First-principles investigations of the pressure-induced phase transformations and properties of crystalline and amorphous AIN

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One-step first principles molecular-dynamics (FPMD) simulations were carried out to investigate structural transformations in wurtzite-type AlN under compression and decompression. The hexagonal transformation path $P6_3mc$ - $P6_3/mmc$ -Cmmm- $Fm\overline{3}m$ was identified during compression at P = 50 GPa and T = 500 K. The inversion of this path of transformation was established at the decompression of compressed rock-salt AlN at 1500 K. The plausible origin of these transformations is established. The occurrence of intermediate and metastable phases was predicted by taking into account their dynamical and elastic instability, and for this purpose, phonon spectra and elastic constant calculations were performed. FPMD simulations were used to generate amorphous—high-density amorphous—rock-salt type was revealed at P = 40 GPa, and the thermodynamic and mechanical properties of crystalline and amorphous AlN were compared. It was found that the one-step FPMD simulations is a viable scheme to predict phase transitions in crystalline and amorphous AlN with higher precision compared with other FPMD approaches with step-wise pressure changes.

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I. INTRODUCTION

Unique physical properties such as high thermal stability, melting point, and hardness are inherent to aluminum nitride (AlN) [1,2], which is an electronic ceramic with a direct energy band gap of ≈ 6.0 eV. AlN is an important material for microelectronic applications, laser diodes, light-emitting diodes, optical detectors, and other devices [3].

Aluminum nitride crystallizes in a hexagonal wurtzite (*B*4, space group $P6_{3}mc$ No. 186) structure with four atoms per unit cell: Al(1/3, 2/3, 0), Al(2/3, 1/3, 1/2), N(1/3, 2/3, h), N(2/3, 1/3, 1/2+h). The zinc-blende cubic structure (*B*3, space group $F\bar{4}3m$) of AlN is epitaxially stabilized as a 1.5–2.0-nm-thin layer [4,5]. AlN undergoes a *B*4-to-*B*1(NaCl-type, space group $Fm\bar{3}m$) phase transformation under pressures of 14.0–22.0 GPa [6–9].

The hexagonal and tetragonal paths were proposed for the *B*4-to-*B*1 phase transformation [10,11]. In the hexagonal path, a *B*4 structure first transforms into a fivefold-coordinated hexagonal transient state with space group $P6_3/mmc$ (the *h*-BN type), and then into a *B*1 structure. In the tetragonal sequence of transformations, a *B*4 phase first transforms into a tetragonal state (space group *I*4*mm*) and then into a *B*1 phase. Previous first-principles calculations [11] suggested that AlN should follow the hexagonal path.

First-principles calculations predict the B4-to-B1 phase transition at 8.3–16.0 GPa [10–17]. First principles moleculardynamics (FPMD) simulations in the NPH ensemble (constant number of atoms, constant pressure, and constant enthalpy), where stepwise change in the cell volume was used, enabled one to establish a first-order B4 to B1 phase transition above 100 GPa and to confirm a hexagonal path for this transition that involved two intermediate states with space groups of P6₃/mmc and Cmcm [18]. Two possible transition B1-to-B4 paths, namely, an indirect $B1 \rightarrow h$ -BN $\rightarrow P4_2/mnm$ (the β -BeO type) \rightarrow B4 path, and a direct B1 \rightarrow h-BN \rightarrow B4 one were identified, as a result of the FPMD decompression of B1-AlN at temperature above 3000 K [19]. The authors of Ref. [19] aimed at a conclusion also that the transition via the $P6_3/mmc$ state is a characteristic feature of the mechanism, whereas the occurrence of the $P4_2/mnm$ phase is not a necessity. A pressure of 29 GPa for the B4-to-B1 transition was also obtained dynamically by using MD simulations based on an empirical potential consisting of two- and three-body terms by increasing the external pressure at a constant temperature of 3000 K [20]. Car-Parrinello molecular dynamics was applied to study the structural properties of amorphous aluminum nitride (a-AlN) [21]. Two successive first-order phase transitions in *a*-AlN were observed through the FPMD simulations [22]. AlN is found to undergo a first-order amorphous-toamorphous phase transition after it crystallizes into a B1 structure with increasing pressure [22]. The mechanical properties of B4-AlN and a-AlN were studied in the framework of an empirical potential model [23].

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An analysis of published data on AlN enabled us to clarify some gaps in the theoretical investigation of this material. In particular, despite numerous studies of the phase transformations in crystalline and amorphous AlN, the origin of the intermediate phases that were observed during compression or decompression was not yet established. Different interpretations on the transient states in *B*1-AlN under decompression were proposed. The temperature of the *B*1-*B*4 transition was not detected. All the suggested models and mechanisms of the structural transformations strongly overestimate either transition pressure or temperature. Finally, so far, there are no comparative first-principles investigations of the thermodynamic and mechanical properties of crystalline and amorphous aluminum nitrides. In this work we aimed at filling these gaps in studying AlN.

The paper is organized as follows. In Sec. II we present our theoretical framework and the computational details. Section III contains the results of the FPMD investigations of the phase transformations in crystalline and amorphous AlN under compression and decompression. In this section a comparative analysis of the vibrational and mechanical properties of *B*4-AlN and *a*-AlN was performed. Finally, Sec. IV contains the main conclusions.

