Machine learning metadynamics simulation of reconstructive phase transition

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Simulating reconstructive phase transition requires an accurate description of potential energy surface (PES). Density-functional-theory (DFT) based molecular dynamics can achieve the desired accuracy but it is computationally unfeasible for large systems and/or long simulation times. Here we introduce an approach that combines the metadynamics simulation and machine learning representation of PES at the accuracy close to the DFT calculations, but with the computational cost several orders of magnitude less, and scaling with system size approximately linear. The high accuracy of the method is demonstrated in the simulation of pressure-induced *B*4-*B*1 phase transition in gallium nitride (GaN). The large-scale simulation using a 4096-atom simulation box reveals the phase transition with excellent detail, revealing different simulated transition paths under particular stress conditions. With well-trained machine learning potentials, this method can be easily applied to all types of systems for accurate scalable simulations of solid-solid reconstructive phase transition.

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I. INTRODUCTION

Reconstructive phase transition (RPT) [1], in which the changes of crystalline phase are driven by the breaking and reconstruction of primary chemical bonds, is of considerable importance in both fundamental and applied material research. It is commonly observed in nature, where matters change their crystalline states under the change of environment. In earth science, RPT plays an important role in the formation of Earth's inner structure and its accretion. In industry, RPTs are often used to manipulate solid materials under high pressure and temperature, such as in steel production, where different forms of ferrites can be grown by a reconstructive mechanism. Currently, elucidation of the mechanism of RPT is still a challenge. It usually proceeds in an abrupt manner with no clearly defined order parameters or groupsubgroup relations between the phases [2]. The existence of one or more common intermediate phases describing the transition path complicates the mechanism [3-5]. Direct experimental observation of RPTs at the atomic level is difficult.

Theoretical simulation provides a complementary approach to trace the atomic movement during RPT. Owing to the rapid advancement of computing power, serious attempts in simulating RPT may now be pursued, but carrying out such simulation in a realistic length/time scale is still daunting. As the current state of the art, density functional theory (DFT)-based simulation is the *de facto* method of choice, but computationally it is very demanding for large-scale systems. Since the computational cost scales as the third power with respect to the number of Kohn-Sham orbitals, DFT-based molecular dynamics (MD) simulation is restricted to systems of a few hundreds of atoms.

An obvious drawback of small-scale simulation is that the simulated phase transition has to proceed collectively, with all chemical bonds reconstructed simultaneously across the simulation box, which increases the activation barrier and makes the transition rarer [6,7]. To circumvent the high activation barrier, the metadynamics (MetaD) method was designed [8,9]. The MetaD method describes the system's location and approximate surroundings in free energy landscape by a number of collective variables (CVs) [10,11]. During the simulation, the system departs from a predetermined energy minimum through molecular motions; meanwhile a series of Gaussian potentials is added to the free energy well to lower the activation barrier and lead the system out to neighboring minima, which enables the simulation of RPT including simulated transition pathways that may proceed via intermediate states. Colloquially known as "filling the free energy wells with computational sand," the MetaD method has been very successful in determining crystal structures occurring at the high-pressure regime by reconstructive mechanism [12–18].

Building on the success of DFT-based MetaD, it is obviously desirable to enhance this method to have the capability not only to simulate the RPT but also to simulate it with a realistic scale simulation box and to some extent account for the heterogeneous processes. To this end, empirical potentials have been employed in several simulations of phase transition, such as solid-solid phase transition [10,12,17] and

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solidification [19,20], however, the accuracy and transferability of the potentials are not always satisfactory. Since the accuracy of atomistic simulation largely depends on the interatomic potentials, constructing appropriate potentials to describe interatomic interactions with the accuracy close to the DFT but at a lower computational cost is central to the problem. Recently, powered by the flexibility to represent arbitrarily complex functions, the machine learning approach has also been used to reconstruct the PES, which leads to a different type of interatomic potentials, namely, the machine learning potential (MLP) [21–27]. They show a satisfactory compromise between accuracy and efficiency in several largescale simulations [28–30].

In this paper, we demonstrate that, by directly learning the data obtained from small-scale DFT calculations, the MLP combined with MetaD can perform a scan of free energy landscape at large length scale at a computational cost similar to the usage of empirical potentials. In contrast to empirical potentials, however, the MLP describes the total energy in terms of individual atoms in given neighboring environments through mathematical fitting rather than parametrizing specific analytical functional forms with physical assumptions. This naturally allows for the description of bond breaking and reconstruction, that is, the change of atoms' local environments, which is ideally suited for simulating RPT. As a proof of principle, we applied the method to a classic example, the B4-B1 phase transition in GaN, using a large simulation box (4096 atoms) under general stress conditions (hydrostatic, uniaxial, and shear). The present simulation clearly reveals the manner of atom rearrangements during the phase transition and influence of external conditions on path selection.

