Microscopic mechanism of the wurtzite-to-rocksalt phase transition of the group-III nitrides from first principles

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There are mainly two kinds of microscopic mechanisms previously proposed for the structural phase transition from wurtzite to rocksalt, that is, the "hexagonal" and "tetragonal" paths. The present work gives a comparative study of these two mechanisms in group-III nitrides (AIN, GaN, and InN) from the energetic point of view based on first-principles calculations. The calculated results indicate that the energy-favored mechanism is dependent not only on the internal compositions but also on the external pressures. AlN and GaN prefer the hexagonal and the tetragonal paths, respectively, in a large pressure range investigated; however, in the case of InN, the tetragonal path is favored under lower pressure but the hexagonal one under higher pressure. In addition, a real-time measurement of the radial distribution function or the axial ratio c/a is suggested to distinguish these two transition paths in experiment. We also propose a simple model to make a rough estimate of the hysteresis cycle of the wurtzite-rocksalt transition and obtain good agreement with the experimental results for AlN and InN.

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I. INTRODUCTION

The group-III nitrides (AlN, GaN, InN, and their alloys) have attracted much attention in recent years due to their enticing potential in the electronic and optoelectronic device technology.¹⁻⁴ A great many of studies have been done to characterize not only their important optical and electronic properties, which are of primary interest, but also their structural and mechanical properties.⁵ Many materials exhibit amazing and interesting behaviors under appropriate pressure and temperature. The group-III nitrides AlN, GaN, and InN crystallize in the wurtzite (B4) phase at ambient conditions. Under high pressure, they go through a phase transition to the rocksalt (B1) phase as most of the fourcoordinated binary compound semiconductors. Upon releasing the external pressure, a reverse transition from B1 to B4 has been reported in GaN and InN, but not in AlN.⁶ Recently, such a phase transition has received considerable interest, especially in the underlying microscopic transition mechanism which may lead to new experiments and possibly the control of transition processes.

The studies of the transition mechanism for a so-called reconstructive phase transition, the B4-B1 transition in this work, mainly focus on two questions:⁷ (1) what is the atom mapping relation between the initial and final phases and (2) what path do the atoms take to accomplish the transition between these two end phases? The mapping question simply deals with how the two structures are related. The path question is more complicated, which deals with the actual cell deformations and atomic displacements in the course of phase transition. It is a challenging problem for both experiment and theory. Up to now, there are still some arguments on the B4-B1 transition mechanism. Mainly two different mechanisms have been proposed in the previous studies (see Sec. II). In this work, we make a comparative study of these two mechanisms in AlN, GaN, and InN from the energetic point of view. The calculated results show that the energyfavored mechanism is dependent not only on the specific composition of the object but also on the various external pressures. It seems more or less complicated but interesting.

The rest of the paper is organized as follows. Section II reviews the previous studies on the B4-B1 transition mechanisms. Section III briefly provides the theoretical methods and calculation details. Section IV contains the calculated results and discussion. In this section, we first estimate the equilibrium transition pressures and some other static properties of AlN, GaN, and InN (Sec. IV A). Second, we investigate the possible transition mechanisms for the three nitrides at selected pressures, and the observations are compared with the previous studies (Sec. IV B). Third, some measurable structural properties are proposed as indicators to identify the actual mechanism in experiment (Sec. IV C). Finally, a theoretical model is proposed to estimate the B4-B1 transition hysteresis cycles and to interpret the related experimental kinetic behaviors (Sec. IV D). Section V is the summary of the present work.

II. REVIEW

The B4-B1 structural phase transition was first described by Corll⁸ using a continual deformation model. Other models have been proposed in recent years from experiments^{9–12} and calculations.^{13–20} Essentially, all these models can be summarized as two different mechanisms characterized by the corresponding intermediate phases, as shown in Fig. 1: one is the "hexagonal" path and the other is the "tetragonal" path. Along each of these two paths, the B4-B1 transition was regarded as a two-stage process approximately.

At the first stage of the hexagonal path, the fractional coordinate *u* changes from ~ 0.375 to 0.50 accompanied with the compression of the axial ratio c/a from ~ 1.6 to ~ 1.2 . The resulting hexagonal intermediate structure is isomorphic to the layered *h*-BN. In this structure, each atom is located at the center of the equilateral triangle formed by unlike atoms and has two opposite bonds along the *c* axis perpendicular to the triangle plane. Then, in the next stage, the hexagonal



FIG. 1. Schematic representation of the two different proposed mechanisms of the B4-B1 phase transition: one path through the "hexagonal" intermediate structure and the other through the "te-tragonal" one. The atom mapping relation is indicated by the numerals labeled in the B4 and B1 structures.

angle γ opens from 60° to 90° and each atom moves horizontally from the center of the triangle to the center of the square resulting from the angle opening; thus, the *h*-BN phase transforms into the B1 phase.

On the other hand, there is an analogous deformation along the tetragonal path, but with the above two stages reversed. In this case, the γ angle at first opens up to 90° accompanied with the atoms moving horizontally to the center of the square, while c/a and u increase slightly. This yields a tetragonal intermediate structure, in which each atom is located at the body center of square pyramid formed by five unlike atoms. The B1 structure is then obtained through a decrease of the c/a ratio which simultaneously brings the atoms from the body center to the base center of the pyramid.