II. COMPUTATIONAL ASPECTS

Geometry optimization for different crystalline structures of AlN was carried out with the first-principles QUANTUM ESPRESSO code [24] using periodic boundary conditions. We used Vanderbilt ultrasoft pseudopotentials [25]. For the exchange-correlation energy and potential, the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [26] was used. The criterion of convergence for the total energy was 1.36×10^{-5} eV/formula unit. The integration in the reciprocal space was carried out using a Gaussian smearing with a width $\sigma = 0.272$ eV. The cutoff energy was 516.8 eV. The initial structures were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [27] by simultaneously relaxing both the cell basis vectors and the atoms inside the cell. Structural optimization was considered to be complete when the atomic forces were less than 7 meV/Å, the stresses smaller than 0.05 GPa, and the total energy during the structural optimization iterative process was changing by less than 1.36 meV. The integration in the Brillouin zone was done by using special sets of kpoints following the Monkhorst-Pack scheme with (12 12 12) and (8 8 6) grids for the 2-atom cubic and 4-atom hexagonal structures, respectively.

We considered the initial 4-atom hexagonal, 8-atom cubic, and 32-atom tetragonal cells that represented the *B*4-AlN phase to clarify the possible origin of the intermediate phases that could form during the compression and decompression of this phase. One-step FPMD simulations in the *NPT* ensemble (constant number of atoms, pressure, temperature) of the relaxed *B*4-AlN structure were carried out at pressure P =50 GPa and temperature T = 500 K. Pressure was applied via the Parrinello-Rahman method [28]. The one-step FPMD decompression of the compressed *B*1-AlN structures was performed at P = 0 and T = 1500 K. The time step was about 10^{-15} s. The system temperature was kept constant by rescaling the velocity with a tolerance of ± 100 K. The variation of the total energy $E_{\rm T}$, cell volume V, average coordination number (ACN), and lattice parameters were controlled during each temperature step. All structures reached their time-averaged equilibrium, and afterwards, the total energy and cell volume of the structures fluctuated only slightly around that equilibrium value. In the case of FPMD simulations for the 32-atom cell, the Γ point was used to save computing time without compromising on accuracy. FPMD calculations for the 4- and 8-atom cells were performed using the (8 8 8) and (4 4 4) Monkhorst-Pack *k*-point meshes, respectively.

A sample of amorphous AlN was generated as follows: First, we generated a 128-atom cubic supercell by the 4 × 4 × 4 translation of the *B*2-AlN (CsCl-type) cell. This initial structure was randomized and then equilibrated for 3 ps during FPMD simulations in the *NPT* ensemble at 4500 K. The melt was cooled down to 500 K for 27 ps and then relaxed. The Γ point and Monkhorst-Pack (2 2 2) mesh were used for the Brillouin-zone integration in FPMD simulations and sample relaxation, respectively. One-step FPMD simulations of the relaxed *a*-AlN sample were carried out at pressure P = 40 GPa and temperature T = 1000 K.

The QUANTUM ESPRESSO code was employed to study the phonon spectra of the crystalline structures in the framework of the density-functional perturbation theory (DFPT) [29]. The phonon density of states of *a*-AlN was determined by using the PHONOPY code [30]. The elastic moduli of the crystalline phases were investigated using the ELASTIC code [31]. The Vickers hardness was estimated by using the calculated elastic moduli in the framework of the approach presented in Ref. [32]. For the calculation of the stress-strain curves, we considered the supercells with the **a** and **c** basis vectors aligned along the [100] and [001] directions, respectively. The tensile stress-strain relations were determined by elongating the cells along the c axis in incremental steps, followed by fixing the c basis cell vector and the BFGS structural relaxation. The stress-shear strain (001)[100] relations were calculated as follows: first, an incremental shear distortion was imposed, then the structures were relaxed with fixed angles [33].

Following Ref. [34], we distinguish metastable and intermediate phases that are stable and unstable after relaxation, respectively. These phases were identified at certain stages of FPMD simulations. An identification of metastable or intermediate structures was carried out with the help of a group-theoretical analysis using the ISOTROPY code [35]. We followed the rule whereby, in the sequence of identified structures G01 - G1 - G2 - G02, G1 should be a subgroup of G01, G2 should be a subgroup (or supergroup) of G1 and a subgroup of G02 [34]. The tolerance of 0.04a (a is a lattice parameter) for cell vectors and atomic coordinates was used in the symmetry analysis [35]. To visualize the structures we used the XCRYSDEN code [36]. The detailed description of the applied procedures for the identification of different structures was done in our previous papers [34,37].

The calculated lattice parameters of *B*4-AlN and *B*1-AlN at equilibrium are a = 3.116 Å, c/a = 1.603, and a = 4.051 Å, respectively, which are comparable to the experimental values of a = 3.111 Å, c/a = 1.600 [PDF 025–1133], and a = 4.045 Å [PDF 046–1200], respectively. The calculated lattice parameters from other authors were a = 3.060-3.151 Å,



FIG. 1. Total energies $E_{\rm T}$ as functions of cell volume V for different structures of AlN at T = 0 K.

c/a = 1.570-1.614, and a = 4.069 Å, respectively [17,18]. The calculated internal parameter *h* was 0.381 that was comparable with the experimental and theoretical values of 0.38–0.383 [18]. These results show that the calculated characteristics are in good agreement with experimental and theoretical values of other authors. A comparison of the calculated elastic constants and moduli with corresponding experimental values will be done below.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the total energies $E_{\rm T}$ as functions of cell volume V of possible structures that could form under pres-



FIG. 2. Cell volume (*V*) and structural parameters (*h*, *a*, *b*, *c* and γ) of *B*4–AlN as functions of simulation time at compression and decompression. The angles α and β were not shown, since they are equal to 90°, and weakly evolve with simulation time.



