

Origin of the Anomalous Piezoelectric Response in Wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ Alloys

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The origin of the anomalous, 400% increase of the piezoelectric coefficient in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys is revealed. Quantum mechanical calculations show that the effect is intrinsic. It comes from a strong change in the response of the internal atomic coordinates to strain and pronounced softening of C_{33} elastic constant. The underlying mechanism is the flattening of the energy landscape due to a competition between the parent wurtzite and the so far experimentally unknown hexagonal phases of the alloy. Our observation provides a route for the design of materials with high piezoelectric response.

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Piezoelectricity is a phenomenon whereby material becomes electrically polarized upon the application of stress. Discovered in 1880 by Pierre and Jacques Curie, the piezoelectric effect is used in many modern devices, like touch-sensitive buttons, cell phones, computers, GPS, bluetooth, WLAN, etc. Moreover, new piezoelectric materials where excellent piezoelectric response is combined with high temperature operation capabilities are currently sought. A fundamental understanding of factors, which influence the piezoelectric properties of materials appears therefore to be of high scientific and technological value.

Recently Akiyama *et al.* [1] have discovered a tremendous $\sim 400\%$ increase of the piezoelectric moduli d_{33} in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys in reference to pure wurtzite AlN around $x = 0.5$. This is the largest piezoelectric response among the known tetrahedrally bounded semiconductors. Since AlN can be used as a piezoelectric material at temperatures up to 1150°C and it easily can be grown as c oriented, the AlN-based alloys with such a high response open a route for dramatic increase in overall performance of piezoelectric based devices. Nevertheless, a fundamental understanding of the phenomenon leading to such a dramatic improvement in piezoelectric properties of AlN is absent. In particular, it is unclear if the enhanced piezoelectric response in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ is related to the microstructure or if it is an intrinsic effect of the alloying. The aim of this Letter is to present the solutions to this problem from *ab initio* theory.

Reliable *ab initio* calculations of polarization in solids have become possible only with the formulation of the Berry-phase approach by King-Smith and Vanderbilt [2,3] in the mid-90s. However, though alloying is known as one of the most efficient ways of improving materials performance, first-principles studies of the piezoelectric response of disordered alloys have appeared only recently [4,5]. In this Letter we show that alloy physics, associated with the tendency towards different coordination preference in different local chemical environments, can lead to a strong change in polarization induced by internal distur-

tions and pronounced softening of C_{33} elastic constant, giving rise to the large piezoelectric effect in $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

The calculations of piezoelectric coefficients in wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys performed in this study are based on density-functional theory within the generalized gradient approximation [6] either by using the projector augmented wave [7] technique implemented into VASP [8] or the Vanderbilt ultrasoft-pseudopotential scheme [9] within the Quantum-ESPRESSO program package [10]. The proper piezoelectric tensor components e_{33} were calculated with the modern Berry-phase approach [2] as proposed by Vanderbilt [11]. To model the alloys, we applied the special quasirandom structure (SQS) method [12], where the ideally random alloys are modeled with cleverly designed ordered superstructures. The 128-atoms wurtzite based SQS supercells were generated for $x = 0.125, 0.25, 0.375,$ and 0.50 by optimizing the Warren-Cowley pair short-range order parameters [13] up to the 7th shell. The Sc atoms were substituted only on the Al sublattice.

Figure 1 demonstrates the resulting behavior of the piezoelectric constant e_{33} of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ versus composition. e_{33} shows a smooth, but nonlinear increase with the

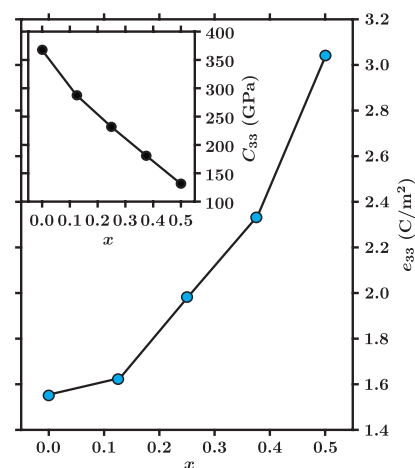


FIG. 1 (color online). The piezoelectric e_{33} and elastic stiffness C_{33} constants of wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys.

amount of Sc, reaching a large, factor of 2 increment at $x = 0.5$. The inset of this figure displays the calculated stiffness constants C_{33} , which exhibit an almost linear decrease. By taking the roughly twofold decrease of C_{33} and the upper bound of $C_{13} \approx C_{13}^{\text{AlN}} = 98$ GPa [5], the acceptable general rule of $R = -(d_{33}/d_{31}) \geq 2$ [14] ensures that $RC_{33} \gg C_{13}$. Consequently, we can reproduce the approximately 400% increase of the piezoelectric moduli $d_{33} \approx (e_{33}/C_{33})$ observed experimentally around $x = 0.5$. These results clearly establish that the observed increase of d_{33} (with units C/N) is definitely inherent for $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys. Hence, our random alloy model should provide valuable insight to explain the microscopic physical origin of the highly increased piezoelectric response in these alloys. The quantitative agreement between our *ab initio*, 0 K results with the reported room temperature experimental results [1] allows us to expect that the phonon contribution to piezoelectricity in ScAlN alloys is small at low and moderate temperatures.

