High-pressure phase behaviors of titanium dioxide revealed by a \(\Delta\)-learning potential

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Titanium dioxide has been extensively studied in the rutile or anatase phases, while its high-pressure phases are less well understood, despite that many are thought to have interesting optical, mechanical and electrochemical properties. First-principles methods such as density functional theory (DFT) are often used to compute the enthalpies of TiO\(_2\) phases at 0 K, but they are expensive and thus impractical for long time-scale and large system-size simulations at finite temperatures. On the other hand, cheap empirical potentials fail to capture the relative stabilities of the various polymorphs. To model the thermodynamic behaviors of ambient and high-pressure phases of TiO\(_2\), we design an empirical model as a baseline, and then train a machine learning potential based on the difference between the DFT data and the empirical model. This so-called \(\Delta\)-learning potential contains long-range electrostatic interactions, and predicts the 0 K enthalpies of stable TiO\(_2\) phases that are in good agreement with DFT. We construct a pressure-temperature phase diagram of TiO\(_2\) in the range 0 < \(P\) < 70 GPa and 100 < \(T\) < 1500 K. We then simulate dynamic phase transition processes, by compressing anatase at different temperatures. At 300 K, we observe predominantly anatase-to-baddeleyite transformation at about 20 GPa, via a martensitic two-step mechanism with highly ordered and collective atomic motion. At 2000 K, anatase can transform into cotunnite around 45-55 GPa in a thermally-activated and probabilistic manner, accompanied by diffusive movement of oxygen atoms. The pressures computed for these transitions show good agreement with experiments. Our results shed light on how to synthesize and stabilize high-pressure TiO\(_2\) phases, and our method is generally applicable to other functional materials with multiple polymorphs.

I. INTRODUCTION

Titanium dioxide is widely used in a range of industries as a white pigment, and in biomedical applications such as drug delivery\(^{11}\). As an intrinsic n-type semiconductor, it also has uses in solar cells\(^{2,3}\), photocatalysis\(^{4}\), and splitting water molecules for hydrogen production\(^{5,6}\). At ambient pressure, titanium dioxide has three common metastable crystalline polymorphs: anatase, rutile, and brookite, of which anatase and rutile are of most interest to industry. There are also a large number of high-pressure metastable structures in the range 0-100 GPa, including TiO\(_2\)(B), hollandite, OI, fluorite, Pca\(_2^2\), ramsdellite, columbite (TiO\(_2\)(II)) and cotunnite\(^{6,8}\). Many of these phases have interesting properties such as high optical absorbance\(^{9}\) and high hardness\(^{10}\). Crucially, many of these high-pressure structures remain stable at ambient pressures due to large kinetic barriers, hence it is useful to be able to understand the metastability of these phases and how they may be synthesised.

Although many applications of ambient-pressure TiO\(_2\) phases have been well-studied, the high-pressure phase behaviors are less understood. Anatase, rutile, and brookite have been known since they can be found in mineral deposits. Experimental work has shown the anatase-to-rutile and brookite-to-rutile transitions to be irreversible, suggesting rutile is the stable phase at low pressures\(^{11,13}\). The first high-pressure phase to be discovered was columbite\(^{14}\), which was made by compressing anatase and brookite using a diamond anvil and using x-ray powder diffraction to identify the structure. Further experimental work using similar methods\(^{15,16}\) demonstrated there is a series of high pressure polymorphs, and the pressures and temperatures at which transitions between these polymorphs occur have been determined\(^{17}\). More recent work has also suggested that phase transitions between polymorphs can be induced by shockwave\(^{18}\) and lasers\(^{19}\). Nevertheless, the kinetic barriers of solid-solid transitions make precise experimental determination of the phase boundaries difficult. Moreover, very little is known about the mechanisms of these transitions, for example whether they are diffusive or martensitic.

