Metadynamics Simulations of the High-Pressure Phases of Silicon Employing a High-Dimensional Neural Network Potential

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We study in a systematic way the complex sequence of the high-pressure phases of silicon obtained upon compression by combining an accurate high-dimensional neural network representation of the density-functional theory potential-energy surface with the metadynamics scheme. Starting from the thermodynamically stable diamond structure at ambient conditions we are able to identify all structural phase transitions up to the highest-pressure fcc phase at about 100 GPa. The results are in excellent agreement with experiment. The method developed promises to be of great value in the study of inorganic solids, including those having metallic phases.

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The study of the phase diagram of simple inorganic crystals is a problem of great academic and practical relevance, which has not yet found a fully satisfactory solution. A typical example for the difficulty one is faced with is Si, which has proven to be experimentally and theoretically challenging. Its behavior under pressure is very complex, and some stable phases have been identified only recently [1,2]. At ambient conditions the thermodynamically stable form of Si is the cubic diamond (cd) structure [3]. Upon compression at 11.7 GPa the β-tin phase is formed. The accurate determination of the transition pressure is complicated by hysteresis implying the existence of significant kinetic effects. Upon further compression at 15.4 GPa it transforms via the *Imma* phase into the simple hexagonal (sh) structure. Further compression at about 38 GPa yields the *Cmca* phase whose complex structure has been resolved only recently [1]. At even higher pressures one finds hcp at 42 GPa and fcc at 80 GPa. Several metastable phases have been discovered upon decompression [3].

If experiments are difficult, theory has also had its own problems. This is in spite of the fact that one of the early successes of density-functional theory (DFT) has been the prediction of the critical pressure of the cd to β-tin transition [4] and that later calculations have shown that DFT can also accurately evaluate the enthalpy ranking of the other structures [3]. In these calculations the crystal structures were assumed and not predicted with the exception of *Imma,* which was guessed before being experimentally found [5]. It would be extremely important to have a method that has the ability not only to predict accurately new structures [6–8] but also to take into account finite temperature effects and to determine transition pathways that are crucial for explaining kinetic effects and plastic behavior [6]. In this respect the method of choice is due to Parrinello and Rahman (PR) [9], which has been later combined with *ab initio* molecular dynamics (MD) and made more efficient by the use of metadynamics [10–12]. Unfortunately, applications of the PR method to Si have so far had limited success [13]. In an early DFT based simulation overpressurization was needed to induce a transition in the short time scale of the simulation. This procedure missed altogether the β-tin phase, which was skipped in favor of the sh phase. A recent calculation that added to the previous scheme the sampling power of metadynamics showed that this can be remedied and both the sh and the β-tin were seen [14]. Still *ab initio* calculations of the needed accuracy are too expensive to thoroughly explore the phase diagram and are beyond present day capabilities. On the other hand, at least the DFT level of theory is needed in order to describe correctly the phase diagram of Si. For instance, the use of a tight binding model can speed up considerably these simulations but leads to loss of accuracy and wrongly predicts that the cd phase transforms directly into sh [11]. Even worse is the accuracy of empirical potentials [15–18] so that PR-like calculations have so far been very rare [19].

Here we show that recent progress in the generation of effective potentials based on neural networks (NN) leads to interatomic potentials of quality comparable with that of the most sophisticated DFT calculations [20]. These potentials combined with an advanced sampling method can account for all the very many Si phases. By applying pressure and temperature, the phases transform into one another in a manner closely resembling that of the experiments, thus providing insight into the transition kinetics. In particular, we find that the cd → β-tin transition is strongly first order and is nucleated by the formation of defects. Given its general character and the successful application to such a classic problem, our approach can be extended to the study of the phase diagram of a variety of inorganic systems.

We recall that in the metadynamics method the free-energy surface is explored as a function of a few collective coordinates [10], and the local minima are filled by adding Gaussian potentials to drive the system out of its current minimum. Experience has shown that the lattice parameters $\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ are excellent collective coordinates [11,12] in the study of structural phase transitions.