FIG. 3. Simulation cell of B4-AlN (h = 0.3807) (a) during different simulation times t at compression (b) t = 118 - 146 ps, (c) t = 146 - 225 ps and (d) t > 225 ps. Simulation cell of B1-AlN (d) at decompression (c) t = 33 - 49 ps, (b) t = 49 - 103 ps and (a) t > 103 ps. Here and in other figures, the large violet circles and small blue circles are the Al and N atoms, respectively. The crystal coordinates of the A1 and A2 atoms are (1/3, 2/3, 1/2) and (1/3, 2/3, 1/2 + h), respectively.

sure of the B4-AlN and a-AlN phases. The results indicate the several possible phase transitions: (i) $B4 \rightarrow h$ -BN type, ii) h-BN $\rightarrow B1$, and (iii) a-AlN $\rightarrow B1$. The h-BN phase can be the metastable one in the $B4 \rightarrow B1$ transition, since the $E_{\rm T}(V)$ dependence in the very small region around $V = 9 \text{ Å}^3/\text{atom}$, where h-BN could be revealed, does not have a minimum. As we will see below, despite this very simplified analysis, the appearance of the metastable h-BN state during the compression of B4-AlN is correctly predicted.

A. Crystalline AlN

Figure 2 shows the volume and structural parameters of the 4-atom cell of B4-AlN as functions of FPMD simulation time during compression at P = 50 GPa and T = 500 K, and decompression at P = 0 and T = 1500 K. The visualization of the atomic configurations at each time step and their comprehensive group-theoretical analysis enabled us to reveal the metastable and intermediate structures that arise during compression and decompression. To single out the metastable and intermediate phases, the structures selected from the FPMD trajectory were relaxed, and the space group was established for both the initial and relaxed structures. The stable $P6_3mc$, identified metastable $P6_3/mmc$, $Fm\bar{3}m$, and intermediate Cmcm structures are shown in Fig. 3. Figure 4 shows the atomic displacements in the stable and metastable phases of AlN according to the phonon modes that will be considered below when describing structural transformations. The transformation path at compression is



FIG. 4. Relative displacement of the atoms according to (a) the optical Γ_1 mode in the $P6_3mc$ structure (b), the Γ_{5+} (c) and Γ_{2-} modes in the $P6_3/mmc$ structure and (d) the X_{5-} mode in $Fm\bar{3}m$ structure [35].

TABLE I. Elastic constants C_{ij} , bulk B, shear G, Young's modulus E (in GPa), and compressibility along (K_1) and perpendicular (K_2) to the c axis (in 10^{-3} GPa⁻¹).

	C_{11}	C_{12}	C_{13}	<i>C</i> ₃₃	C_{44}	C_{66}	В	G	Ε	K_1	<i>K</i> ₂
	380	127	98	362	113	127	196	124	307	1.9	1.6
	394 ^a	134	95	402	121	130	202 ^b	117 ^b	295 ^b		
$P6_3mc, P=0$	411 ^c	149 ^c	99°	389 ^c	125°	131°	206 ^d	126 ^d	315 ^d		
	369 ^e	144 ^e	100 ^e	392 ^e	91 ^e	113 ^e	220 ^f	154 ^f	374 ^f		
	376 ^g	127 <mark>8</mark>	97 ^g	355 <mark>8</mark>	112 ^g	125 ^g	194 <mark>8</mark>	122 ^g			
$P6_3mc, P = 60$ GPa	586	261	227	513	163	167	347	165	426	1.2	0.9
$P6_3/mmc, P = 0$	650	453	164	866	330	98	414	208	534	0.86	0.78

^aExperiment, Ref. [39]; ^bExperiment, Ref. [43]; ^cExperiment, Ref. [40]; ^dExperiment, Ref. [44]; ^eDFT, Ref. [41]; ^fExperiment, Ref. [45]; ^gDFT, Ref. [42].

 $P6_3mc$ - $P6_3/mmc$ -Cmcm- $Fm\overline{3}m$. At decompression, the reverse sequence is realized.

The same sequence was obtained for the 8- and 32-atom simulation cells, indicating that the paths of the structural transformations of AlN were insensitive to the shape and size of the initial simulation cells. Also, we identified the same sequence of structural transformations at high temperatures at compression (500 K $\leq T \leq$ 2000 K) and decompression (1500 K $\leq T \leq$ 2500 K). These results show that the "hexagonal deformation path" (i.e., without the formation of a tetragonal intermediate structure) takes places in B4-AlN at compression and decompression, in agreement with the prediction of other theoretical investigations [10,11,18,19]. However, the transition pressure of 50 GPa is lower than that established in other FPMD investigations (above 100 GPa [18]), and simulation temperature of the *B*1-to-*B*4 transition of 1500 K was lower compared with the transition temperature of above 3000 K [19], which can be due to different conditions of FPMD simulations. These results indicate that the one-step FPMD scheme turns out to be more accurate than other variants of FPMD procedures. Also, our simulations did not reveal the tetragonal P42/mnm intermediate state detected in Ref. [19] during decompression of B1-AlN. We suppose that the indirect $Fm3m \rightarrow P6_3/mmc \rightarrow$ $P4_2/mnm \rightarrow P6_3mc$ transformation path [19] is unlikely, since the $P4_2/mnm$ space group is a subgroup of neither the $P6_3/mmc$ space group nor the $P6_3mc$ space group [35].