A number of theoretical studies have used density functional theory (DFT) to determine the relative stability of the phases. DFT generally shows very good agreement with experiment, except for the well-known problem that the enthalpy of rutile is significantly over-estimated, often suggesting anatase is the stable phase at 0 GPa\(^{20}\), which is in disagreement with the experimental data cited above. It is thought that this discrepancy may be due to unphysical delocalisation of titanium’s 3d electrons\(^{21}\), but it is not well-understood. Nevertheless, DFT, in particular using the PBEsol function, remains a useful tool for studying the high-pressure behaviour\(^{22,23}\). It is also possible to overcome the incorrect ordering of phases using semi-empirical methods, such as DFT+U\(^{24}\) and DFT+D\(^{25}\). Alternatively, Quantum Monte Carlo (QMC) methods includ-
low pressure is subject to debate that the accuracy of (semi-)local DFT functionals for TiO$_2$ shows better agreement with experimental lattice constants than the PBE and LDA functionals. It is worth mentioning that the accuracy of (semi-)local DFT functionals for TiO$_2$ at low pressure is subject to debate since for example rutile is not predicted to be a stable phase, although DMC shows good agreement in the ranking of static-lattice energies of phases with a number of DFT functionals. In addition, three functionals, LDA, PBE and PBEsol, all give consistent results regarding the ranking of stabilities for the known polymorphs of TiO$_2$. We employed the CASTEP ab initio simulation package, and full details of the DFT set-ups and configurations can be found in the input files supplied in the Supplementary Information. The 0 K enthalpies computed as above are shown in Fig. 1. The DFT data suggests that anatase should be the lowest enthalpy phase at very low temperature, followed by baddeleyite at 10 - 20 GPa, followed by cotunnite for $\geq 30$ GPa. Columbite is also competitive around 10 GPa, and Olphase and Pca2$_1$ are competitive around 30 GPa. Experimentally, it is well known that the stable phases under increasing compression follow the order rutile $\rightarrow$ columbite $\rightarrow$ baddeleyite $\rightarrow$ Ol $\rightarrow$ cotunnite, which is true for HfO$_2$ and ZrO$_2$ as well as TiO$_2$. Kinetic barriers make precise experimental determination of the phase diagram very challenging, however it is generally found that bulk anatase transforms to columbite at approximately 5 GPa. In polycrystalline anatase, columbite is not formed, but baddeleyite is instead formed at 13 GPa. On starting from bulk rutile, a transformation to columbite is sometimes seen at 7-10 GPa, followed by a transformation to baddeleyite at 15 GPa, however, it is more common to see a transformation directly from rutile to baddeleyite near 12 GPa. Baddeleyite transforms to cotunnite at approximately 60 GPa at 1700 K. Hence, we may consider DFT data as being a good predictor for the purpose of determining the phase diagram, with the exception of the rutile phase as discussed above.

### B. Parameterising an empirical potential

One of the most widely used empirical potentials for modelling titanium dioxide is the Matsui-Akaogi (MA) potential. This includes both a Buckingham potential and the usual Coulomb repulsion, where $q_1$ and $q_2$ are the effective charges of Ti and O:

$$V = A e^{-r/\rho} - \frac{C}{r^6} + \frac{q_1 q_2}{4\pi \varepsilon_0 r},$$

where $A$, $C$, and $\rho$ are empirical parameters. However, when comparing the relative enthalpy of the metastable polymorphs computed by the MA potential with that computed by DFT, the performance of the MA potential is poor, as seen in Fig. 1. In particular, from 15-65 GPa the MA potential predicts that pyrite is the stable phase, yet according to DFT pyrite has a significantly higher enthalpy than the stable phases, baddeleyite and cotunnite. Despite this, it remains one of the most widely used potentials for the large time-scale and length-scale molecular dynamics simulations required to study nanoparticle, surface physics, crack propagation, and other complex phenomena.