II. METHODS

A. Machine learning potential

The MLP is a data-driven interatomic potential for the representation of potential energy surface (PES) for systems with high degrees of freedom. The total energy *E* of a system containing *N* atoms is dictated by atomic coordinates \mathbf{R}_i and atomic number Z_i ,

$$E = f(\mathbf{R}_1, \dots \mathbf{R}_i, \dots \mathbf{R}_N; Z_1 \dots, Z_i \dots Z_N).$$
(1)

To describe high dimensional PES, Behler and Parrinello represent the *E* as a sum of atomic contributions ε_i , mapped to each atom by atomic feature vector (descriptor) **d**_{*i*} [31],

$$E = \sum_{i} \varepsilon_{i}(\mathbf{d}_{i}).$$
 (2)

The descriptor \mathbf{d}_i accounts for the chemical environment of atom *i*, which depends on positions and chemical identities of all neighboring atoms within a given cutoff radius R_c . It should retain the symmetries as the atomic energy ε_i is invariant under translation and rotation, as well as the permutation among atoms of same chemical element. It also should be smooth with respect to displacement of atoms to obtain continuous derivatives. By construction, the atomic energy ε_i is short ranged, but standard terms representing long-range interactions (electrostatic, van der Waals) may be added to Eq. (2) as needed [32–34].

The atom centered symmetry function (ACSF) [35] proposed by Behler and Parrinello is a well-used descriptor that models local environment via radial and angular distributions of atomic neighbor density. However, the downside of traditional ACSFs is that the number of symmetry functions increases nonlinearly with the number of species, that is, the numbers of radial and angular symmetry functions increase with the number of species (N_c) by a factor of N_c and $\frac{1}{2}[N_c(N_c+1)]$, respectively. In the present study, to overcome this undesirable scaling we use the weighted atom-centered symmetry functions (wACSFs) based on conventional ACSFs, in which weight parameters are assigned to each atomic species to distinguish their contributions [36,37]. Therefore, the number of the symmetry functions remains the same for systems with different N_c s. Specifically, the radial and angular symmetry functions are written as

$$G_{i}^{\text{rad}} = \sum_{j} \omega_{j} e^{-\eta (R_{ij} - R_{s})^{2}} f_{c}(R_{ij}), \qquad (3)$$

$$G_{i}^{\text{ang}} = 2^{1-\zeta} \sum_{j,k \neq i} \omega_{j} \omega_{k} (1 + \lambda \cos \theta_{ijk})^{\zeta} e^{-\eta (R_{ij}^{2} + R_{ik}^{2} + R_{jk}^{2})} \times f_{c}(R_{ij}) f_{c}(R_{ik}) f_{c}(R_{jk}). \qquad (4)$$

Here, θ_{ijk} denotes the bond angle extended by atoms *i*, *j*, and k, i.e., $\cos \theta_{ijk} = \frac{\mathbf{R}_{ij} \cdot \mathbf{R}_{ik}}{R_{ij} R_{ik}}$. η , R_s , λ , and ζ are adjustable parameters (hyperparameters) that set the position and width of Gaussian function, and the range and shape of angular density function, which are parametrized carefully to ensure the precision of MLP. f_c is a cutoff function which ensures that only the energetically relevant regions close to the atom iare encoded in wACSFs. By construction, f_c decays smoothly to zero in value and slope at R_c . The weight parameters ω_i and ω_k are element specific and are used to distinguish contributions from different atomic species. They are determined during the training process using grid search. Details on setting hyperparameters are provided in the Supplemental Material [38]. For GaN ($N_c = 2$) with the current settings of hyperparameters (Table S1 [38]), the number of symmetry functions is 66 in wACSFs, while it would be 87 in traditional ACSFs. As the number of species in the system increases, the advantage of wACSFs would become more obvious.

In MLPs, the total energy as a sum of atomic energies ε_i is fitted to the computed reference data using methods such as neural network (NN) [31,45], Gaussian process regression (GPR) [46], and linear regression (LR) [47,48]. In the current implementation, we use GPR as the regression model for potential fitting with the wACSF as descriptors. The advantages of this combination are (1) the fitting is determined by simple linear algebra, which is computationally more efficient than optimizing multimodal functions as in the case of NN, and (2) both energies and derivatives of energies (interatomic forces, virial stress) can be treated at equal footing in the training set. The second point is particularly desirable for simulating RPTs, where the weight and accuracy of potential fitting may be biased toward interatomic forces. Detailed implementations of the GPR are similar to those in the Gaussian approximation potential [21,46].