To understand the origin of this sequence of structural transformations we calculated elastic constants and moduli of AlN under pressure and investigated the phonon spectra of all the above-mentioned phases. The calculated elastic constants C_{ij} , Hill elastic bulk *B*, shear *G*, and Young's modulus *E* for polycrystalline materials and compressibility along and perpendicular to the **c** axis (K_1 and K_2 , respectively) [38] are summarized in Table I. For the sake of comparison, in Table I we show the elastic constants and moduli obtained in other experimental and theoretical investigations. A rather good agreement is found between the experimental and theoretical results.

1. Compression: $P6_3mc \rightarrow P6_3/mmc$ phase transition

An analysis of the atomic configurations at different stages of FPMD compression shows that the $P6_3mc \rightarrow P6_3/mmc$ phase transition occurs owing to a vertical displacement of the nitrogen atoms within the cell, and to the compression of the c axis [cf. Figs. 3(a) and 3(b)]. The homogeneous reduction of cell volume at a constant c/a ratio did not result in any phonon mode softening and structural transformations. We calculated the elastic constants for both phases at different pressures and found that the criteria of elastic stability for hexagonal crystals [46],

$$C_{11} > |C_{12}|,$$

$$2C_{13}^2 < C_{33}(C_{11} + C_{12}),$$

$$C_{44} > 0,$$

$$C_{66} > 0,$$

are satisfied for all the structures (cf. Table I), indicating that the phase transition is not related to their elastic instability. The structural parameters and the frequency of the optical Γ_1 phonon mode of *B*4-AlN as functions of pressure are shown in Fig. 5. Drastic structural changes are seen to occur at pressure $P \approx 65$ GPa, which is related to the $P6_3mc \rightarrow P6_3/mmc$ transformation. At the initial stage of compression, the c/aratio decreases, and, correspondingly, the ε_{zz} strain can be considered as a primary order parameter. Such a reduction can be explained by the fact that, for *B*4-AlN, $K_1 > K_2$ (cf. Table I). In our further analysis the optical Γ_1 phonon was singled out [cf. Fig. 4(a)] because it is the only one to be related the vibration of the N sublattice relative to the Al sublattices along the *c* axis and the ε_{zz} strain [35].

To explain the influence of the ε_{zz} strain e_3 on the Γ_1 optical phonon, a Landau free-energy expansion was considered for the pressure-induced $P6_3mc \rightarrow P6_3/mmc$ phase transition:

$$F = F_{\rm e} + F_{\rm U} + F_{\rm eU}.$$
 (1)

Here $F_{\rm U}$ is the free energy associated with the Γ_1 optical mode, $F_{\rm eU}$ refers to the coupling between the atomic displacements and strains, and $F_{\rm e}$ corresponds to homogeneous elastic and strains [35]:

$$\begin{split} F_{\rm e} &= 1/2C_{11} \left(e_1^2 + e_2^2 \right) + C_{12} e_1 e_2 + C_{12} e_3 (e_1 + e_2) \\ &+ 1/2 \, C_{33} e_3^2 + 1/2 C_{44} \left(e_4^2 + e_5^2 \right) + 1/4 (C_{11} - C_{12}) e_6^2, \\ F_{\rm U} &= \alpha U_{\rm z} + \beta U_{\rm z}^2 + O(U^3), \\ F_{\rm eU} &= A e_3 U_{\rm z} + B e_3 U_{\rm z}^2 + C e_3^2 U_{\rm z} + O(U^3, e^3), \end{split}$$

where α and β are normal Landau coefficients, **e** is the complete set of spontaneous strains, *A*, *B*, and *C* are strain-atomic



FIG. 5. Frequency of the Γ_1 optical phonon, $\omega(\Gamma_1)$, parameter *h*, cell volume *V*, and *c/a* ratio for *B*4-AlN as functions of pressure *P*.

displacement coupling coefficients, and C_{ij} are the bare elastic constants. Spontaneous atomic displacements according to the Γ_1 optical mode ($U_x = U_y = 0$, $U_z \neq 0$) and elastic strains follow from the equilibrium conditions:

$$\frac{\partial F}{\partial U_z} = 0 \text{ and } \frac{\partial F}{\partial e} = 0,$$
 (2)

respectively. At the initial stage of compression, we determine the atomic displacements

$$U_{\rm z} = -\frac{1}{2} \frac{Ae_3 + Ce_3^2}{\beta + Be_3}.$$

It follows that a compression of the *c* axis (the ε_{zz} strain) causes the consequent vertical displacement of the N sublattice relatively to the Al sublattice related to the Γ_1 optical phonon [cf. Fig. 4(a)]. On the other hand, the softening of the Γ_1 optical mode causes a spontaneous increase of ε_{zz} strain (i.e., the *c/a* ratio, cf. Fig. 5):

$$e_3 = -\frac{AU_z + BU_z^2 + C_{12}(e_1 + e_2)}{2CU_z + C_{33}}.$$

As a result, the formation of the $P6_3/mmc$ phase occurs with h = 0.5 [cf. Fig. 3(b)]. The structural transformation is accompanied by a softening of the Γ_1 optical phonon, a reduction of cell volume and c/a ratio (cf. Fig. 5), indicating that this transformation can be closer to a first-order phase transition.