In the present description, an arbitrary intermediate state during the B4-B1 transition can be characterized by six free parameters. Besides the cell edges *a* and *c* and the base angle γ , there are three more fractional coordinate parameters, namely, u, v, and δ . The parameter u denotes the relative displacement of the two sublattices along the c axis, i.e., in the direction of [001], v relates to the relative sliding of the two adjacent (001) planes of the cation (or anion) sublattice in the direction of [110], and δ defines the relative displacement of the two different sublattices also in the [110] direction. Note that in the commonly mentioned four phases shown in Fig. 1, δ is always equal to zero; however, in other phases along the transition paths, δ may deviate from zero a little. Thus, the origin (0, 0, 0) is occupied by one atom, and the fractional coordinates (δ, δ, u) , (v, v, 0.5), and $(v - \delta, v)$ $-\delta, u+0.5$) describe the positions of the other three atoms, respectively. Such a free parameter set actually defines the symmetry restriction $Cmc2_1$ for both the hexagonal and tetragonal paths.¹⁸ Those mechanisms described in the space group of $Pna2_1$ (Refs. 18 and 19) can be regarded as a modification of the $Cmc2_1$ case. The only difference is the arrangement manners of the four-atom unit cells to build up the crystal (see more details in Appendix).

The first comparative study on these two transition paths was given by Saitta and Decremps from the dynamical point of view, which led to the conclusion that the wurtzite semiconductors containing d electrons, such as GaN, InN, and ZnO, preferred the tetragonal path, but the hexagonal path was only possible for those containing light cations, such as AlN and wurtzite SiC.¹⁶ However, the recent experiment by Liu *et al.*²¹ shows the competition between the two transition paths in the ZnO case. Thus, a more detailed study is necessary to improve our understanding of the important B4-B1 phase transition. As shown in Fig. 1, these two mechanisms share the same atom mapping relation between the initial B4 phase and the final B1 phase. Therefore, the present task is to answer the question of which path the atoms take to accomplish the phase transition from B4 to B1. In this paper, we focus on the group-III nitrides and make an investigation of the underlying mechanism from the energetic point of view. The activation enthalpy, which is the least cost crossing over the enthalpy barrier, is taken as the criterion to select the most probable transition path, i.e., the energy-favored path.

III. METHODOLOGY

A. Ab initio calculation

Details of the *ab initio* calculation technique are as follows. We adopt the density-functional theory (DFT) framework and the local-density approximation (LDA) for the exchange and correlation potentials,²² as implemented in the VASP code.²³ The electron-ion interaction was described using Vanderbilt's ultrasoft pseudopotentials.²⁴ In the case of the Ga and In atoms, the *d* electrons were treated as valence electrons, since this is known to be important to obtain reliable results. The valence electronic wave functions were expanded in a plane-wave basis set up to a kinetic-energy cutoff of 350 eV for the three nitrides. The Brillouin-zone integrations were performed by sampling on gamma-centered Monkhorst-Pack grids with $7 \times 7 \times 4$ division of the reciprocal unit cell.

B. Potential-energy surface

The computational approach is very appealing to reveal the underlying mechanism of phase transitions because of the difficulties of the real-time experimental measurement to monitor the fast transition process. A particularly fruitful method is to regard the phase-transition process as a concerted movement of all atoms in the system on a highdimensional potential-energy surface (PES).²⁵ The PES is defined as the hypersurface $H=H(\Omega)$, where Ω is the free structural parameter set and H(=E+PV) is the chemical enthalpy as a function of Ω . Once the PES is obtained, it can be used to determine several points of interest such as the minimum points (corresponding to stable or metastable states) and the saddle points (corresponding to transition states). Moreover, it can be used to determine the transition path by continuously tracing back from the transition state in the steepest-descent direction to the initial and final phases.²⁶ The obtained path clearly represents the atomic shifts and cell deformations occurring during the phase-transition process.

We have known that the common intermediate state for the B4-B1 transition is characterized by six parameters (a, c, c) γ , u, v, and δ). Thus, the complete PES of the B4-B1 transition is six dimensional (6D). However, it is not an easy task for ab initio calculations. Then, it is necessary to introduce some simplifications. As shown in Fig. 1, the parameters γ and u can distinctly characterize the difference between the hexagonal and tetragonal paths. So, instead of the 6D PES, we calculate a two-dimensional PES $H(\gamma, u)$ by fixing γ and *u* and optimizing the enthalpy with the other parameters fully relaxed. The computation details are as follows. The variable range is defined as $(\gamma, u) = [57.5^{\circ}, 92.5^{\circ}] \times [0.37, 0.51]$, which covers the initial B4 phase [corresponding to $(60.0^{\circ}, \sim 0.375)$] and the final B1 phase [corresponding to $(90.0^{\circ}, 0.50)$]. We divided the γ -u space with a 15 × 15 mesh grid. At each grid point, the parameters a, c, v, and δ were fully relaxed to reach the enthalpy minimum. The conjugate gradient algorithm was used for the energy minimization. After obtaining the data of the 15×15 mesh grid, the PES $H(\gamma, u)$ can be figured out as a contour plot by using the spline interpolation method to obtain smooth isolines. To study the pressure effect on the transition mechanisms, the calculations for each nitride were performed at three different pressures: the ambient pressure (~ 1 bar=10⁻⁴ GPa), the equilibrium transition pressure (P_t) , and a higher pressure than the P_t value.