The large nonlinearity of e_{33} highly diminishes the impact of the linear, compositional alloying and points to other alloying related effects, such as internal strain [15]. Consequently, the physical origin of the large piezoelectric response should be explored more in relation to intrinsic structural properties of these alloys. Though, in the *ab initio* computational technique we applied supercell geometries, further analysis of the resulting data is done by projecting to a single wurtzite unit cell using site averaging. Therefore, the piezoelectricity can be discussed like for III–V nitrides [16] by using the expression,

$$e_{33}(x) = e_{33}^{\text{clamped-ion}}(x) + \frac{4eZ^*(x)}{\sqrt{3}a(x)^2} \frac{du(x)}{d\delta}, \quad (1)$$

where e is the electronic charge, a stands for the equilibrium lattice parameter, u for the wurtzite internal parameter and Z^* is the dynamical Born or transverse charge in units of e . δ is the macroscopic applied strain. The first, *clamped-ion* term expresses the electronic response to strain, while the second term describes the effect of internal strain on the piezoelectric polarization.

Although the *clamped-ion* term is not expected to contribute to the strong increase of e_{33} , it was considered in our investigation as the first term in Eq. (1). As Fig. 2(a) shows, a monotonic decrease (from -0.47 to -0.56 C/m²) has been found for this quantity up to $x = 0.375$, followed by an increase up to -0.51 C/m² at $x = 0.5$. The more important characteristic of the local structural sensitivity to macroscopic axial strain δ is expressed in the second term of Eq. (1). Figures 2(b)–2(d) show our calculated compositional weighted and site resolved contributions. The figures unambiguously demonstrate that the change in polarization in these alloys is mainly induced by internal distortions around the Sc sites. One finds a factor of 2 higher sensitivity of u parameter for the Sc sites than for the Al ones. At low Sc fraction the value of $du/d\delta$ ap-

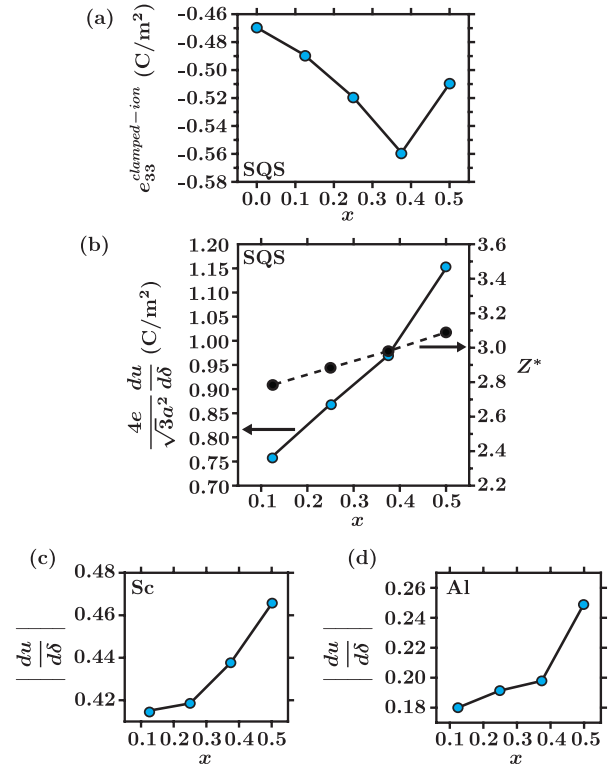


FIG. 2 (color online). The calculated contributions of e_{33} as introduced by Eq. (1). (a) shows the *clamped-ion* term. (b) gives the strain contributions and the Born charges Z^* calculated from Eq. (1). (c) and (d) exhibit the Sc and Al site resolved internal strain sensitivity of wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

proaches -0.18 , which is just the value of pure wurtzite AlN. This justifies our projected single cell approach.