2. Compression: $P6_3/mmc \rightarrow Cmcm \rightarrow Fm\bar{3}m$ phase transitions

Figure 5 shows that no structural transformations are observed after 65 GPa, indicating that the compressed $P6_3/mmc$

structure is stable up to very high pressure. However, a small displacement of the atoms along the long diagonal of the xy cell plane [cf. Fig. 4(b)] resulted in the formation of the *Cmcm* structure [cf. Fig. 3(c)]. This structure differs from the $P6_3/mmc$ structure by the position of the A1 and A2 atoms: in the new cell their crystal coordinates are $(1/3 \pm U)$, $2/3 \pm U$, 1/2) and $(1/3 \pm U, 2/3 \pm U, 1/2)$, respectively. An expectation of the atomic configurations of AlN during FPMD simulations shows that the atomic displacement, $U_{\rm x} = U_{\rm y} = U$, $U_{\rm z} = 0$, can be considered as the driving order parameter for the $P6_3/mmc \rightarrow Cmcm$ phase transition. The group-theoretical analysis of this atomic displacement indicates that it corresponds to the Γ_{5+} phonon mode in the $P6_3/mmc$ phase [35] [cf. Fig. 4(b)]. When this mode softens, spontaneous elastic strains can be induced through the coupling between the atomic displacements and macroscopic strains. These strains can be established by taking into account the following expansion for the symmetric square of $[\Gamma_{5+} \times$ Γ_{5+}] = $\Gamma_{1+} + \Gamma_{5+}$: Only the strains $\eta_0 = \varepsilon_{xx} + \varepsilon_{yy}$, ε_{zz} , $\eta_1 =$ $\varepsilon_{xx} - \varepsilon_{yy}$, and $\eta_2 = -2\varepsilon_{xy}$ transform according to the Γ_{1+} and Γ_{5+} representation [35]. Since η_0 does not influence the crystal symmetry, we will focus on the η_1 and η_2 strains. Given this finding, the Landau free-energy expansion for the $P6_3/mmc \rightarrow Cmcm$ phase transition can be written [35]

$$F_{e} = \lambda (\eta_1^2 + \eta_2^2) + O(\eta^3),$$

$$F_{eU} = D\eta_1 (U_x^2 - U_y^2) - 2D\eta_2 U_x U_y,$$

where λ and D are constants. Since $U_x = \sqrt{3}U$, $U_y = U$, and $U_z = 0$ (in lattice coordinates) [35], spontaneous elastic strains follow from the expressions (1) and (2):

$$\eta_1 = -\frac{DU^2}{2\lambda}, \quad \eta_2 = \frac{\sqrt{3}DU^2}{\lambda}$$

For these strains |a| = |b|, and the angle between a and b, $\angle(a, b) \neq 60^\circ$. The closer the A1 and A2 atoms are to the center of the xy cell plane, the closer the angle $\angle(a, b)$ is to 90°. The rhombic deformation of the unit cell is accompanied by an increase of the c/a ratio and by a decrease of cell volume due to the η_0 , η_1 , and η_2 strains (cf. Figs. 2 and 3). The $Fm\bar{3}m$ structure forms when $\angle(a, b) = 90^\circ$ and $c/a = \sqrt{2}$. The average volume of the compressed B1-AIN structure of 7.3 Å³/atom is comparable with the theoretical (6.75 Å³/atom [18]) and experimental (7.75 Å³/atom [8]) values.

3. Decompression: $Fm\bar{3}m \rightarrow Cmcm \rightarrow P6_3/mmc$ phase transitions

When B1-AlN formed during FPMD simulations, we performed a decompression of this phase at P = 0 and T =1500 K. No phase transformation occurs at temperatures lower than 1500 K. A visualization of the FPMD structures at each time step enabled us to identify the metastable and intermediate phases that appeared during decomposition. The sequence of phase transitions $Fm\bar{3}m \rightarrow Cmcm \rightarrow$ $P6_3/mmc \rightarrow P6_3mc$ was established (cf. Figs. 2 and 3). The phonon spectrum of B1-AlN was investigated at different cell volumes and led to the conclusion that the $Fm\bar{3}m \rightarrow Cmcm$ transition could be caused by the collapse of the transversal



FIG. 6. Frequencies of the optical X_{5-} and Γ_{2-} phonon modes in the $Fm\bar{3}m$ and $P6_3/mmc$ structures of AlN, respectively, as functions of cell volume V.

 X_{5-} phonon mode at large volumes. The atomic displacement according to this mode is shown in Fig. 4(d). In Fig. 6 we show the frequency of this mode as a function of the cell volume V. One can see that, upon achieving $V_0 \approx 11$ Å³/atom, the vibrations related to this mode vanish. The value of V_0 is larger than the equilibrium cell volume of B4-AlN (10.5 Å³/atom), and a large fluctuation of cell volume is only possible at high temperatures. This fact explains why the structural transformation in B1-AlN starts at high temperatures.