Here we adopt the functional form of the MA potential in Eqn. (1), and fitted the parameters $q_1$, $q_2$, $A$ and $C$. The fit was performed by minimizing the difference in the relative energies of 893 liquid TiO$_2$ configurations of 144 atoms compared to the PBEsol reference. These liquid configurations were generated by molecular dynamics (MD) simulations employing the MA potential at $0 - 100$ GPa. We call this new empirical potential for TiO$_2$ the reMA potential, and the parameters are provided in the Supplementary Information, as a LAMMPS input file.
FIG. 1. Enthalpies of known TiO$_2$ polymorphs at 0 K computed using (a) the MA potential, (b) the Δ-learning MLP, and (c) PBEsol DFT. Note that for the MA potential the oxygen-displaced fluorite (Pca2$_1$) structure is not (meta)stable, and the ramsdellite and OI phases are somewhat different from the experimentally reported structures.

C. Training the MLP

The MLP is constructed using the framework originally proposed by Behler and Parinello as implemented in RuNNer. 90 symmetry functions are used, each modulated by a hyperbolic tangent cutoff function at up to 16r$_{\text{Bohr}}$. The neural network consists of two hidden layers with 20 and 10 nodes respectively, and each with a hyperbolic tangent activation function.

The training set consists of 7,336 structures, each having either 135 or 144 atoms. Amongst these, 3,483 liquid structures were generated by running molecular dynamics simulations using both the MA and reMA potentials and selecting structures from the trajectory separated by a time interval that larger than the decorrelation time, and 3,853 solid structures were constructed by adding random displacements of atoms to the structures of known phases at different pressures. The set includes a wide variety of geometries from cubic to triclinic at densities from 0.15 f.u./Å$^3$ to 0.6 f.u./Å$^3$, which is adequate to cover the range of pressures and temperatures we investigate. A projection of the training set using principal component analysis is shown in Fig 2.

In the MLP, the atomic environments are described by a set of symmetry functions (SFs). Initially a large, comprehensive set of SFs are generated with a maximum cutoff radius of 16r$_{\text{Bohr}}$. The SFs that make the most important contributions to modelling the interactions (without unnecessarily increasing computational cost) are selected using a decomposition algorithm similar to the CUR decomposition. In addition to the CUR, the method is also biased to select an SF if it is strongly correlated with the magnitude of the forces in the dataset. We attempted training with 90, 117, and 150 unique SFs and found that using 90 SFs resulted in the best precision, due to overfitting when using greater numbers of SFs.

After training for 30 epochs using the Kalman Filter to update the 2,282 weights, we obtain the test and training errors which are summarised and compared with characteristic values for the training set in Table I. The 30th epoch was chosen for subsequent calculations as it had the minimum RMS force error.

It should be stressed that the purpose of the MLP we have trained is to provide a small correction to the behavior of the empirical reMA potential, and their effects must be superposed to produce accurate behavior. Due to the reMA baseline, even for the regions not covered by the training set, the combined empirical potential and MLP will behave reasonably and remain stable.
TABLE I. Test and training RMSEs are compared with the standard deviations (SD) of the PBEsol training set before and after subtracting the contribution from the reMA potential (PBEsol-reMA).

|                         | Energy / eV at$^{-1}$ | Forces / eV Å$^{-2}$ |
|-------------------------|-----------------------|----------------------|
| RMS Test Error          | 0.0110                | 0.725                |
| RMS Training Error      | 0.0099                | 0.713                |
| PBEsol Set SD           | 0.38                  | 3.14                 |
| PBEsol-reMA Set SD      | 0.23                  | 1.21                 |

D. Enthalpies of TiO$_2$ predicted by the $\Delta$-learning potential

We benchmark the accuracy of the $\Delta$-learning potential by comparing the enthalpy as a function of pressure at 0 K with that expected from DFT and that predicted by the MA potential (see Fig. 1). Although the relative stabilities of several metastable phases noticeably differ from the DFT reference, the $\Delta$-learning potential is able to correctly predict the relative enthalpies of the stable phases. For instance, anatase is the stable phase at pressures up to 1 GPa, where baddeleyite becomes the stable phase until the compression reaches approximately 18 GPa, whereupon both it and OI are competitive. Above 26 GPa cotunnite remains the stable phase. The enthalpy curves predicted by the $\Delta$-learning potential are considerably more similar to the DFT predictions than the predictions of the MA potential, which predicts pyrite to be the stable phase over most of the pressure range, when in fact it is approximately 500 meV/f.u. higher in enthalpy than the stable phase. Therefore, in what follows we will use the $\Delta$-learning potential to study the phase behaviors of the stable phases, as well as the transition processes between them.