Coupling of the metadynamics method with on-the-fly DFT calculations is especially demanding for the metallic high-pressure phases of Si, which require an accurate sampling of **k** space. However, in recent years due to their high flexibility NNs have become a valuable tool for the accurate and efficient representation of DFT potential-energy surfaces [21–24]. In the present work we employ a new high-dimensional NN scheme, which we have introduced recently to construct a reliable potential for silicon [20]. This potential has been fitted using DFT calculations in the local density approximation employing the plane-wave pseudopotential method [25]. For the details of the method we refer to Ref. [20]. The NN, which is about 5 orders of magnitude faster than DFT for the systems studied in this work, also provides analytic forces and the stress tensor as needed in metadynamics simulations.

Employing this NN-based metadynamics scheme, we have carried out a large number of simulations for silicon starting from different initial structures at different temperatures and pressures in a 64 atom cell. Each metastep consists of one picosecond MD to equilibrate the system and another picosecond to average the stress tensor.

We start with the cd structure, which is stable at ambient conditions. The transition from the semiconducting diamond to the metallic β-tin phase includes a significant rearrangement of bonds and thus involves a high energy barrier. For a long time these barriers caused difficulties in measuring exactly the transition pressure and also hampered theoretical simulations [13]. With metadynamics we do not need to overpressurize the system and we see (Fig. 1) that at 300 K and 12 GPa the system transforms.

In order to obtain a clearer picture of the structures visited, we remove the fluctuations by performing at the end of each metadynamics step a full enthalpy optimization by relaxing the matrix **h** and the atomic positions. We emphasize that this is done for the purposes of analysis only and it is not part of the metadynamics protocol. The system remains in the cd structure basin (a) up to metastep 38, where it climbs a high enthalpy barrier. With all the caution due to the use of periodic boundary conditions and of a small MD cell, this intermediate state can be described as a nucleation step, in which a thin layer of a new phase is created. This nucleation halves the barrier relative to what is calculated by assuming that the diamond to β-tin transition occurs as a morphing of one structure into the other [26]. At metastep 43 the system undergoes a very large volume change, $\frac{\Delta V}{V} \approx 17\%$, and the *Imma* phase is found first, followed by the sh one until the β-tin phase is reached, which is the stable phase at this pressure.

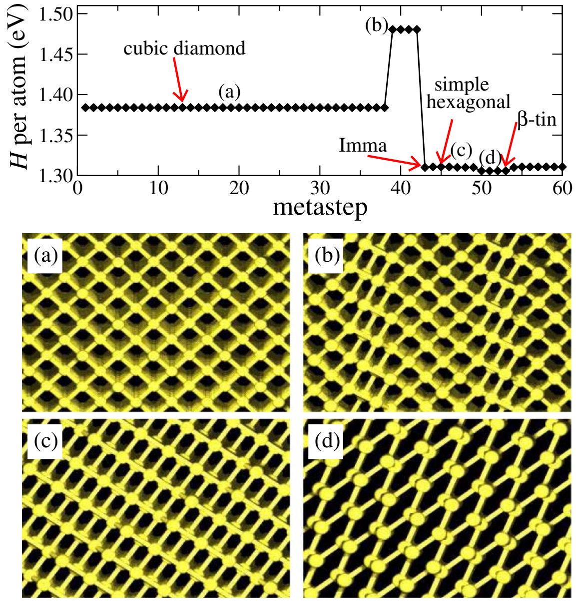

FIG. 1 (color online). Enthalpies of the optimized crystal structures obtained in a metadynamics simulation at 300 K starting from the cubic diamond structure at an external pressure of 12 GPa.

We repeated this simulation several times, always finding a high barrier. However, the first structure after the transition could be any of the three seen above. This is not too surprising since at these thermodynamic conditions the enthalpies of these phases are very close. Our findings of a high enthalpy barrier separating the diamond structure from a basin in which many other highly similar structures compete is compatible with experiment.