IV. RESULTS AND DISCUSSION

A. Equilibrium transition pressure

The equilibrium transition pressure P_t is defined as the pressure at which the enthalpy of the initial B4 phase is equal to that of the final B1 phase. Usually, it can be determined by taking the common tangent of energy-volume curves of the two end phases. So, we calculated the cohesive energy curves of B4 and B1 phases for AlN, GaN, and InN. The result of AlN is shown in Fig. 2 as an example. The common tangent gives the P_t value of 9.8 GPa. We have also performed additive calculations with different energy cutoffs for the plane-wave expansion to check the reliability of our *ab initio* calculations (see Fig. 2), which shows that the energy cutoff of 350 eV is enough to produce reliable results and is a good choice for time-saved consideration.

In Table I, the calculated P_t values of AlN, GaN, and InN are listed together with the structure parameters (a, c/a, and u) of the equilibrium states. Theoretical and experimental values by others are given as comparison. Overall agreement is obtained. It is also interesting to compare the results of GaN and InN obtained by treating the *d* electrons of the cation explicitly in the valence with those results freezing the *d* electrons. As presented in Table I, the agreement with the available experimental data is better when the *d* electrons are included in the valence for both GaN and InN. Noticeably, the calculated P_t values increase when the *d* electrons are relaxed.



FIG. 2. (Color online) Cohesive energy as a function of volume for the B4-AlN and B1-AlN. The equilibrium transition pressure P_t is estimated at about 9.8 GPa from the common tangent construction. The *ab initio* calculations are performed with different precisions. The medium precision denotes a kinetic-energy cutoff of 350 eV which is used for all the left calculations. The high and the low precisions denote a higher energy cutoff (440 eV) and a lower one (260 eV), respectively.

All the above results support the reliability of the present *ab initio* calculations. This encourages the subsequent calculations to investigate the microscopic mechanisms. It requires huge computational efforts to acquire the potentialenergy surfaces as given in Sec. IV B for the three nitrides, respectively.

B. Potential-energy surface and transition mechanism

1. AlN

Figure 3 shows the calculated potential-energy surfaces for AlN. There are three minima located at the lower-left, upper-left, and upper-right corners in each contour plot, which, respectively, correspond to the B4, hexagonal intermediate, and B1 phase along the hexagonal path illustrated in Fig. 1. Obviously, the tetragonal path, across the lowerright part of the contour plot, is not energy favored since there is a relatively high-energy barrier; however, the hexagonal path is most favored in the AlN case regardless of the various external pressures.

In addition, the hexagonal intermediate phase occurs as a metastable state on the hexagonal path, referred to as MS_h. Because of the existence of MS_h, the B4-B1 transition can be regarded as a multistage process of two steps for AlN. The first step is transition from B4 to MS_h, and the second is from MS_h to B1. For each step, there is one transition state (TS) (shown as a saddle point of the PES). We label the TS of the first step as TS_h1 and the second one as TS_h2. The structural parameters of these states and their corresponding enthalpies are listed in Table II.

The enthalpy corresponding to TS_h2 is larger than that of TS_h1. It indicates that TS_h2 is the least resistance required to overcome for the AlN B4-B1 transition. Thus, TS_h2 is also the global transition state or the "activation state." The corresponding enthalpy defines the activation enthalpy of the

TABLE I. Structural parameters at zero pressure for the wurtzite (B4) and rocksalt (B1) structures of AlN, GaN, and InN. Calculated and experimental values by others are given as comparison. Particularly, the values in parentheses correspond to the experimental data and the values in square brackets correspond to freezing the semicore d electrons of the cation. Note that the parameters for the B1 phase are also given in a four-atom unit cell representation (see Fig. 1) instead of a conventional cubic cell.

	Phase	a (Å)	c/a	и	P_t (GPa)
AlN	B4	3.06	1.606	0.382	9.8
		3.061 ^a	1.600 ^a	0.382 ^a	9.2, ^a 9.5, ^b 8.3 ^c
		(3.111 ^a)	(1.601^{a})	(0.3821^{a})	
	B1	2.843	1.414	0.5	
		2.813 ^a			
		(2.860^{a})			
GaN	B4	3.145 [3.133]	1.633 [1.631]	0.376 [0.377]	44.5 [36.0]
		3.180 ^a	1.632 ^a	0.376 ^a	42.9, ^a 43.7, ^b 33.5 ^c
		(3.160-3.190 ^a)	$(1.622 - 1.632^{a})$	(0.377^{a})	
	B1	2.956	1.414	0.5	
		2.987"			
InN	B4	3.507 [3.488]	1.620 [1.613]	0.378 [0.379]	12.1 [5.6]
		3.525 ^a	1.613 ^a	0.379 ^a	11.1, ^a 11.12, ^b 11.7 ^c
		(3.533^{a})	(1.611^{a})	(0.375^{a})	
	B1	3.282	1.414	0.5	
		3.278 ^a			

^aRef. 27 and references therein.