E. MD simulations using the $\Delta$-learning potential

MD simulations using the $\Delta$-learning potential were carried out using LAMMPS [53] patched with N2P2 [54]. The hybrid/overlay potential style in LAMMPS was used to combine the reMA component and the MLP correction. The simulations were performed using a 1 fs timestep, with Nose-Hoover barostatting and canonical sampling thermostatting. The simulation cell is allowed to relax such that all of the cell lengths and angles can vary independently. Full details of all MD simulations and geometry-optimisations are given in the Appendix.

III. PHASE DIAGRAM

The metastability of the TiO$_2$ phases at non-zero temperatures is determined by their relative chemical potentials, instead of the enthalpies at 0 K. We thus computed the Gibbs free energies via the thermodynamic integration method - the method is briefly outlined in the Appendix and discussed in detail in Ref. [55]. The free energy is computed at intervals of 100 K and 10 GPa, then interpolated to determine the phase boundaries illustrated in Fig. 3.

IV. SOLID-SOLID PHASE TRANSITIONS

In practice, high pressure phases such as cotunnite are usually made by compression of anatase or rutile using a diamond anvil and heating the sample either electrically or by laser, then decompressing back to ambient pressure and quenching [55]. However, different experiments have predicted different phases will be formed.

Furthermore, it has not previously been possible to elucidate the transition mechanisms either experimentally - due to the difficulty of making in-situ measurements of very short-timescale processes - or theoretically, due to the computa-
tional cost of \textit{ab initio} methods and the poor accuracy of empirical potentials. The $\Delta$-learning potential that we have developed is capable of correctly ordering the metastability of some of the phases, while being computationally cheap enough to be able to perform long timescale MD simulations.

We demonstrate this by compressing anatase from 0 to 70 GPa over a period of 1 ns. A timestep of 1 fs is used and the thermostat and barostat routines are the same as above. Both the lengths and angles of the simulation cell are allowed to vary independently. The simulation is repeated using three different system sizes, 128, 432, or 1024 TiO$_2$ formula units (f.u.), as well as 12 different random seeds for each size. We performed independent simulations at 300 K, 500 K, 800 K, 1000 K, 1500 K, and 2000 K. The enthalpy and volume evolution of the systems during the compression at 300 K and 2000 K is given in Fig. 4 and the rest of the results are in the Appendix. For comparison, the results from the compression simulations of baddeleyite and cotunnite are also included. In order to better distinguish between the different phases, both enthalpy and volume are plotted as moving averages over 100 timesteps and the enthalpies are given relative to a linear fit of the enthalpy of cotunnite.

At 300 K using the small system size of 128 f.u. (the 12 sets of blue curves in Fig. 4b), most (9 out of 12) simulations exhibited a two-step transition, with the first transition at about 20 GPa and the second one at about 40 GPa, and amongst them 8 simulations reached the baddeleyite phase. With the system size of 432 f.u. (the light blue curves in Fig. 4b), 7 out of 12 show the same two-step transition, and 6 became baddeleyite. With the 1024 f.u. simulation cell, 4 runs have the same transition, and all ended up as baddeleyite. As such, the transition process is quite consistent at the three different system sizes.

To understand the two-step transition mechanism better, we plot the displacement vectors of all the atoms in the small system along with the snapshots before and after the two transitions in Fig. 5. The displacement vectors show the atomic movement $\mathbf{q}(t) - \mathbf{q}(t_0)$, where $\mathbf{q}(t_0)$ and $\mathbf{q}(t)$ are the coordinates just before and after the transition. Fig. 5 shows that, in both steps, all the atoms follow a highly ordered and collective motion, and the most prominent feature is the sliding of two of the $\{010\}$ planes over each other. Such transitions are analogous to the diffusionless Martensitic transition.