B. Metadynamics

MetaD is an efficient method for simulating pressureinduced phase transitions. In this method, the free energy surface is explored on a few carefully constructed CVs. Initial work by Parrinello and Rahman adopted the lattice matrix **h** of the simulation box as CVs [49]. The **h** matrix contains six nonzero order parameters (h_{11} , h_{22} , h_{33} , h_{12} , h_{13} , h_{23}) representing six independent degrees of freedom, arranged in upper (or lower) triangular form in order to freeze unphysical box rotations [10]. The atomic degrees of freedom are assumed to be coupled to the **h** matrix by molecular dynamics equilibrium. By this construction, the energy wells are six dimensional, whose curvatures are determined by second derivatives of the Gibbs free energy *G* with respect to the deformation of the simulation box. Close to a given minimum $G(\mathbf{h}^0)$, the free energy well can be approximated harmonically,

$$G(\mathbf{h}) \approx G(\mathbf{h}^0) + \frac{1}{2}(\mathbf{h} - \mathbf{h}^0)^T \mathbf{A}(\mathbf{h} - \mathbf{h}^0), \qquad (5)$$

where **A** is the elastic response matrix, or Hessian matrix. At a local minimum, the **A** matrix has positive real eigenvalues (λ^i) and can be diagonalized by an orthogonal matrix **O**. To treat all degrees of freedom on equal footing, which is crucial for dramatic structure changes in RPT, it is convenient to diagonalize the **A** matrix by expressing **h** in a set of new variables **s** [11],

$$h_i - h_0 = \sum_j O_{ij} \frac{1}{\sqrt{\lambda^j}} s_j. \tag{6}$$

With the new variables, the energy well becomes spherical which eliminates sampling problems resulting from a highly anisotropic shape of energy well.

The centerpiece of the metadynamics algorithm is that the Gibbs potential is continuously modified by a series of Gaussian potentials until the system is pushed out the local minimum. The G is therefore history dependent, expressed in term of \mathbf{s} ,

$$G'(\mathbf{s}) = G(\mathbf{s}) + \sum_{t' < t} W e^{-|\mathbf{s} - \mathbf{s}'|^2 / 2\delta s^2}.$$
 (7)

Here W and δs are the height and width of the Gaussian, which are adjusted to reach an optimal speed of energy well filling. For a given G^t , the driving force is the negative of its derivative, $\mathbf{F}^t = -\partial G^t / \partial \mathbf{s}$, which guides the evolution of the simulation box as

$$\mathbf{s}^{t+1} = \mathbf{s}^t + \delta s \frac{\mathbf{F}^t}{|\mathbf{F}^t|}.$$
 (8)

For convenience, the driving force is calculated in terms of matrix \mathbf{h} using Eq. (6),

$$\frac{\partial G'}{\partial s_i} = \sum_j O_{ji} \frac{1}{\sqrt{\lambda^i}} \frac{\partial G'}{\partial h_j},\tag{9}$$

with the derivative of *G* obtained from [49]

$$-\frac{\partial G}{\partial h_{ij}} = V[\mathbf{h}^{-1}(\mathbf{p} - P)]_{ji} - V_0 [\mathbf{h}_0^{-1} \Sigma \mathbf{h}_0^{T-1} \mathbf{h}^T]_{ji}.$$
 (10)

Here the V is the volume of the simulation box, i.e., $V = |\det \mathbf{h}|$. **p** is the internal stress tensor of the system. To adopt a general strain condition, the (target) external pressure

is decomposed into hydrostatic (*P*) and anisotropic (Σ) components, i.e., $\mathbf{P}_{\text{ext}} = \Sigma + P$ and $P = \text{Tr}(\mathbf{P}_{\text{ext}})/3$.

In practice, for systems at temperatures far below the melting temperature, the change in enthalpy is a good measure of the change in free energy for a solid phase transition since the change in entropy is relatively low. Therefore, in many cases, the free energy *G* is replaced by enthalpy *H* in Eqs. (5)–(10). The MetaD simulation of a RPT will progress in metasteps. In each metastep, the system is equilibrated in a relatively short MD simulation, from which the **p** and *H* are obtained by ensemble average. The driving force \mathbf{F}^t is calculated using Eqs. (9) and (10), which are then used to update the simulation box using Eq. (8).

In the present study, the MD simulations and structure optimizations are carried out using our MLP package interfaced with the atomic simulation environment package (ASE) [50]. Each metastep consists of a MLP-driven MD simulation employing a canonical ensemble (*NVT*) using a Berendsen thermostat with 1000 time steps for a total simulation time of 1.0 ps. The Hessian matrix is constructed from the finite differences of the stress tensors at deviated simulation box. This breaks down to 13 fixed cell optimizations which include 12 distorted boxes (6 +/- symmetrically distorted **h**) and one undistorted box **h**₀. The limited-memory BFGS algorithm is used as an optimizer in fixed cell optimizations in which the atomic positions are relaxed until the maximum force on the atom is reduced to below 0.01 eV/Å.