The kink observed for the *clamped-ion* term at $x = 0.375$ in Fig. 2(a) seems to be connected to those shown in Figs. 2(b)–2(d). Hence, this kink refers to the rapidly increasing internal strain sensitivity around the Al sites, which should be determined by electronic effects. To adequately discuss the strong increase of e_{33} in Fig. 1, based on the terms introduced in Eq. (1), one should consider also the dielectric effects represented by the dynamical Born charge Z^* . The dashed line in Fig. 2(b) shows Z^* calculated from Eq. (1). Z^* varies within about 15% around the expected ionic nominal value of 3. In comparison, the structural strain part shown by the solid line in Fig. 2(b) changes by around 60%, which derogates the dielectric contribution associated with Z^* . Consequently, the strongly increased internal axial strain sensitivity, coming primarily from the Sc sites, is mostly responsible for the nonlinear enhancement of the piezoelectric constant e_{33} in wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys. Therefore in this system the observed large piezoelectric response and large elastic softening should be governed by local structural instabilities.

From a structural point of view, the parent wurtzite AlN (w-AlN) has the pyroelectric point group symmetry $6mm$

and the value $u = 0.38$ of the wurtzite internal parameter. The inset of Fig. 3 exposes the wurtzite (B4) structure with its fourfold (tetrahedral) coordination and u parameter. Thus, w-AlN exhibits spontaneous polarization and three nonvanishing independent piezoelectric tensor components. The ground state crystal structure of the other parent compound, ScN, is cubic rocksalt, but the existence of a metastable nearly fivefold coordinated layered hexagonal phase (h-ScN) with a flattened bilayer structure $u = 0.5$ (see the inset of Fig. 3) has been proposed theoretically [17]. Its wurtzite phase turned out to be unstable. Accordingly, h-ScN shows the centrosymmetric point group $6/mmm$ and thus poses no polar properties.

Figure 3 shows the calculated wurtzite internal parameter u of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ as a function of Sc concentration. Interestingly, around the Al sites, the found average u^{Al} value shows strong stability, it is actually frozen to its parent w-AlN value, $u = 0.38$. Around the Sc atoms one finds a monotonic increase of u^{Sc} , though it is still well below the value 0.5 of the hexagonal phase. In accordance with Figs. 2(c) and 2(d), this behavior is in clear correspondence with the larger sensitivity of the Sc sites to axial strain.

The possible phase transition from wurtzite to hexagonal structure, set up by the parent binary phases, can in principle result in enhanced piezoelectric behavior. This issue has been discussed in detail for ordered $\text{Sc}_x\text{Ga}(\text{In})_{1-x}\text{N}$ alloys [18]. Nonetheless the direct influence of this phase transition on our results, in general, can be ruled out. One would observe a jump in the structural internal parameter u [19]. Our calculated composition weighted average wurtzite internal parameters u , as shown in Fig. 3, display instead a small and smooth increase from 0.384 to 0.406. Accordingly, the N coordination in these alloys is still fairly tetrahedral and not fivefold. In the nearly fivefold coordinated hexagonal phase at $x = 0.5$ we found the value $u = 0.49$ corresponding to insignificant piezoelectric activity. The tendency toward different coordination prefer-

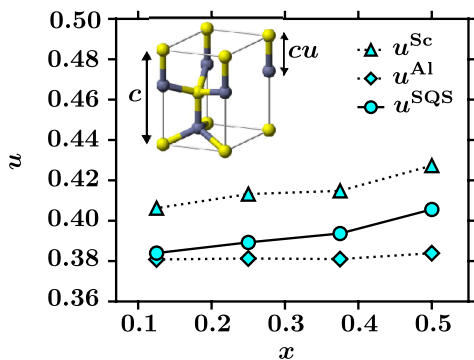


FIG. 3 (color online). The averaged wurtzite internal parameter u as a function of Sc concentration. The dotted lines show the Sc and Al site resolved values, while the solid line is the compositional weighted of $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

ence in different local chemical environments is evident from our calculations.

In order to gain microscopic insights into the observed huge axial softening responsible for the anomalous increase of the piezoelectric coefficient in Sc-doped AlN, as indicated by Fig. 1, we calculated the energy landscape of $\text{Sc}_{0.50}\text{Al}_{0.50}\text{N}$ showing the largest enhancement of e_{33} . The resulting landscape is presented in Fig. 4(a) where each contour line represents an energy step of 5 meV/f.u. The landscape of pure w-AlN is shown in the inset of Fig. 4(a) for comparison and reflects how strongly the elastic properties are affected by Sc alloying. The shallow region in (a) connects the wurtzite derived global energy minimum with a residue of the h-ScN phase present at $c/a \approx 1.27$. The topology of the minimum energy region is considerably elongated in the c/a direction, which guarantees that it affects the alloy properties mostly along lattice parameter c . Since the elastic stiffness constant C_{33} is the curvature of the total energy with respect to c , it gives an explanation of our results shown in the inset of Fig. 1. Note that the existence of a Gibbs free-energy flattening in ferroelectric perovskite crystals has been discussed by Budimir *et al.* [20] in the framework of the phenomenological Landau-Ginsburg-Devonshire theory. Here, it appears explicitly as a result of *ab initio* quantum mechanical calculations.