We have examined in more detail the transitions between the β-tin, the *Imma,* and the sh structure at a slightly increased pressure of 16 GPa and 300 K (Fig. 2). It has been previously suggested that the β-tin to *Imma* transition may be second order, while the *Imma* to sh transition is weakly first order [27], which implies that transition barriers are small or nonexistent. This might have posed problems to metadynamics, which was designed to overcome large barriers. This is not the case, and confirming the low barrier scenario of Ref. [27] we observe that the system accesses in a random sequence the three phases. We note that the NN potential can reproduce the tiny differences between these phases, which are at the limit of DFT accuracy. The enthalpy of the *Imma* phase is found to be the lowest at the given conditions, in agreement with DFT, while the sh phase becomes stable above 22 GPa. It is particularly noteworthy that the *Imma* phase was found since it has not been included in the DFT data set used to construct the NN potential. Still, this structure is correctly

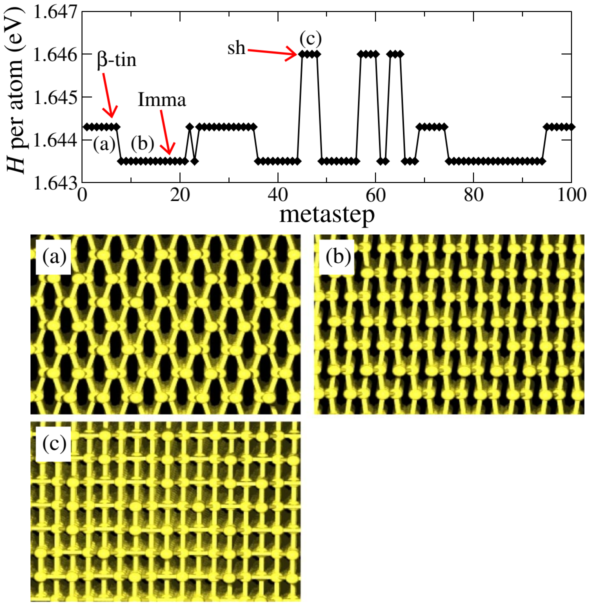

FIG. 2 (color online). Enthalpies of the optimized crystal structures obtained in a metadynamics simulation at 300 K starting from the β-tin structure at an external pressure of 16 GPa. Note the much smaller enthalpy differences compared to Fig. 1.

identified in the simulations and placed in the right DFT enthalpic order, thus providing further confidence in the predictive power of our method. These structures, all of comparable volumes, transform easily into one another, reflecting the fact that they are very similar and that their metallicity diminishes the directional character of the bonds.

We then proceeded to the much higher pressure of 45 GPa to explore the phase transitions starting from the sh phase (Fig. 3). At 300 K we found a direct transition to the hcp phase, which can be obtained by a concerted sliding of atomic planes from the sh structure. At higher temperature (800 K), however, we did observe the formation of the *Cmca* phase, which is the thermodynamically stable phase at this pressure and whose formation has not yet been observed in simulations. The increase of temperature facilitates the atomic distortions that transfer the sh to the very complex *Cmca* structure containing 16 atoms per unit cell. Also in experiment annealing at about 400 K was necessary to obtain the transition [1]. The sh and *Cmca* structures are compared in Figs. 3(a) and 3(b), and from this perspective the hexagonal pattern of the sh structure can still be recognized in the *Cmca* phase, but the distortion pattern is very complex.

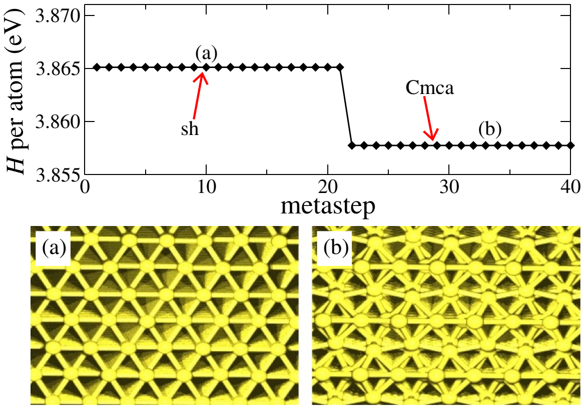

FIG. 3 (color online). Enthalpies of the optimized crystal structures obtained in a metadynamics simulation at 800 K starting from the simple hexagonal (sh) structure at an external pressure of 45 GPa.

By increasing the pressure to 50 GPa at 300 K we observe a transition to the thermodynamically stable hcp structure (Fig. 4). As for the sh → *Cmca* transition, a complex atomic rearrangement is required, but in this case no increase of temperature is necessary. Instead, initially two different coexisting hcp domains are formed between metasteps 29 and 90. The relative size of the two domains can vary, yielding two distinct enthalpy values, which we have observed in several simulations. In the lower enthalpy structure formed in metastep 46 both domains have about the same size. Finally, in metastep 91 the domains merge to yield a perfect hcp lattice. Again, the precise values of the enthalpies in the transition region are affected by the size of the simulation cell.