III. RESULTS AND DISCUSSION

A. Constructing machine learning potential

Since the objective is to simulate a reconstructive phase transition, we need to construct the PES taking into account the structures before and after the phase transition (local minima), as well as the distorted/randomized structures describing the regions between energy minima. Sampling the PES is a highly nontrivial task [29,30]; to do it efficiently we designed five data sets that represent different regions of the PES. Each data set includes three element groups, i.e., total energies, interatomic forces, and stress tensors of the cell, which were constructed by DFT calculation using the Vienna *ab initio* simulation Package (VASP) [51]; see the Supplemental Material [38] for details.

The first data set consists of 2000 randomized structures generated using the home-made CALYPSO package [52–55]. These structures were generated randomly from all space groups which are meant to coarsely sample the PES. The number of Ga or N atoms in the unit cell was set in [10, 20] range, and the atomic volume in [8.0, 12.0] Å³. Total energies, interatomic forces, and stress tensors for these structures were obtained using self-consistent-field (SCF) calculation. The data were then used as the initial training set, from which a coarse MLP was trained. The energy and volume distributions for the first data set are presented in Fig. 1(a) (black hexagonal dots). As one can see, this set of structures has a very diverse distribution in the high-energy region of the PES. The second data set consists of the B4 and B1 structures optimized at different volumes using VASP, which are meant to precisely describe the energy minima on the



FIG. 1. Summary of the training data set and test calculations for the MLP. (a) Left: Distribution of energies and volumes for all structures in the training sets calculated using VASP. Structures in five data sets are distinguished by different colors and shapes. Right: energy distribution of randomized (data set 1) and coarse-MLP-relaxed structures (data set 3). (b) Calculated enthalpies for the *B*4 and *B*1 phases in the pressure range 0–80 GPa using MLP (points) and VASP (lines). The enthalpies of the *B*4 phase calculated by VASP (red line) are taken as the zero-energy reference. (c) The RDFs of N-N, Ga-N, and Ga-Ga obtained from the *NVT* simulation of *B*4 phase at 50 GPa and 300 K using VASP and MLP respectively.

PES. The energy distribution of this data set is situated at the low-energy region of the PES [blue diamond dots in Fig. 1(a)], separated from the first data set by an energy gap of more than 1.0 eV/atom. To sample the region within the gap, the third data set was generated with 1000 randomized structures and subsequently relaxed using the coarse MLP for 60 conjugate-gradient (CG) steps at randomly chosen pressures between 0 and 100 GPa. After relaxation, the energies, forces, and stress tensors were obtained using the SCF which covers the relatively low energy region of PES [red circular dots in Fig. 1(a)]. Here we emphasize that the number of CG steps should be set carefully since the coarse MLP is not sufficient for fine calculations and therefore too many CG steps will lead to unreasonable configurations. The fourth data set was constructed by instantaneous structures evenly sampled from MD trajectories obtained on B4 and B1 structures with a 64-atom simulation cell at 50 GPa and 300 K in the isothermic isobaric (NPT) ensemble using VASP [green up triangular dots in Fig. 1(a)]. These structures are included in the training data set to describe the dynamic part of the PES and account for the anharmonic effects. Finally, the fifth data set contains 24 distorted structures (64 atoms/cell) of B4 and B1 phases at 50 GPa [dark green down triangular dots in Fig. 1(a)]. These structures describe the two energy wells and ensure that the elastic moduli and Hessian matrix are reproduced precisely. The numbers of structures chosen from the five data sets for

the training set are given in Table S2 [38]. A total 3682 structures cover a broad range of energies and volumes [Fig. 1(a)]. Learning from a diverse variety of relevant structures is a key to successful training of the MLP, in particular, for potentials to have a high degree of predictive power. The weights on the energies, forces, and stresses of the five training data sets in Gaussian process regression are provided in Table S3 in the Supplemental Material [38].

The performance of the trained MLP was tested in total energy and force calculation, structural optimization, and MD simulation (the errors and computational costs of the MLP compared with DFT have been illustrated in Table S3 and Figs. S1 and S2 in the Supplemental Material [38]). Figure 1(b) shows the enthalpies of B4 and B1 structures calculated at different pressures using MLP and VASP. The excellent agreement in the evolution of enthalpy and critical transition pressure at about 45 GPa reveals a high accuracy of the MLP. We note here that since we target simulations at room temperature (far below the melting point), enthalpy should be a good measure of the change in free energy for a solid phase transition since the change in entropy is expected to be low. To examine the reliability of the trained MLP in dynamic processes, we carried out separate MD simulations using MLP and VASP, and compared the statistics through the radial distribution function (RDF) gathered from thermal trajectory. The B4 structure is used for MD simulation at

TABLE I. Bulk modulus (B), shear modulus (G), Young's modulus (Ym) and Poisson ratios (Pr) of *B*4 and *B*1 phases under 50 GPa obtained from MLP and VASP.