The mechanism of the phase transition related to the collapse of the X_{5-} mode in *B*1-SiC was described in detail in Ref. [34]. The same mechanism is applicable for an explanation of the structural transformations in B1-AlN. Together with the details mentioned in Ref. [34] here is the reasoning. There are three equivalent X points, $k_1 = 2\pi/a(1, 0, 0)$, $k_2 = 2\pi/a(0, 1, 0)$, and $k_3 = 2\pi/a(0, 0, 1)$ in the Brillouin zone. Let us consider k_1 . Then the order parameters Uassociated with the X₅₋ mode are $U_y(\mathbf{k}_1)$ or $U_z(\mathbf{k}_1)$. For the X_{5-} representation, $[X_{5-} \times X_{5-}] = X_{1+} + X_{3+}$. Then, if $U_z(\mathbf{k}_1) = U \neq 0$, spontaneous elastic strains $e_V = \varepsilon_{xx} + \varepsilon_{yy}$ $\varepsilon_{yy} + \varepsilon_{zz}$, $e_{E1} = 2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}$ that transform according to the X_{1+} and X_{3+} representations arise [35]. The atomic displacement and $e_{\rm V}$, $e_{\rm E1}$ strains lead to (i) a shift of the A1 and A2 atoms along the diagonal of the square of the tetragonal cell, (ii) a decrease of the angle $\angle(a, b)$, and (iii) a contraction of the c axis [cf. Figs. 3(d) and 3(c)]. As a result, the intermediate Cmcm structure forms. This unstable structure further transforms into the metastable $P6_3/mmc$ phase. Since the $Fm\bar{3}m \rightarrow P6_3/mmc$ transformation occurs by means of a tetragonal deformation of the cell, this structural transformation should show the features of a first-order phase transition.

4. Decompression: $P6_3/mmc \rightarrow P6_3mc$ phase transitions

To describe the $P6_3/mmc \rightarrow P6_3mc$ phase transition let us clarify why a phonon mode is responsible for this transition. The group-theoretical analysis shows that only the atomic displacement according to the optical Γ_{2-} phonon mode in the $P6_3/mmc$ structure can lead to the formation of the $P6_3mc$ phase. The Γ_{2-} phonon mode is related to the atomic vi-



FIG. 7. Supercell volume V, total energy $E_{\rm T}$, and average coordination number (ACN) of *a*-AlN as functions of simulation time t under compression at P = 40 GPa and T = 1000 K.

brations of the N sublattice relatively to the Al sublattice along the *c* axis [cf. Fig. 4(c)]. The frequency of this mode is shown in Fig. 6 as a function of cell volume. One can see that the frequency of the optical Γ_{2-} phonon approaches zero with increasing volume *V* at decompression. The softening of this mode leads to a reduction of the *h* parameter from 0.5 to 0.3807. As a result, the *P*6₃/*mmc* phase transforms into the *P*6₃*mc* phase. An expansion for the symmetric square of $[\Gamma_{2-} \times \Gamma_{2-}] = \Gamma_1 + \Gamma_{2-}$ implies that this phonon mode couples with the $\varepsilon_{xx} + \varepsilon_{yy}$, ε_{zz} strains, and the atomic displacements should be accompanied by a change in *c/a* ratio and a volume jump, indicating that the formation of the *P*6₃*mc* phase will occur according to a mechanism of a first-order phase transition.

B. Amorphous AlN

An amorphous aluminum nitride sample was generated to investigate a possible phase transition in *a*-AlN under pressure and its thermodynamic and mechanical properties in comparison with those of *B*4-AlN. The structural parameters of the generated sample were compared with those obtained for *a*-AlN in Refs. [20–23], and very good agreement was achieved (not shown here). The generated sample was used in one-step FPMD simulations at P = 40 GPa and T = 1000 K. Cell volume, total energy $E_{\rm T}$, and average coordination number (ACN) as functions of simulation time are shown in Fig. 7. Three stages were identified: $t_1 = 0-1200$ fs, $t_2 = 1200-5000$ fs, and $t_3 > 5000$ fs. Typical atomic configurations of *a*-AlN at these stages are shown in Fig. 8. During the first stage, t_1 , a gradual decrease in cell volume and an increase in $E_{\rm T}$ and



FIG. 8. Atomic configurations of *a*-AlN at different stages of compression at 40 GPa: (a) t = 0, (b) t = 2700 fs, and (c) t = 6000 fs (cf. Fig. 7).

ACN occur. The average coordination number increases from ≈ 4 to ≈ 5 . The steady state is reached at the t_2 stage. During this stage, V and E_T oscillate around the corresponding equilibrium values, and ACN \approx 5. In Ref. [22], this state was identified as a high-density amorphous (HDA) phase. Indeed, Fig. 8 shows that the structure of HDA is denser than the structure of the *a*-AlN phase at t = 0. Therefore, it would be reasonable to name the latter phase the low-density amorphous (LDA) phase. The LDA \rightarrow HDA transformation is not a first-order transition, since the cell volume gradually changes during the transformation. This finding contradicts the results of FPMD simulations with step-wise volume change, since, at the transition point, V abruptly decreases [22]. We assume that this discrepancy can be due to different FPMD schemes used in both approaches. Finally, the HDA-to-B1 first-order phase transition occurs at the t_3 stage, since it is accompanied by an abrupt decrease in the total energy and cell volume, as well as by an increase in ACN up to ≈ 6 [cf. Figs. 7 and 8(c)]. Typical atomic clusters for the fourfold coordinated LDA, fivefold-coordinated HDA, and sixfold-coordinated B1 phases are shown in Fig. 9. One can see that four atoms of the Al₀-N₁ N₂ N₃ and N₀-Al₁ Al₂ Al₃ units are located on the corresponding planes, which is inherent to the $P6_3/mmc$ and Cmmm structures [cf. Figs. 3(b) and 3(c)]. The HDAto-B1 transition at P = 65 GPa was predicted in Ref. [22]. Unfortunately the results of both approaches cannot be further analyzed in more detail since the transition temperature in the stepwise FPMD simulations [22] is not reported. The pair correlation functions and bond angle distribution of a-AlN at different stages of simulations are shown in Figs. 10 and 11. The results presented in Figs. 10, 11, and 9 clearly show that the fivefold coordinated HDA phase can be considered as an intermediate state in the LDA-to-B1 phase transition like the $P6_3/mmc$ state in the $B4 \rightarrow B1$ transformation. So, we can