At 300 K and with all three different system sizes, a one-step transition mechanism was sometimes observed, during which the sharp change happens at about 20 GPa, and the final structure has a density between that of baddeleyite and cotunnite, and an enthalpy that is higher than baddeleyite. We show the displacement vector analysis for this one-step transition in Fig. 5. It can be seen that the arrangement of Ti atoms in the ending configuration resembles baddeleyite, but the oxygen atoms are less ordered. The displacement vectors again show highly ordered and collective motion. Comparing the one-step transition with the first transformation in the aforementioned two-step process, our results suggest that while the pressure at which this transition begins is consistent (about 20 GPa), the product state of the phase transition is determined probabilistically between the baddeleyite and the oxygen-disordered baddeleyite-like state.

Fig. 4b shows the evolution of volume and enthalpy during the compression of anatase at a high temperature of 2000 K. In this case, a fraction of the end product from simulations with the small system size (the 12 sets of blue curves in Fig. 4b) are the thermodynamically-stable cotunnite, while the rest are in the oxygen-disordered baddeleyite-like state. This is in contrast to the low temperature simulations at 300 K, where none of the products were cotunnite. With larger system sizes, as shown using the light blue and the orange curves in Fig. 4b, all the final structures have the oxygen-disordered baddeleyite-like character. This suggests that simulations run with smaller system sizes are more likely to end in the stable polymorph.

In all the simulation runs, the volume and enthalpy curves show a sharp drop at about 20 GPa, follows by gradual and somewhat stochastic changes in both volume and energy between about 20 GPa-30 GPa. During the runs that ended up in cotunnite, there is also a third sharp transition at a pressure between 45 GPa and 55 GPa depending on the initial random seed of the simulation. These transition pressures are slightly higher than predicted by the phase diagram, but this in not unexpected as the kinetic barriers must be overcome and the rate of compression is very high. We show the displacement vector analysis for such three-step process in Fig. 5. For the first and the third transition, the motion of both Ti and O atoms are sudden as well as highly-coordinated, and the shuffling of the whole atomic planes are visible as well. During the second transition, from $t = 300$ ps to $t = 400$ ps and pressure from about 20 GPa-30 GPa, however, the displacements of the Ti atoms are relatively small, while the O atoms undergo large displacements with seemingly random orientations. These oxygen motions thus appear diffusive, and such diffusion-like behaviors are typically associated with thermal activation. If oxygen diffusion is indeed required in the anatase to cotunnite transformation process, it would explain why the simulations run with smaller system sizes are more likely to end in this stable polymorph, and why this transformation is never seen in simulations at lower temperatures.

Experimental results for the compression of anatase are mixed and are dependent on the microstructure of the initial material. For example, it has been shown that single crystal anatase transforms to columbite at 7 GPa, whereas in polycrystalline anatase this transformation is suppressed, and it instead transforms to baddeleyite when compressed to 18 GPa and heated to 850-900 K. While we would expect our results to reflect the single crystal case, we find that the transformation to columbite is suppressed. Nevertheless, the anatase-baddeleyite transition pressure is in good agreement and the temperature dependence of the transition is consistent with our suggestion that it may involve oxygen diffusion.

Under further compression, baddeleyite has been shown experimentally to transform to cotunnite when compressed to 61 GPa and heated to 1100 K. Our simulations with the MLP show this transformation occurring only at high temperatures between 46 and 57 GPa.
FIG. 4. Volume and enthalpy over the course of rapid compression of anatase from 0 to 70 GPa over 1 ns at (a) 300 K and (b) 2000 K. The compression was repeated 12 different times using different random seeds, for 3 different system sizes. For reference, baddeleyite and cotunnite are also included.