		B (GPa)	G (GPa)	Ym (GPa)	Pr
<i>B</i> 4	MLP	364	86	238	0.39
	VASP	379	89	247	0.39
<i>B</i> 1	MLP	373	214	539	0.26
	VASP	365	208	525	0.26

300 K and 50 GPa, with a $16 \times 8 \times 4$ simulation cell for MLP (4096 atoms) and a $4 \times 2 \times 2$ simulation cell for VASP (128 atoms). The RDFs obtained in the two simulations [Fig. 1(c)] reveal that the MLP is very accurate in reproducing the MD statistics, in that both the position and shape of RDF peaks are reproduced. To test the ability of the MLP in reproducing the elastic properties, we calculated the bulk (*B*), shear (*G*), and Young's (Ym) moduli and estimated the Poisson ratio (Pr) using Voigt-Reuss-Hill (VRH) approximation [56], i.e., Pr = [(3B - 2G)/2(3B + G)], for *B*4 and *B*1 structures at 50 GPa (Table I). The MLP shows a very good accuracy reproducing the elastic moduli with the largest deviation less than 4% from the VASP values.

To further assess the performance of the current MLP for more strange configurations, we further performed NVE MD simulations using VASP and MLP at ~4500 K and ~60 GPa where GaN is melted. Configurations sampled from the trajectory of VASP MD are used as testing data set. The results for RDFs, energies, forces, and stresses are shown in Table S3 and Fig. S1 in the Supplemental Material [38]. It is seen that the RDFs obtained from the two simulations agree well with each other, and the errors of MLP compared with VASP for the liquid configurations is also moderate.

B. MetaD simulations of B4-B1 transition in GaN

In this section, we use a classical example of RPT, the *B*4-*B*1 transition in GaN, to demonstrate the MLP enhanced large-scale MetaD simulation. With this method, we are able to elucidate the details of atom rearrangements during the transition. We start this section by explaining the significance of this phase transition and questions to address.

GaN is a wide band-gap semiconductor with a fourcoordinated wurtzite structure (B4, space group $P6_3mc$). Under pressure, the wurtzite structure transforms to a sixcoordinated rocksalt structure (B1, space group Fm-3m) with a large hysteresis (37–54 GPa). The B4-B1 transition is rather common in nitrides, such as GaN, AlN, and InN, etc., but the mechanism is yet to be elucidated. Since the B4 and B1 structures do not comply to the group-subgroup relation, there are multiple possible reconstructive paths, each represented by a common subgroup. This transition has three variables: (1) the relative spacing *u* between Ga and N sublattices changes from 0.38 to 0.5; (2) the angle γ extended by the cell basal axes decreases from 120° to 90° ; and (3) the *c/a* ratio reduces from 1.633 to 1.414. Different paths are envisioned upon switching the orders of the transition steps, among which the two major ones are "tetragonal path (iT)" [57] and "hexag-



FIG. 2. The "tetragonal" and "hexagonal" transition paths. Both paths consist of two steps, closure of angle γ and increase of the relative spacing *u*, but have opposite sequences. The Ga and N atoms are represented by green (larger) and blue (smaller) balls, respectively.

onal path (*iH*)" [58] (Fig. 2). In the *iT* path, the angle γ changes first bypassing a five-coordinated tetragonal intermediate (space group I4mm), and then u increases along with the change of c/a ratio. The *iH* path has reversed orders where uchanges before the closure of the angle γ , bypassing a fivecoordinated hexagonal intermediate (space group $P6_3/mmc$). In finding the true transition path, many methods have been used including static modeling [59], classical and *ab initio* MD [60,61], transition path sampling [62], and DFT-MetaD [63]. While the results obtained from different methods do not have fundamental discrepancy, the limitations such as a small simulation box in DFT or inadequate description of the PES by classical potentials, confine the simulations to restricted models. Consequently, we choose to simulate this phase transition using a large-scale simulation box (4096 atoms) at an accuracy comparable to DFT to examine the MLP-MetaD method and reveal in-depth details.