^bDFT-LDA (ABINIT code) (Ref. 28).

^cDFT-LDA (PWSCF code) (Ref. 16).

phase transition. As given in Table II, with the pressure increased from ambient condition up to 15 GPa, the activation enthalpy for the AlN B4-B1 transition decreases from 0.438 to 0.219 eV/pair which results in the increasing occurrence probability of the phase transition.

2. GaN

Figure 4 shows the calculated potential-energy surfaces for GaN, which is quite different from those of AlN and shows some diversities under different pressures.

First, as shown in Fig. 4(a), the hexagonal intermediate state located at $(\gamma, u) = (60^{\circ}, 0.5)$ is not a minimum point (MS h) but a saddle point (TS h1) at ambient pressure; however, the tetragonal intermediate state at the lower-right corner is observed as a metastable state, referred to as MS_t. It indicates that the tetragonal path becomes favorable for the GaN B4-B1 phase transition. The existence of MS_t separates the tetragonal path into two steps: the first one from B4 to MS t and the second one from MS t to B1. Likewise, we label the two saddle points as TS_t1 and TS_t2, respectively. Second, as shown in Fig. 4(b), when the pressure increases up to the equilibrium transition pressure (\sim 44.5 GPa for GaN), TS_t2 and MS_t disappear from the PES and only TS t1 remains on the tetragonal path. Third, with the pressure increased further, MS h comes out and TS h1 shifts toward B4 along the hexagonal path [see Fig. 4(c)].

The structural parameters and the corresponding enthalpies of the representative states for GaN are listed in Table III. Compared with the hexagonal one, the tetragonal path is of a relatively small activation enthalpy in the pressure ranges investigated here. Therefore, the tetragonal path is more favored than the hexagonal path in the GaN case, which is contrary to the case of AlN. It is likely that the energy consideration of the B4-B1 transition has confirmed the results from the dynamical point of view for AlN and GaN,¹⁶ as reviewed in Sec. II. However, analogous calculations in InN, which also contains *d* electrons as GaN, will show some new results.

3. InN

The calculated potential-energy surfaces for InN are shown in Fig. 5. The structural parameters and the corresponding enthalpies of several representative states are listed in Table IV. As shown in Fig. 5, with the pressure increased, the PES of InN clearly shows the similar "reforming" as in the GaN case: MS_t occurs at low pressure, whereas MS_h occurs at high pressure. However, the similarity is only at the qualitative level. If we make a careful comparison of the activation enthalpies of the two transition paths (Table IV), we can find that the preferred path changes from the tetragonal one under lower pressure to the hexagonal one under higher pressure. At ambient pressure, the activation enthalpy ΔH of the hexagonal path is about 0.488 eV/pair which is higher than the value 0.457 eV/pair of the tetragonal path. At equilibrium transition pressure (~12.1 GPa),



FIG. 3. Contour plot of the minimized enthalpy of AlN as a function of γ and u at (a) ambient pressure (~1 bar), (b) equilibrium transition pressure (~9.8 GPa), and (c) 15 GPa. The dashed line indicates the hexagonal path.

the corresponding activation enthalpies are 0.240 and 0.249 eV/pair, respectively. Herein, these two activation enthalpies are comparable with each other though the hexagonal path is of a little lower barrier. As the external pressure is



FIG. 4. Contour plot of the minimized enthalpy of GaN as a function of γ and u at (a) ambient pressure (~1 bar), (b) equilibrium transition pressure (~44.5 GPa), and (c) 100 GPa. The dashed lines are shown as a guide of the hexagonal and tetragonal paths.

up to 20 GPa, the activation enthalpies are 0.131 and 0.151 eV/pair, respectively, which enhances the preference of the hexagonal path. Therefore, we suggest that these two paths are competitive in the InN case and the tetragonal one



FIG. 5. Contour plot of the minimized enthalpy of InN as a function of γ and u at (a) ambient pressure (~1 bar), (b) equilibrium transition pressure (~12.1 GPa), and (c) 20 GPa. The dashed lines are shown as a guide of the hexagonal and tetragonal paths.

is more preferable under lower pressure but the hexagonal one under higher pressure.