To interpret these results one can consider the different coordination preferences of ScN and AlN. The tetrahedral coordination of nitrogen in w-AlN is strikingly different as compared to the octahedral coordination in rocksalt ScN and also to the nearly fivefold coordination in h-ScN. In $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys the Al and Sc atoms compete about the coordination of nitrogen thus weakening both the internal resistance against nitrogen displacement as well as the resistance against changing the c/a ratio. As the Sc composition increases this competition becomes more evident [21] and at $x = 0.50$ the structural parameters have become extremely sensitive to external stress underlined by the near energy degeneracy of the two parent phases. The previously discussed kink in the piezoelectric *clamped-ion* term and in the strain sensitivity shown in Fig. 2(d) clearly demonstrate the amplified effect. The fact that the h-ScN derived phase of $\text{Sc}_{0.50}\text{Al}_{0.50}\text{N}$ is not really a local energy minimum with respect to change in c/a , but rather an energy saddle point is seen clearly in Fig. 4(b). The absence of an energy barrier between the two phases is likely to be connected to the fact that we are considering a real random alloy where the presence of chemically different local environments around the nitrogen atoms, all with different preferences for the local coordination, smears out the dependence of the energy on the c/a ratio. This smearing results in smaller curvature, what is seen as a decrease of the elastic constant C_{33} (inset of Fig. 1). Thus, it is underlined that the high piezoelectric response in the $\text{Sc}_x\text{Al}_{1-x}\text{N}$ system is really due to alloy physics of the

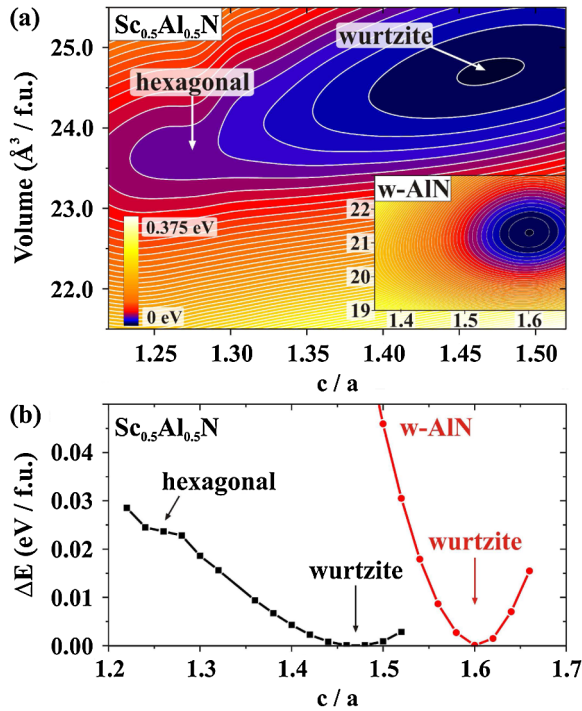


FIG. 4 (color online). The energy landscape of wurtzite $\text{Sc}_{0.5}\text{Al}_{0.5}\text{N}$. (a) presents it as a function of c/a and volume with both wurtzite and hexagonal phases of the alloy, while the inset shows the energy surface of the parent wurtzite AlN . (b) shows minimum energy cross sections of the energy landscapes.

wurtzite phase rather than an actual phase transition. Nevertheless, the close presence, both in energy and volume, of the similar phases with different coordination preference, as in $\text{Sc}_{0.50}\text{Al}_{0.50}\text{N}$, seems to be the signature of an ideal semiconductor alloy system with a potential for large piezoelectric responses. It can thus be used as a criteria in search of better piezoelectric materials.

In summary, we present the theory that reveals the origin of the observed anomalous enhancement of piezoelectric response in wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys. Our first-principles calculations confirm that the 400% increase of the piezoelectric constant is an intrinsic alloying effect. The energy-surface topology is found to be strongly influenced by the alloying, being elongated around the global minimum along c/a direction. This leads to the large elastic softening along the crystal parameter c , and raises significantly the intrinsic sensitivity to axial strain resulting in the highly increased piezoelectric constant. The role of the local environment effects characteristic for disordered alloys is demonstrated. The preference of Sc atoms to bind rather hexahedrally than tetrahedrally to nitrogen results in a frustrated system with a strong response to strain. The effect is particularly accentuated at intermediate compositions where the elongated double-minimum energy landscape is flattened due to the energy proximity of the wurtzite and hexagonal phases of these alloys. Note also,

that the hexagonal phase of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloy at 50% composition appears at the saddle point rather than in an energy minimum. Therefore, it is dynamically unstable, and most probably could not be synthesized experimentally. Accordingly, we conclude as a rule, that structural phase competition similar to the one observed in this work can be a general key point to search for materials systems with substantial enhancement of the piezoelectric response. This establishes a novel route for the design of materials to be used in piezoelectric applications.

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