FIG. 9. Atomic clusters formed in the (a) LDA, (b) HDA, and (c) *B*1 phases of AlN. For the HDA clusters, the atoms belonging to the Al_0 - N_1 N_2 N_3 and N_0 - Al_1 Al_2 Al_3 units are located on the N_1 N_2 N_3 and Al_1 Al_2 Al_3 planes, respectively.



FIG. 10. Pair correlation functions of *a*-AlN at different stages of compression at 40 GPa: t = 0 (solid line), t = 2700 fs (red dashed line), and t = 6000 fs (blue dotted line) (cf. Fig. 7).

consider the HDA phase as the amorphous counterpart of the metastable $P6_3/mmc$ phase.

Now let us analyze the behavior of amorphous structures of AlN and SiC under pressure. Both AlN and SiC undergo the B4-to-B1 structural transformation under pressure and exist in an amorphous state [22,34]. However, in contrast to *a*-AlN, in the case of *a*-SiC, molecular-dynamics simulations [47] did not reveal the formation of the B1 phase under high pressure.



FIG. 11. Bond angle distribution $g(\theta)$ for *a*-AlN at different stages of compression at 40 GPa: t = 0 (solid line), t = 2700 fs (red dashed line), and t = 6000 fs (blue dotted line) (cf. Fig. 7). For the sake of comparison, $g(\theta)$ for the $P6_3/mmc$ structure of AlN is also shown (green dash-dotted line).



FIG. 12. Calculated phonon density of states (PHDOS) of *B*4-AlN (2), *a*-AlN (3) in comparison with experimental PHDOS (1) [48].

Figure 10 clearly shows that *a*-AlN is chemically ordered, i.e., there are only hetero-polar bonds in the nearest-neighbor surrounding of each atom, whereas, the *a*-SiC network is composed of both heteropolar and homopolar bonds [47]. We suppose that the availability of the homopolar bonds makes it impossible to form the perfect heteropolar Si-C network in *a*-SiC under pressure.

C. Thermodynamic and mechanical properties of *B*4-AlN and *a*-AlN

In Fig. 12 we show the calculated phonon density of states for *B*4-AlN, *a*-AlN (LDA) in comparison with the experimental phonon density of states (PHDOS) [48]. One can see that both theoretical and experimental PHDOS for crystalline AlN agree rather well. The phonon spectrum of the amorphous sample is smoothed compared with that of *B*4-AlN due to the impact of the random amorphous network. The gap between 68 and 75 meV in the PHDOS of *B*4-AlN disappears in the spectrum of *a*-AlN.

The calculated PHDOSs of the crystalline and amorphous phases were used to estimate the heat capacity at constant volume $(C_{\rm V})$. The results are presented in Fig. 13. For comparison, in Fig. 13 we also show the experimental evolution of $C_{\rm P}(T)$ [49,50]. Despite the fact that the PHDOS of crystalline and amorphous AlN differ significantly (cf. Fig. 12), their heat capacities are very close. The difference is observed in the low-temperature region, up to 600 K, where the $C_V(T)$ curve of B4-AlN is slightly lower than that of a-AlN. There is a scatter of experimental points at temperatures higher than 600 K. Nevertheless, one can see that the calculated curve for B4-AlN reproduces the experimental $C_{\rm P}(T)$ curve rather well in the temperature region up to 1000 K. This means that the simplest model that only involves phonon spectra is capable of describing the thermodynamic properties of B4-AlN, in particular the heat capacity, as well as entropy and vibrational energy (not shown here) with an acceptable accuracy in the temperature range up to 1000 K.

The calculated stress-strain curves of *B*4-Al and *a*-AlN are shown in Fig. 14. The curves inform us about the behavior of these systems under tensile and shear stresses. The ideal strengths (i.e., maximum stress before failure) for *B*4-AlN



FIG. 13. Calculated heat capacities at constant volume (C_V) as functions of temperature for *B*4-AlN (red line, 3) and *a*-AlN (dark dashed line, 4). Experimental temperature dependence of heat capacities at constant pressure, $C_P(T)$ [49] (dark circles, 1) and [50] (open circles, 2).

at tension, $\sigma_{\rm T} = 39.5$ GPa, and shear, $\sigma_{\rm S} = 19.6$ GPa, are more than two times higher compared with $\sigma_{\rm T} = 16.7$ GP and $\sigma_{\rm S} = 12.4$ GPa for *a*-AlN. First-principles calculations of *B*4-AlN under tensile and shear strains showed that $\sigma_{\rm T} =$ 35–40 GP and $\sigma_{\rm S} = 20–22$ GPa [51], which are very close to those obtained in the present work. A worst agreement of the calculated values of $\sigma_{\rm T}$ is observed with the ideal tensile strengths of \approx 24 GPa and \approx 6 GPa for *B*4-AlN and *a*-AlN, respectively, obtained using an empirical model [Ref. [23], Fig. 5(a)].