4. Comparison with previous studies

Our *ab initio* calculation results have shown that the energy-favored transition path is dependent not only on the internal compositions but also on the external pressures. Such a kind of pressure dependence, to our knowledge, was little discussed in previous theoretical studies. Based on the

elastic behaviors upon pressure, Saitta and Decremps pointed out that both InN and GaN prefer the tetragonal path, but AlN prefers the hexagonal path.¹⁶ Serrano et al. investigated the relative stability of the group-III nitrides in the pressure range up to 200 GPa wherein InN and AlN transform from B4 into MS_h but GaN remains stable in B4.27 The results of Serrano et al. indicate that the preferred path of InN is similar to that of AlN rather than that of GaN, which is contrary to the statement of Saitta and Decremps.¹⁶ In other words, the results of these two groups agree with each other for AlN and GaN but not for InN. Now, the inconsistency in the case of InN can be understood if a pressure-dependence effect is considered. The present work makes it clear that AlN always prefers the hexagonal path and GaN always prefers the tetragonal one in a large range of pressure, whereas in the InN case the tetragonal path is more preferable under lower pressure but the hexagonal one under higher pressure. In our point of view, the elastic response to pressure gives a reasonable result in the low-pressure range; on the contrary, the structural stability under pressure gives a reasonable result in the high-pressure range. The former might be more suitable for displacive phase transitions than for reconstructive transitions.⁶

Also, based on the calculated results, it is not definitive for the preference of the transition path whether d electrons are contained in the concerned system or not. The full electrons might make a coherent effect on this point, which needs further study in future work. A phenomenological explanation for the different responses of these three nitrides might be due to the different ionic sizes (refer to the lattice constants, as shown in Table I). A relatively large ionic size of In may lead to a relatively large changeability of the highpressure behavior in the InN structure and result in the obvious competition between the two possible paths for InN.

It is also interesting that the B4-B1 transition can be considered as a two-step process for AlN, as shown in Fig. 3, where the hexagonal intermediate state acts as a metastable state. However, this is not always the case for GaN and InN, as shown in Figs. 4(b) and 5(b), respectively. That is to say, a metastable state is not necessary for the B4-B1 transition of GaN and InN, which is inconsistent with the assumption in the work of Saitta and Decremps.¹⁶

C. Indicator of transition mechanism

In Sec. IV B, we have made a comparative study of the hexagonal and tetragonal paths in AlN, GaN, and InN from the energy point of view. It is also important to identify which path is the preferred one with the help of experimental measurement. To shed light on this issue, we will have a look at the evolution of some measurable properties along the two different transition paths, taking InN as an example.

As shown in Fig. 1, the atomic coordination environment is significantly different between the hexagonal and tetragonal intermediate states. The radial distribution function (RDF) is a kind of description of the coordination. Figure 6 shows the change of RDFs for the B4-B1 phase transition in InN. With respect to the RDF of the initial B4 structure, there will be an additive peak on the right of the first peak along



FIG. 6. Comparison of the RDFs of InN in the B4, B1, hexagonal, and tetragonal structures.

the hexagonal path; however, there will be an additive peak on the left along the tetragonal path. This is a result of the 3+2 and 1+4 coordinations in the hexagonal and the tetragonal intermediate structure, respectively (see Fig. 1). The different changes of the RDF are likely to be a good indicator to distinguish these two transition mechanisms.

Figure 7 shows the contour plots of the ratio c/a and the fractional coordinate v as a function of u and γ obtained in the above calculation for InN at the pressure of P_t =12.1 GPa. The hexagonal and tetragonal transition paths are also approximately outlined in the contour plots which helpfully exhibit the evolution of the structural parameters along the corresponding path. As shown in Fig. 7(a), the c/aratio decreases firstly and then increases along the hexagonal path, whereas it increases slightly at first and then decreases along the tetragonal path. That is to say, the variation of c/ais quite different along these two paths on the qualitative side, which implies that the measurement of c/a ratio is a suitable choice to identify the hexagonal or tetragonal path in experiment since there is no need of an accurate quantitative measurement. However, the parameter v, as shown in Fig. 7(b), changes monotonously along both paths. Obviously, the structure parameters u and γ also change monotonously along both paths. Thus, compared with the case of c/a, measurements of any one of the parameters v, u, and γ might not reveal particularly significant differences between the two paths. In some sense, we think that the c/a ratio is a relatively good choice to identify the hexagonal or tetragonal path on the experimental side. It is also very interesting that the change of v almost depends on the γ angle only, even in the full contour graph [see Fig. 7(b)]. This implies a strong coupling between the coordinate v and the angle γ .

Now, we have proposed the RDF and axial ratio c/a as indicator for experimental measurements to distinguish the two possible transition paths proposed for the B4-B1 phase transition. Obviously, there is a need for real-time observation of these parameters *during* the transition process. However, the fast transition process brings forward a challenging problem on the high time-resolving power for the experimental measurements. Most of the previous experiments fo-



FIG. 7. Contour plots of the ratio c/a (a) and the fractional coordinate v(b) as a function of u and γ for InN at the pressure of $P_t=12.1$ GPa. Several key points of the hexagonal and tetragonal paths are marked by diamonds and squares, respectively. The dashed lines are shown as a guide of the hexagonal and tetragonal paths.

cused on the changes of structural parameters with increasing pressure *before* the onset of phase transitions. Experimentally, the axial ratio c/a of GaN exhibits no evident change with pressure, whereas the axial ratios of AlN and InN decrease with increasing pressure; (see Fig. 8 in Ref. 30). Furthermore, there is a distinct drop of c/a observed immediately before the onset of the transition for the case of InN. These results were also confirmed by *ab initio* calculations.²⁵ If they are compared with the calculated results of c/a changing along the two paths during the pressure process [see Fig. 7(a)], it might imply that, before the onset of the transition along the hexagonal path, whereas GaN does not.