1. Small-scale benchmark simulations

Before the large-scale simulation, a benchmark test was performed using a 64-atom simulation box. This box has a tetragonal dimension with $h_{11} = 6.03$ Å, $h_{22} = 10.44$ Å, and $h_{33} = 9.85$ Å. The B4 structure is situated in a tetragonal setting in the simulation box, i.e., h_{22} would follow the hexagon edge, h_{11} is perpendicular to it, and h_{33} is normal the hexagonal plane. In this simulation, the Gaussian parameters were set as $\delta s = 50$ (kbar Å³)^{1/2} and W = 2500 kbar Å³, respectively, which are found suitable for simulation at room temperature. The hydrostatic pressure P was set to 50 GPa and for the nonhydrostatic case, the anisotropic component was loaded along the [001] direction with the magnitude set as 10% of the *P*, i.e., $\Sigma_{33} = -2\Sigma_{11} = -2\Sigma_{22} = 6.67\% P$, and zero for all off-diagonal elements. The eigenvalues and corresponding eigenvectors of the Hessian matrix of the B4 phase calculated by MLP and VASP at 50 GPa are shown in Table S4 [38].



FIG. 3. Evolution of the enthalpy in 64-atom MetaD simulation using MLP under isotropic and uniaxial pressures starting from the *B*4 structure at 300 K and 50 GPa.

The two methods yield the same set of eigenvectors and very similar eigenvalues. This reveals that the MLP can reproduce the energy well as accurately as the DFT calculation. Note that for most eigenvectors the MLP and VASP values have opposite signs; this means that the energy well is depicted from opposite sides by the two methods, which should not affect the simulation since the energy well is symmetric by construction.

Figure 3 shows the time evolution of the enthalpy during the 64-atom MetaD simulation using MLP under isotropic and uniaxial pressures at 300 K and 50 GPa. Under both stress conditions, the phase transition from B4 to B1 is recovered, identified by an abrupt, large drop of enthalpy. Notably, the phase transition under uniaxial compression appears quicker (at step 76) but it is associated with a higher barrier (\sim 0.18 eV/atom). In hydrostatic compression, the phase transition occurs at step 229 and the energy barrier is about 0.14 eV/atom. The slow increase of the enthalpy before the phase transition shows the gradual filling of the free energy well with Gaussian potentials. In either case, the energy barrier is far beyond the reach of an atom's kinetic energy $(\sim 0.03 \text{ eV/atom at } 300 \text{ K})$, which manifests the capability of the MetaD method. Once the initial energy well is filled, the configuration is pushed into a neighboring minimum that causes a sudden drop of energy. The simulated transition path is found to be dependent on the stress conditions. In the hydrostatic case, the transition undergoes the tetragonal path [Fig. S3(a) [38]]. At step 229, the angle γ has changed to 90° while the spacing u has increased slightly to 0.41, which converts the six rings to four rings on the $h_{11}h_{22}$ (001) layers and yields a tetragonal intermediate. Afterward, the u has a quick increase to 0.5 and completes the transition at step 233. In contrast, under uniaxial compression, u increases to 0.46 at step 76 while the $h_{11}h_{22}$ (001) layer maintains its six-ring configurations, resulting in a hexagonal intermediate [Fig. S3(b) [38]]. From step 76 to step 82, the angle γ closes and convert the six rings to four rings. We emphasize that because of the thermal fluctuations, the system does not pass exactly through the saddle point, or transition state, but will cross the

TABLE II. Eigenvalues (in unit of kbar Å) and corresponding eigenvectors of the Hessian matrix for *B*4 phase consisting of 4,096 atoms at P = 50 GPa calculated using MLP.

Eigenvalues										
	<i>s</i> ₁	<i>s</i> ₂	<i>s</i> ₃	s_4	<i>s</i> ₅	<i>s</i> ₆				
	72,981	73,212	18,662	30,712	94,405	641,778				
Eigenvectors										
h_{11}	0.0	0.0	0.0	0.796	0.563	-0.225				
h_{22}	0.0	0.0	0.0	-0.606	0.751	-0.263				
h_{33}	0.0	0.0	0.0	-0.021	-0.346	-0.938				
h_{12}	0.0	0.0	1.0	0.0	0.0	0.0				
h_{13}	0.0	1.0	0.0	0.0	0.0	0.0				
h_{23}	-1.0	0.0	0.0	0.0	0.0	0.0				

free energy barrier somewhere nearby. This explains why the simulated transition path always has a small degree of mixing. Overall, the transition paths and their stress dependence obtained here using MLP are in very good agreement with the previous simulation carried out using DFT with the same-size simulation box, in which the tetragonal path is activated under isotropic compression but the hexagonal path is achieved under the uniaxial stress conditions [63]. At this point, the MLP combined with MetaD is proven to be a reliable method for simulating RPT.