FIG. 5. The displacement vector plots for the TiO$_2$ system before and after each transition during the rapid compression simulations (0 GPa at $t = 0$ ps and 70 GPa and $t = 1$ ns). The titanium atoms are plotted as gray spheres, and the associated displacement vectors are plotted as thin gray lines. The oxygen atoms and their displacements are both plotted in the red color. The snapshots of atomic coordinates were averaged over a time window of 2 ps. For each transition, both the starting and the ending configurations are provided, and the displacement vectors shown on top of both configurations are essentially the vectors that show the change of the positions of atoms. (a) shows a two-step transition between anatase and baddeleyite at 300 K. (b) illustrates an one-step transition between anatase and a baddeleyite-like phase with disordered oxygen atoms at 300 K. (c) depicts a three-step process for the transformation between anatase and cotunnite, with diffusive movement of oxygen atoms during the second step.
V. CONCLUSIONS

We have trained a stable, long-range MLP with significantly higher accuracy than empirical potentials for titanium dioxide using the Δ-Learning method, where the training data consists of the difference between the energies and forces computed using DFT (using the PBEsol functional) and a reparametrised version of the MA potential (reMA). The computational cost is $O(N)$ and approximately one order of magnitude higher than reMA, compared to $O(N^3)$ for DFT.

The relative enthalpy of the metastable phases shows good agreement with DFT at 0 K from 0-70 GPa, and predicts that the anatase, brookite, baddeleyite, and cotunnite phases would be the stable phase in different regions of $P$-$T$ space.

We have investigated the phase transformations that occur on compressing anatase from 0 to 70 GPa at selected temperatures ranging from 300 K to 2000 K. We observed several distinct solid-solid transition mechanisms: At low $T$, anatase can either undergo a two-step martensitic transformation to baddeleyite, with the first step involving the crystallographic planes gliding over each other, or a single-step transformation to an oxygen-disordered baddeleyite-like state. At high $T$, anatase can transform into cotunnite via a thermally activated process that involves both gliding of the planes and diffusive movements of oxygen atoms. The transition pressures for the anatase-baddeleyite and the baddeleyite-cotunnite transformations in our simulations agree well with experiments.

From the methodology side, future work could involve designing more sophisticated empirical potentials as the baseline of the Δ-learning potential, which may include charge redistributions. Another direction is to use a higher-level electronic structure method as the reference for constructing MLPs, in order to avoid the known issues of DFT for the system of TiO$_2$. For applications, further work could be done using the MLP we have developed to investigate the many other phase transitions in titanium dioxide in order to develop more sustainable synthetic routes, in addition to further research into other complex phenomena such as polymorphous phases and surface physics.

VI. APPENDIX

A. Details on geometry optimisation

Starting with DFT-optimised structures of the known phases from Ref. [29] at 0 K and 0 GPa, the geometry is re-optimised using the MLP at 0 K and 0 GPa. The box is allowed to relax by up to 10% in volume to reach the target pressure and both the lengths and angles of the simulation cell are free to change during the relaxation. Following the box relaxation, the quadratic conjugate gradient minimisation algorithm is used to optimise the atomic positions. To avoid trapping in a shallow local minimum, the optimization is repeated four times, using sequentially smaller tolerances. The potential energy of the final structure is minimised to a precision of $10^{-10}$.

The 0 K, 0 GPa is then used as the starting structure for geometry optimisation at 0 K, 5 GPa, and the structure is optimised in the same way. This is repeated in 5 GPa intervals up to 70 GPa. This is done for all phases in order to calculate the enthalpy curves shown in Fig. [1].

B. Details on free energy calculations

For each polymorph of TiO$_2$, we first perform a molecular dynamics simulation at each pressure of interest at a low temperature $T_0 = 100$ K, starting with the corresponding structure optimised at 0 K. This is run for $30,000 \times 1$ fs timesteps in the isobaric-isothermal (NPT) ensemble using the Nose-Hoover barostat with a damping time of 500 fs. The required temperature is maintained using stochastic velocity rescaling thermostat with a damping time of 100 fs. The dimensions of the simulation cell are allowed to change anisotropically but the cell angles are fixed.

The resulting geometries are optimised in a similar manner to the 0 K structures and their internal energies $U(T_0)$ are found. Where a local minimum is found, the Hessian matrices of the structures are computed using the program [63] using the finite-difference method. The Hessian matrix enables us to construct a reference harmonic crystal, where the forces between the atoms are defined by the phonon modes. An MD simulation is run on the harmonic crystal in the isochoric-isothermal (NVT) ensemble to determine its internal energy $U_{\text{har}}(T_0)$.