D. Hysteresis cycle

In Sec. IV A, we have estimated the equilibrium transition pressure (P_t) by common tangent construction, which is frequently used to compare directly with the experimental transition pressure (P_e) in the past. However, it is realized recently that there are large kinetic barriers that impede the

transition at P_t , leading to a hysteresis between the forward and backward transitions,¹⁵ in which the transition pressure observed on increasing the pressure is larger than that observed on decreasing the pressure. The pressure for the onset of the forward transition can be considered as an upper limit of the P_t value, while the pressure for the onset of the backward transition is the lower limit.¹⁴ These two limits define the hysteresis cycle of phase transition.

It may also be significative to estimate the hysteresis cycle on the theoretical side. For this purpose, we first introduce a concept of "activation temperature." The activation enthalpy ΔH corresponds to the height of the largest enthalpy barrier along the transition path. To overcome such a barrier, the crystal system at least needs a critical internal energy Ecomparable to ΔH . It means a temperature of T for the system from the thermostatistics view, where T is determined by the Dulong and Petit law $E=3k_BT$ and is defined as the activation temperature (T_a) in this work. The physical meaning of the activation temperature could be understood as a temperature threshold for the onset of the phase transition at a given pressure. If the external pressure is high enough, the enthalpy barrier disappears which indicates a zero activation temperature. In particular, T_{\rightarrow} and T_{\leftarrow} denote the activation temperature of the forward $B4 \rightarrow B1$ transition and the backward $B1 \rightarrow B4$ transition, respectively. The calculated values for AlN, GaN, and InN are listed in Tables II-IV, respectively. We also plot the activation temperature as a function of external pressure in Fig. 8. The plots clearly show that, with the increasing pressure, the activation temperature decreases for the forward $B4 \rightarrow B1$ transition but increases for the backward $B1 \rightarrow B4$ transition. In other words, with the increasing temperature, the transition pressure decreases for the forward $B4 \rightarrow B1$ transition but increases for the backward $B1 \rightarrow B4$ transition.

Though the B4-B1 transition is pressure induced, the temperature really has influence on the experimental transition pressure. For example, the pressure determined for the B4-B1 transition in ZnO by Decremps et al.³¹ decreases from 9 GPa at 25 °C toward 6 GPa at 600 °C. We note that the activation temperature should be interpreted as the sample temperature instead of the environment temperature. Moreover, the sample temperature of the transition kernel can be varied during the transition process and might be much higher than the initial sample temperature.³² Thus, the sample temperature might not be easily given in experiment. For the preliminary analysis, we assume a sample temperature of 300 K. Then, the forward and backward P-T curves can determine the hysteresis cycle by the two intersections with the horizontal axis positioned at the assumed sample temperature 300 K, as shown in Fig. 8.

For AlN [see Fig. 8(a)], the pressure of ~21 GPa is required for the onset of the forward $B4 \rightarrow B1$ transition, whereas the backward $B1 \rightarrow B4$ transition will not begin even at zero pressure. Experimentally, the B4-B1 transition in AlN was reported to start at about 20.0 GPa.³³ Upon releasing pressure from the B1 phase, this structure persists down to atmospheric pressure.³⁴ Therefore, good agreement is obtained for the theoretical and experimental results in the case of AlN. For InN [see Fig. 8(c)], the hysteresis cycle is estimated at around 6–17.5 GPa, which is comparable with

TABLE II. Representative points on the potential-energy surface of AlN. TS and MS denotes the transition state (a saddle point) and the metastable state (a local minimum point). The postfix "h" denotes the hexagonal path. The (γ, u) value of each point is given together with the corresponding enthalpy ΔH (with respect to the B4 state). The forward and backward activation temperatures T_{\rightarrow} and T_{\leftarrow} are also listed for the corresponding activation state (see text in Sec. IV D). The bold font highlights the activation enthalpy and activation temperature at a given pressure.

	B4	TS_h1	MS_h	TS_h2	B1					
AlN at 1 bar										
γ (degree)	59.8	59.9	60.4	78.0	90.0					
и	0.382	0.471	0.507	0.501	0.500					
ΔH (eV/pair)	0.000	0.212	0.207	0.438	0.240					
T_{\rightarrow} (K)		410		847						
T_{\leftarrow} (K)		0		383						
		AlN at 9.8	GPa							
γ (degree)	60.0	60.3	59.9	75.6	90.0					
и	0.383	0.464	0.501	0.500	0.500					
ΔH (eV/pair)	0.000	0.152	0.131	0.287	0.000					
T_{\rightarrow} (K)		295		556						
T_{\leftarrow} (K)		295		556						
AIN at 15 GPa										
γ (degree)	60.0	60.0	60.3	74.5	90.1					
и	0.383	0.456	0.500	0.500	0.501					
ΔH (eV/pair)	0.000	0.125	0.095	0.219	-0.119					
T_{\rightarrow} (K)		242		423						
T_{\leftarrow} (K)		473		653						