2. Large-scale simulations with 4096 atoms

After establishing the method, we expand the simulation to a 4096-atom box. Apart from testing the scalability of the MLP method, we wish to reveal microscopic events that are critical to RPT but are not accessible in a small simulation box, such as the homogeneous process of the formation of the new phase. The 4096-atom simulation box is constructed from an $8 \times 4 \times 2$ expansion of the 64-atom simulation box (Fig. S4 [38]). This box has a tetragonal dimension with $h_{11} = 48.27$ Å, $h_{22} = 41.78$ Å, and $h_{33} = 19.70$ Å. The calculated eigenvalues and corresponding eigenvectors of the Hessian matrix for the 4096 atom simulation box are shown in Table II. The geometry of the initial energy well is characterized by collective variables s. s_1 and s_2 describe the shearing of two tetragonal planes, one extended by h_{22} and h_{33} and the other extended by h_{11} and h_{33} (Fig. S4 [38]), with similar eigenvalues (72,981 and 73,212 kbar Å). s₃ describes the shearing of the hexagonal plane extended by h_{11} and h_{22} . This mode is much softer compared to s_1 and s_2 , shown by a smaller eigenvalue 18,662 kbar Å. s₄ describes a rectangular distortion by simultaneous elongation of h_{11} and shortening of h_{22} . s_5 describes a simultaneous increment of h_{11} and h_{22} , and shortening of h_{33} . s_6 describes a simultaneous reduction of h_{11} , h_{22} , and h_{33} . For an efficient simulation in this model, Gaussian parameters were scaled up to $\delta s = 500 \, (\text{kbar } \text{\AA}^3)^{1/2}$ and W = 250,000 kbar Å³, respectively.

Figure 4 shows the snapshots of the 4096-atom simulation box selected at different times from the MetaD trajectory under hydrostatic compression at 50 GPa (figures are generated using OVITO [64]). A phase transition is clearly revealed by the change of atoms' coordination numbers. The evolution of the CVs shows that this transition



FIG. 4. Snapshots of the 4096-atom simulation box of the *B*4 phase in MetaD simulation using MLP at 50 GPa under hydrostatic conditions. In (a)–(f), Ga and N atoms are not distinguished but colored by coordination numbers (CN) determined by a cutoff radius 2.3 Å. Blue, grey, and red represents atoms with CN = 4, 5, and 6, respectively. For clarity, a nucleation center is enlarged from the snapshot at metastep 33. In (g), only Ga atoms are shown and colored by their atomic energy obtained from MLP and the lowest atomic energy is taken as the reference. The shearing caused by soft s_3 mode and the direction of atomic realignment along the face diagonal are highlighted. Figures are generated using OVITO [64].

follows the *iT* path, activated by modes s_3 and s_6 [Fig. S5(a) [38]]. s_3 becomes negative and decreases dramatically from metastep 29 to metastep 39 (29-39 ps), causing the $h_{11}h_{22}$ (001) plane to shear [Figs. 4(b)-4(f)]. During the same time, s_6 becomes positive and increases dramatically, resulting in the reduction of h_{33} and a sudden drop of the volume, which is the manifesto of a first-order phase transition. A significant finding is the formation and growth of centers for the tetragonal intermediate phase (grey atoms) in the B4 matrix [Figs. 4(b)-4(d)]. Once the intermediate phase is fully established, new centers of the B1 phase (red atoms) start to form randomly and quickly grow throughout the crystal [Figs. 4(e) and 4(f)]. In this step, the major change is in the spacing *u*, which does not change the geometry of the $h_{11}h_{22}$ (001) plane but brings neighboring planes together and increases the coordination number to 6.

The simulation above reveals details on the manner of atom rearrangements during the phase transition, from which some points can be made. The B4 and tetragonal intermediate phases are shown as six rings and four rings on the $h_{11}h_{22}$ (001) plane, respectively. Under thermal fluctuation, four rings (nucleation centers) may form randomly on the plane, but most of them will go back to six rings under the large strain induced by the phase mismatch. From a metastep around 30, the s_3 shearing mode is activated, which obviously cause the angle γ to change promoting the formation of nucleation centers. As the shearing progresses, more and more adjacent six rings are converted to four rings around nucleation centers. However, this growth is not random, but follows a direction with the lowest interfacial energy. Because of the anisotropy of crystalline phases, the interfacial energy at a solid-solid phase boundary can vary from low values for fully coherent interfaces to high values for incoherent interfaces. For the said transition, the soft s3 mode causes the atoms to realign along the face diagonal direction, which results in