Given the internal energies of the real and harmonic crystals, as well as the Helmholtz energy of the harmonic crystal $F_{\text{har}}(T_0)$ (which is the sum of the phonon energies) we can transform to the isobaric-isothermal (NPT) ensemble to determine the Gibbs energy using the equation,

$$G(P, T_0) = F_{\text{har}}(V, T_0) - k_B T_0 \ln \left( \exp \left( \frac{U - U_{\text{har}}}{k_B T_0} \right) \right)_{V,T_0}.$$

Further MD simulations at higher temperatures $200 \leq T \leq 1500$ K are performed to determine the enthalpy of each polymorph under these conditions. Thermodynamic integration is then used to determine the Gibbs energy at higher temperatures,

$$\frac{G(P, T_1)}{k_B T_1} = \frac{G(P, T_0)}{k_B T_0} - \int_{T_0}^{T_1} \frac{\langle H \rangle_{P,T}}{k_B T^2} dT.$$

The measured properties, such as volume, enthalpy, etc., were extracted from the final 20% of each MD simulation, when it has reached a stable equilibrium.

C. More results on the anatase compression simulations

In the main text, we analyze the simulations of compressing anatase from 0 to 70 GPa over a period of 1 ns at 300 K and 2000 K (see Fig. [4]). In Fig. [5] we show the analogous enthalpy and volume curves from simulations at $T = 500, 800, 1000,$
and 1500 K. The observations in Sec. [IV] are valid for these simulations at the intermediate temperatures; the product state of the phase transition is determined probabilistically, and the final state is more likely to be cotunnite when the temperature is high.

