mixing the *h*-ScN, which exhibits a phase that is quite different from the wurtzite phase of GaN, should lead to a number of structural, dielectric and optical anomalies. Therefore, we predict that these findings will allow the fabrication of technologically promising devices whose optimal functioning requires large piezoelectric properties and /or certain optical properties.

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