a fully coherent two phase interface without any dislocation [Fig. 4(g)]. As such, the atoms at the phase boundary have low energies that facilitate continuous growth. Along the vertical h_{33} [001] direction, the neighboring planes have essentially the same geometry so that the whole crystal is viewed as a two-phase inhomogeneous mixture propagating along the h_{33} [001] direction. Once the regions occupied by four rings reach the critical value, they will no longer convert back to six rings but will continue to grow throughout the crystal. To verify this process, we performed another simulation using the same simulation box but with additional shear stress added along the s_3 direction. The magnitude of additional stress is about 2 GPa, i.e., $\Sigma_{21} = 4\% P$, which is designed to aggravate the s3 mode and bias the structure toward its shallow energy valley. The MetaD trajectory for this simulation is shown in Fig. S7 [38]. As expected, the transition path is essentially unchanged under additional shear but the transition speed is notably higher-the whole transition completes in 29 ps. Clearly, the formation of centers for tetragonal intermediate phase is resonant to the enforced shearing, and the growth pattern is better structured and aligned. The two phases form alternating 2D slabs according to the shearing [Fig. S7(d) [38]]. This observation confirms that the s_3 shearing mode activates the *iT* transition path and progresses through the nucleation and growth.

Next we carry out a large-scale simulation under the uniaxial stress condition at P = 50 GPa to examine the effects of uniaxial stress on the transition path. Additional uniaxial stress of 5 GPa was loaded on the h_{33} [001] direction, i.e., $\Sigma_{33} = -2\Sigma_{11} = -2\Sigma_{22} = 6.67\% P$. The snapshots of the MetaD trajectory selected at different times for this simulation is shown in Fig. 5. This time the transition path is changed to the *iH* path via five-coordinated hexagonal intermediate ($P6_3/mmc$). The evolution of CVs shows that the uniaxial stress blocks the s_3 mode but activates the s_5 mode,



FIG. 5. Snapshots of the 4096-atom simulation box of the *B*4 phase in MetaD simulation using MLP at 50 GPa under uniaxial stress conditions. Additional uniaxial stress of 5 GPa is loaded in h_{33} [001] direction. Ga and N atoms are not distinguished but colored by coordination numbers (CN) determined by a cutoff radius 2.3 Å. Blue, grey, and red represents atoms with CN = 4, 5, and 6, respectively.

which, along with the s_6 mode, drives the phase transition [Fig. S5(b)]. The s₅ becomes positive and increases dramatically from metastep 6 to metastep 13 (6-13 ps). This causes the $h_{11}h_{22}$ (001) plane to expand with slight rectangular distortion (due to a faster increase of h_{22} than h_{11}) and the distance between neighboring planes to decrease. Under this distortion, the six rings on the $h_{11}h_{22}$ (001) plane maintain a basic hexagonal shape but the spacing u increases and the c/a ratio reduces which altogether brings neighboring planes close and increases the CN to 5 [Fig. 5(b)]. Clearly, the initial change of u and c/a results from a greater pressure load on the h_{33} axis, which pushes the configuration toward hexagonal intermediate. Afterward, the six rings located on the $h_{11}h_{22}$ (001) plane convert to four rings [Figs. 5(c)-5(e)] similar to the first transition stage under hydrostatic stress. During the transition, the s₆ becomes positive and increases rapidly, resulting in a large volume drop which significates a first-order phase transition.

These simulations demonstrate the capability of the MLPbased MetaD method in simulating RPT at a large scale not possible for DFT-based methods but at an accuracy close to that of DFT. The simulated B4-B1 phase transition in GaN reveals the manner of atom rearrangements with unprecedented quality and details, which provides insight into this well-known phase transition. In particular, the microscopic transition path may be manipulated using shear and uniaxial stress to reach different intermediate phases, which helps us to reconcile the experimental and theoretical uncertainty regarding the transition path for the *B*4-*B*1 transition [57,65,66]. The unique combination of machine learning potential and metadynamics method will certainly lead to significant improvement of the simulation of phase transitions. The method can be easily expanded and transferred to other systems with well-constructed potentials.

IV. CONCLUSION

In this study, we demonstrate that well-trained machine learning potentials combined with metadynamics method can provide a highly accurate survey of potential energy surface required for large-scale atomistic simulation of reconstructive phase transitions. The machine learning potential is constructed by learning directly from the data consisting of energies, interatomic forces, and unit cell stresses experienced by structures in a well-designed structures set, as obtained by density functional calculations. The potential is fitted in terms of individual atoms in given neighboring environments and therefore is capable of expanding to an arbitrary system size and to complex potential energy surface. As a test case, we apply the method to simulate the pressure induced B4-B1 phase transition in gallium nitride using a 4096 atom simulation box under general stress conditions including hydrostatic, uniaxial, and shear stress. The simulation reveals the transition path with excellent quality. Microscopic events that are critical to reconstructive phase transition but not possible with small-scale DFT simulation, and their responses to changing stress conditions, are clearly reproduced in our simulation. This provides a different dimension for the understanding of reconstructive phase transition. It should point out that the manner of atom rearrangements revealed by the current approach should not be the exact mechanism of real-world RPT but offer an important insight for understanding it.

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