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Data availability statement All original data generated for the study, and the Δ-learning potential for TiO2 constructed in this study are in the repository https://github.com/jacobglee1/tio2-mlp
high pressures,” Solid State Communications 34, 799–802 (1980).
44 H. Arashi, “Raman spectroscopic study of the pressure-induced phase transition in tio2,” Journal of Physics and Chemistry of Solids 53, 355–359 (1992).
45 L. Gerward and J. Staun Olsen, “Post-rutile high-pressure phases in tio2,” Journal of Applied Crystallography 30, 259–264 (1997).
46 R. A. Buckingham, “The classical equation of state of gaseous helium, neon and argon,” Proc. R. Soc. Lond. A 168, 264–283 (1938).
47 P. K. Naicker, P. T. Cummings, H. Zhang, and J. F. Banfield, “Characterization of titanium dioxide nanoparticles using molecular dynamics simulations,” J. Phys. Chem. B 109, 15243–15249 (2005).
48 V. N. Koparde and P. T. Cummings, “Molecular dynamics simulation of titanium dioxide nanoparticle sintering,” The Journal of Physical Chemistry B 109, 24280–24287 (2005) pMID: 16375425, https://doi.org/10.1021/jp054667p.
49 M. Heyhat, M. Abbasi, and A. Rajabpour, “Molecular dynamic simulation on the density of titanium dioxide and silver water-based nanofluids using ternary mixture model,” Journal of Molecular Liquids 333, 115966 (2021).
50 Y. Xu, M. Wang, N. Hu, J. Bell, and C. Yan, “Atomic investigation into the mechanical behaviour of crystalline and amorphous tio2 nanotubes,” RSC advances 6, 28121–28129 (2016).
51 J. Behler and M. Parrinello, “Generalized neural-network representation of high-dimensional potential-energy surfaces,” Phys. Rev. Lett. 98, 146401 (2007).
52 B. Cheng, R.-R. Griffiths, S. Wengert, C. Kunkel, T. Stenczel, B. Zhu, V. L. Deringer, N. Bernstein, J. T. Margraf, K. Reuter, and G. Csanyi, “Mapping materials and molecules,” Accounts of Chemical Research 53, 1981–1991 (2020) pMID: 32794697, https://doi.org/10.1021/acs.accounts.0c00403.
53 R. K. Cersovsky, B. Helfrecht, E. A. Engel, S. Kliavinek, and M. Ceriotti, “Improving sample and feature selection with principal covariates regression,” Machine Learning: Science and Technology (2021).
54 G. Imbalzano, A. Anelli, D. Giofré, S. Klees, J. Behler, and M. Ceriotti, “Automatic selection of atomic fingerprints and reference configurations for machine-learning potentials,” The Journal of Chemical Physics 148, 241730 (2018) https://doi.org/10.1063/1.502461.
55 A. P. Bartok and G. Csanyi, “Gaussian approximation potentials: A brief tutorial introduction,” International Journal of Quantum Chemistry 115, 1051–1057 (2015) https://onlinelibrary.wiley.com/doi/pdf/10.1002/qua.24927.
56 S. Plimpton, “Fast parallel algorithms for short-range molecular dynamics,” J. Comput. Phys. 117, 1–19 (1995).
57 A. Singraber, T. Morawietz, J. Behler, and C. Dellago, “Parallel multistream training of high-dimensional neural network potentials,” Journal of Chemical Theory and Computation 15, 3075–3092 (2019) pMID: 30995035, https://doi.org/10.1021/acs.jctc.9b00192.
58 B. Cheng and M. Ceriotti, “Computing the absolute gibbs free energy in atomistic simulations: Applications to defects in solids,” Phys. Rev. B 97, 054102 (2018).
59 J. C. Janieson and B. Olinger, “Pressure-temperature studies of anatase, brookite rutile, and TiO2(II): A discussion,” American Mineralogist 54, 1477–1481 (1969), https://pubs.geoscienceworld.org/ammin/article-pdf/54/9-10/1477/4249594/am-1969-1477.pdf.
60 X. Che, L. Li, J. Zheng, G. Li, and Q. Shi, “Heat capacity and thermodynamic functions of brookite tio2,” The Journal of Chemical Thermodynamics 93, 45–51 (2016).
61 S. V. Swamy, N. A. Dubrovinskaia, and L. S. Dubrovinsky, “Compressibility of baddeleyite-type tio2 from static compression to 40 gpa,” Journal of Alloys and Compounds 340, 46–48 (2002).
62 S. V. Swamy, L. S. Dubrovinsky, N. A. Dubrovinskaia, A. S. Simonovici, M. Drakopoulos, V. Dimitriev, and H.-P. Weber, “Compression behavior of nanocrystalline anatase tio2,” Solid State Communications 125, 111–115 (2003).
63 V. L. Deringer, N. Bernstein, G. Csányi, C. B. Mahmoud, M. Ceriotti, M. Wilson, D. A. Drabold, and S. R. Elliott, “Origins of structural and electronic transitions in disordered silicon,” Nature 589, 59–64 (2021).
64 M. P. Teter, M. C. Payne, and D. C. Allan, “Solution of schrödinger’s equation for large systems,” Phys. Rev. B 40, 12255–12263 (1989).
65 G. Bussi, D. Donadio, and M. Parrinello, “Canonical sampling through velocity rescaling,” J. Chem. Phys. 126, 014101 (2007).
66 V. Kapil, M. Rossi, O. Marsalek, R. Petraglia, Y. Litman, T. Spura, B. Cheng, A. Cuzzocrea, R. H. Meißner, D. M. Wilkins, B. A. Helfrecht, P. Juda, S. P. Bienvenue, I. Poltavsky, S. Vandenbrande, J. Kessler, I. Gavino, P. Van Speybroeck, and M. Ceriotti, “i-pi 2.0: A universal force engine for advanced molecular simulations,” Computer Physics Communications 236, 214–223 (2019).
67 M. Ceriotti, J. More, and D. E. Manolopoulos, “i-pi: A python interface for ab initio path integral molecular dynamics simulations,” Computer Physics Communications 185, 1019–1026 (2014).
FIG. 6. Enthalpy and volume curves for anatase as it is compressed from 0 - 70 GPa at $T = 500, 800, 1000, 1500$ K. Cotunnite and baddeleyite are also shown for reference.