For *a*-AlN, the elastic moduli *G* and *E* were calculated from the data of Fig. 14 taking into account the structural homogeneity of the amorphous sample. The modulus *B* was calculated from the equation of states. The elastic moduli of *a*-AlN were found to be B = 182 GPa, G = 87 GPa, and E = 189 GPa. Comparing these values with those presented in Table I, we see that the amorphous sample exhibits much lower elastic moduli than the crystalline sample. Given the calculated elastic moduli, the values of Vickers hardness (H_V) for the crystalline and amorphous phases were estimated. The hardness of 16.5 GPa for *B*4-AlN turned out to be two times higher than the value of $H_V = 8.4$ GPa for *a*-AlN. These values are lower than the corresponding ideal shear strengths



FIG. 14. Stress-strain relations for *B*4-AlN [0001] (1), (0001)[2–1–10] (2), *a*-AlN [001] (3), and (001)[100] (4).

(cf. Fig. 14), and this fact justifies the applicability of the approach for estimating the hardness based on the elastic moduli calculated at equilibrium. The experimental values of hardness for *B*4-AlN are in the range of 16–18 GPa [45], indicating that the calculated and experimental values of hardness are in good agreement.

The B/G ratio is related to the ductility of a material: if B/G > 1.75, it will be ductile, otherwise it will be brittle. The values of B/G are equal to 1.6 and 2.1 for B4-AlN and *a*-AlN, respectively, indicating that the crystalline phase should be brittle, whereas the amorphous phase should be ductile.

IV. CONCLUSIONS

One-step FPMD simulations of crystalline and amorphous AlN were carried out under compression and decompression. The sequence $P6_3mc \rightarrow P6_3/mmc \rightarrow Cmmm \rightarrow Fm\bar{3}m$ of phase transitions was revealed upon compression of B4-AlN at P = 50 GPa and T = 500 K. At the initial stage of the $P6_3mc \rightarrow P6_3/mmc$ transformation, the c/a ratio decreases since the compressibility of B4-AlN is higher along the caxis than perpendicular to this axis. This causes the spontaneous atomic displacement according to the Γ_1 optical mode $(U_x = U_y = 0, U_z \neq 0)$ and the subsequent elastic strains ε_{zz} . In further transformations, the driving order parameter in the $P6_3/mmc$ phase is supposed to be the atomic displacement, $U_{\rm x} = U_{\rm y} = U$, $U_{\rm z} = 0$, according to the Γ_{5+} phonon mode. When this mode softens, spontaneous elastic strains $\eta_0 =$ $\varepsilon_{xx} + \varepsilon_{yy}, \varepsilon_{zz}, \eta_1 = \varepsilon_{xx} - \varepsilon_{yy}, \text{ and } \eta_2 = -2\varepsilon_{xy} \text{ can be induced.}$ As a result, the angle between a and b axes changes from 120° to 90° , and the sequence of the $P6_3/mmc \rightarrow Cmmm \rightarrow$ $Fm\bar{3}m$ phase transitions takes place.

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The $Fm\bar{3}m \rightarrow Cmcm \rightarrow P6_3/mmc \rightarrow P6_3mc$ pathway was established at decompression at 1500 K. The $Fm\bar{3}m \rightarrow Cmcm \rightarrow P6_3/mmc$ sequence of transformations can be caused by the collapse of the transversal X_{5-} phonon mode at a high cell volume with subsequent strains $e_V = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$, $e_{E1} = 2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}$. A fluctuation of cell volume should be large enough to initiate the phase transformations. The collapse of the optical Γ_{2-} phonon mode in the $P6_3/mmc$ structure during further decompression was found to cause the $P6_3/mmc \rightarrow P6_3mc$ phase transition.

The second-order low-density amorphous (LDA) \rightarrow highdensity amorphous (HDA) phase transition and the first-order HDA $\rightarrow Fm\bar{3}m$ phase transition were identified at compression of *a*-AlN at P = 40 GPa and T = 1000 K.

The phonon spectra and heat capacities of both crystalline and amorphous phases were studied. Despite the fact that their phonon spectra differ significantly, the heat capacity of *a*-AlN is only slightly higher than that of *B*4-AlN at low temperature.

The ideal strengths for *B*4-AlN at tension, $\sigma_{\rm T} = 39.5$ GPa, and shear, $\sigma_{\rm S} = 19.6$ GPa, are more than two times higher compared with $\sigma_{\rm T} = 16.7$ GPa and $\sigma_{\rm S} = 12.4$ GPa for *a*-AlN. With the calculated elastic constants and moduli, the Vickers hardness of both the phases was estimated. The hardness of 16.5 GPa for *B*4-AlN turned out to be almost two times higher than $H_{\rm V} = 8.4$ GPa for *a*-AlN. It was found that the crystalline phase will be brittle, whereas the amorphous one will be ductile.

Finally, we found that the one-step FPMD scheme enabled one to predict the phase transitions in crystalline and amorphous AlN with higher precision compared with other FPMD approaches based on stepwise pressure changes.

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