The final transition from the hcp to the perfect fcc structure is difficult to observe because of the tiny enthalpy differences between the different stacking sequences of the silicon layers reflecting an even higher degree of metallicity, and indeed in many simulations we obtained stack-

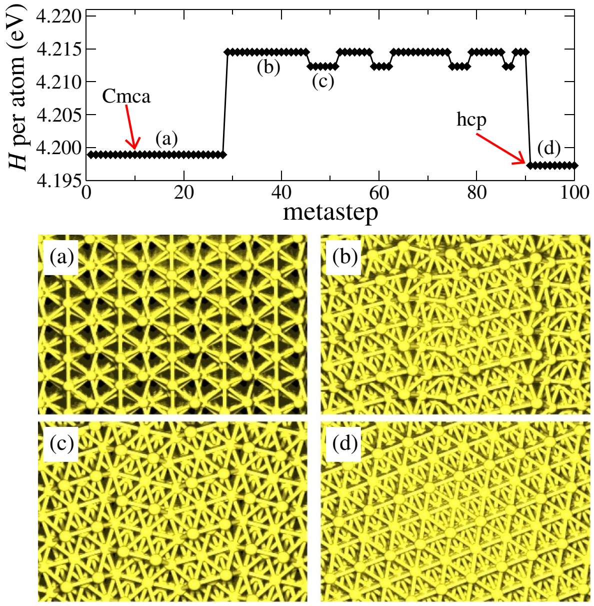

FIG. 4 (color online). Enthalpies of the relaxed structures obtained in a metadynamics simulation at 300 K starting from the *Cmca* structure at an external pressure of 50 GPa.

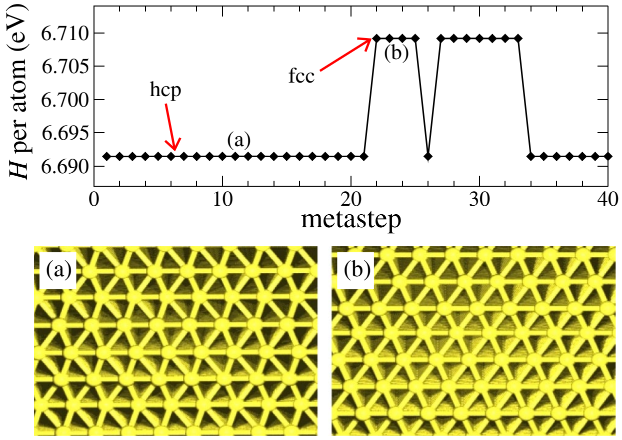

FIG. 5 (color online). Enthalpies of the relaxed structures obtained in a metadynamics simulation at 300 K starting from the hcp structure at an external pressure of 90 GPa.

ing faults. An additional complication is that we are here at the limit of validity of our NN, which has been fitted at pressures between 0 and 100 GPa. The DFT transition pressure is 104 GPa, and, although this value is accurately predicted in static NN calculations, we have some reason to believe that some of the transition configurations might not be correctly described. For this reason we have reduced the external pressure to the safer value of 90 GPa (cf. Fig. 5). At metastep 22 a perfect fcc lattice is formed, which at this pressure has a higher enthalpy than the hcp. The formation of the fcc structure is particularly remarkable, since we started the simulation in a $4 \times 4 \times 2$ supercell of the hcp structure containing four layers of atoms in each direction. For this initial structure it is not obvious that the stacking of the fcc structure can be realized in a straightforward way. Yet, during the metadynamics, the shape of the simulation cell adapts to facilitate the transition.

In summary, we have shown that upon compression the full sequence of high-pressure phases of silicon up to the highest-pressure fcc phase can be obtained by a sequence of metadynamics simulations starting from the cubic diamond structure, and new insight into these transitions has been gained. The NN potential employed in the metadynamics simulations yields results essentially indistinguishable from a direct application of DFT, which is prohibitively expensive. The observed transitions are in excellent agreement with the experimental data. The method has predictive power and can be applied to a wide range of systems.

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