the experimental result that the B4-B1 transition was reported to occur at about 13.5 GPa (Ref. 35) and the reverse B1-B4 transition was reported to start at about 3.0 GPa.³⁶ For GaN, the B4-B1 transition was reported to occur at above 50.0 GPa,³² and the reverse B1-B4 transition was reported at 30.0 GPa.³⁷ Our theoretical model estimates the hysteresis at about 20–80 GPa [see Fig. 8(b)]. If our model is accepted, the relatively large discrepancy in the GaN case might be interpreted as follows. First, the transition pressure for GaN is much larger than the one for AlN or InN. Higher pressure may cause a higher temperature inside the sample, especially in the transition kernel. If the sample temperature is assumed at a higher value 600 K in Fig. 8(b), one can estimate a hysteresis cycle at around 35-53 GPa, which arrives at improved agreement with the experimental results. Moreover, the actual sample temperature might not be a constant value during the whole transition process. Therefore, our model is oversimple for GaN though it is relatively effective for AlN and InN. There is also clear evidence in experiment that phase transition tends not to occur as a single homogeneous domain.¹⁵ The actual complicated nucleation process is currently unclear which might be important to estimate the hysteresis cycle theoretically. Therefore, we note that the model proposed here is a rather rough one.

TABLE III. Representative points on the potential-energy surfaces of GaN. TS and MS denote the transition state (a saddle point) and the metastable state (a local minimum point). The postfixes "h" and "t" denote the hexagonal and the tetragonal paths respectively. The parameters are of the same definitions as in Table II. The bold font highlights the activation enthalpy and activation temperature for the hexagonal or tetragonal path at a given pressure.

	B4	TS_h1	MS_h	TS_h2	TS_t1	MS_t	TS_t2	B1		
GaN at 1 bar										
γ (degree)	60.0	60.0		81.9	84.8	89.0	89.6	90.0		
и	0.375	0.500		0.500	0.395	0.399	0.460	0.500		
ΔH (eV/pair)	0.000	0.483		0.948	0.832	0.819	0.891	0.870		
T_{\rightarrow} (K)		935		1834	1608		1722			
T_{\leftarrow} (K)		0		151	0		39			
	GaN at 44.5 GPa									
γ (degree)	60.0	59.9		72.2	78.9			90.0		
и	0.376	0.499		0.501	0.400			0.501		
ΔH (eV/pair)	0.000	0.339		0.418	0.384			-0.011 ^a		
T_{\rightarrow} (K)		656		808	742					
T_{\leftarrow} (K)		677		830	763					
GaN at 100 GPa										
γ (degree)	60.0	60.0	60.0	62.1	72.5			90.0		
и	0.377	0.465	0.500	0.500	0.395			0.501		
ΔH (eV/pair)	0.000	0.177	0.167	0.168	0.109			-0.866		
T_{\rightarrow} (K)		342		325	210					
T_{\leftarrow} (K)		2017		2001	1885					

^aReference 29.

	B4	TS_h1	MS_h	TS_h2	TS_t1	MS_t	TS_t2	B1
			InN	Vat 1 bar				
γ (degree)	60.0	60.0		80.3	82.2	90.0	90.0	90.0
и	0.378	0.500		0.500	0.393	0.405	0.450	0.500
ΔH (eV/pair)	0.000	0.242		0.488	0.446	0.419	0.457	0.388
T_{\rightarrow} (K)		468		945	863		884	
T_{\leftarrow} (K)		0		195	113		134	
			InN a	at 12.1 GPa				
γ (degree)	60.0	60.0		75.0	78.9			90.0
и	0.379	0.496		0.501	0.398			0.500
ΔH (eV/pair)	0.000	0.149		0.240	0.249			0.004
T_{\rightarrow} (K)		289		465	482			
T_{\leftarrow} (K)		282		458	476			
			InN a	at 20.0 GPa				
γ (degree)	60.5	60.2	60.0	71.2	76.5			89.9
и	0.380	0.469	0.500	0.500	0.399			0.499
ΔH (eV/pair)	0.000	0.100	0.094	0.131	0.151			-0.221
T_{\rightarrow} (K)		194		253	293			
T_{\leftarrow} (K)		621		680	720			

TABLE IV. Same as Table III but for InN.



FIG. 8. (Color online) Activation temperatures of the $B4 \leftrightarrow B1$ phase transition vs external pressures for (a) AlN, (b) GaN, and (c) InN. The activation temperature decreases with the increasing pressure for the forward $B4 \rightarrow B1$ transition (downward lines) but increases for the backward $B1 \rightarrow B4$ transition (upward lines). Triangles and squares are used to denote the hexagonal and the tetragonal paths, respectively. The forward and the backward *P*-*T* curves explicitly define the hysteresis cycles.

Now, we would like to address the problem of what the two competitive mechanisms mean in InN. For convenience, we define a critical pressure (P_c) at which the hexagonal and tetragonal paths share the same activation enthalpy or activation temperature. Thus, the pressure dependence of the energy-favored mechanism in InN can be described as that the tetragonal path is more preferable at a pressure smaller than P_c but the hexagonal one larger than P_c . If the phase transition of InN can take place at a pressure far lower than

 P_c , we may imagine that InN will transform into its B1 phase along the tetragonal path if the external pressure is gradually increased (slow compression mode) but the hexagonal path instead if an instantaneous pressure much larger than P_c is loaded (shock compression mode). This does not happen for AlN and GaN since they always take a single path in a rather large pressure range. Unfortunately, such an interesting phenomenon for InN seems not likely to be observed in experiment. As shown in Fig. 8(c), the value of P_c is estimated at about 8 GPa which is evidently smaller than the accepted transition pressure of 13.5 GPa. That is to say, the above assumption and conjecture are not true in practice for InN. The hexagonal path might always be the most probable mechanism for the InN B4-B1 transition. With a further consideration of the reversed B1-B4 transition for InN, we note that the transition pressure is smaller than P_c , as shown in Fig. 8(c). In this situation, InN will recover to its ambient phase mostly along the tetragonal path instead of the hexagonal one.

In addition, the equilibrium transition pressure can also be estimated more accurately from experiment at higher temperature, which is readily a conclusion from the P-T curves. As usual in experiment, the middle of the hysteresis cycle is taken as a crude approximation to the equilibrium transition pressure, and the half-width of the interval as a measure of its uncertainty. From the calculated results shown in Fig. 8, the hysteresis cycle will become smaller if the sample temperature increases. Thus, it suggests that high-temperature experiments may give a good estimation of the equilibrium transition pressure.

V. CONCLUSION

In the present work, we make a comparative study on the microscopic mechanism of the B4-B1 phase transition in group-III nitrides (AlN, GaN, and InN) based on ab initio calculations. The calculated potential-energy surfaces for these three nitrides at various pressures become a base to select or to determine the energy-favored transition path. We have pointed out that AlN and GaN prefer the "hexagonal" and the "tetragonal" paths, respectively, in a large range of pressure, whereas these two different mechanisms are competitive in the InN case which is significantly affected by the external pressure. That is to say, the microscopic mechanism of B4-B1 phase transition is dependent not only on the internal compositions but also on the external pressures. It seems to us that the variety of transition mechanism should be interpreted through the electronic properties of these systems under different pressures, which is left for further study.

It is also interesting that RDF or c/a might be a good indicator to distinguish these transition paths by experimental measurement. Besides, we introduce the concept of "activation temperature" and plot it as a function of external pressure. The *P*-*T* curves are suggested to roughly estimate the hysteresis cycle of the B4-B1 transition. Good agreement with the experimental results is obtained for AlN and InN. However, such an oversimple model produces a larger hysteresis than the experimental observation in the case of GaN. The P-T curves also suggest that the equilibrium transition pressure can be estimated more accurately from experiment under higher temperature.

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APPENDIX

In this appendix, we give a more detailed explanation for the symmetry correlation between the mechanisms with $Cmc2_1$ symmetry restriction and any other possible mechanisms with different space-group symmetry restrictions including $Pna2_1$ discussed in Refs. 18 and 19.

In Fig. 9, we illustrate the similarities and differences of $Cmc2_1$, $Pna2_1$, and other possible symmetry restrictions in the description of the mechanisms proposed for the B4-B1 phase transitions. From the top view of the hexagonal B4 structure, if the adjacent four-atom unit cells are arranged with translational symmetry, the global description of the transition is in the $Cmc2_1$ space group [see Fig. 9(a)], while with reflective symmetry, it turns into the $Pna2_1$ symmetry restriction [see Fig. 9(b)]. Further, any other arrangement patterns may be allowable if they can build up the whole plane. When each of the four-atom unit cells in a large crystal transformed from the fourfold-coordinated phase to the sixfold-coordinated phase, as sketched out in Fig. 1, the B4-B1 structural phase transition takes place in the crystal. In other words, any rhombus division of the closed-pack plane leads to one possible microscopic mechanism. The DFT calculations of Shimojo et al. reveal very similar energy barriers or activation enthalpies among these mechanisms defined as different arrangements of the four-atom unit cell.¹⁹ Therefore, without consideration of the long-range arrangement differences, all the above mechanisms can be explained by the same one described with the $Cmc2_1$ symmetry.¹⁸ The four-atom cell can be regarded as the "transition unit" for all mechanisms discussed here. Therefore, at least for B4-B1 phase transitions, point-group symmetry might be more reasonable and convenient to define a transition path than space-



FIG. 9. (Color online) Schematic projection of the different arrangements of four-atom unit cells in the B4 structure. Each rhombus stands for one four-atom unit cell and will transform into squares together with the c/a compression companying the B4-B1 transition: (a) is the "translational" arrangement and corresponds to the $Cmc2_1$ restriction, (b) is the "reflective" arrangement and corresponds to the $Pna2_1$ case, and (c) is another sample by combining the translational and reflective arrangements.

group symmetry. Thus, we suggest the point group *mm*² as a unified description of all the above mechanisms proposed for B4-B1 phase transitions.

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