# Direct Transformation of Vacancy Voids to Stacking Fault Tetrahedra

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Defect accumulation is the principal factor leading to the swelling and embrittlement of materials during irradiation. It is commonly assumed that, once defect clusters nucleate, their structure remains essentially constant while they grow in size. Here, we describe a new mechanism, discovered during accelerated molecular dynamics simulations of vacancy clusters in fcc metals, that involves the direct transformation of a vacancy void to a stacking fault tetrahedron (SFT) through a series of 3D structures. This mechanism is in contrast with the collapse to a 2D Frank loop which then transforms to an SFT. The kinetics of this mechanism are characterized by an extremely large rate prefactor, tens of orders of magnitude larger than is typical of atomic processes in fcc metals.

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It is well established that materials, upon irradiation, exhibit embrittlement and swelling that can often be traced to the atomic scale processes of defect accumulation. Defects (interstitials and vacancies) are produced; these diffuse and aggregate, leading to interstitial and vacancy clusters. When a supersaturation of vacancies is created, vacancy clusters can grow to the point that the material swells and fails.

Much work has been done to elucidate the structure of the vacancy clusters formed during irradiation and it is well known that stacking fault tetrahedra (SFTs) are the dominant vacancy cluster in most face-centered-cubic (fcc) metals [1,2]. It is less well understood how they form, but it is postulated that vacancy voids collapse into Frank loops (a disk of vacancies in a {111} plane) which then dissociate into SFTs [3–5]. Other mechanisms have been proposed [6]. Early simulations showed that, under nonequilibrium conditions, voids could collapse into Frank loops at 800 K [7] or that SFTs could form when the region around a void was set to 9000 K [8]. Later, it was shown that SFTs could form directly in molecular dynamics (MD) simulations of collision cascades (e.g., [9]). None of these studies considered the actual thermal evolution of a vacancy void.

In this Letter, we show that voids can thermally transform directly to SFTs without passing through a Frank loop. The mechanism demonstrated here is different from any reviewed by Jossang and Hirth [6]. The transformation of very small voids, containing as few as 6 vacancies, to SFT-like structures has been observed in MD simulations [10]. However, the thermal barrier to transform larger voids directly to SFTs has been considered to be too great to occur in most metals [2]. Furthermore, it has been assumed that, even if the transformation could occur, it would require passing through a Frank loop structure.

In what follows, we describe the direct transformation of vacancy voids in Cu to SFTs. This transformation proceeds stepwise through a series of three-dimensional structures without collapse to a Frank loop. While we find that the potential energy barrier for the transformation is very large, the kinetics involve an extremely large rate prefactor that more than compensates for the barrier, enabling high rates even at temperatures as low as 400 K. We have compared the stability of voids versus SFTs for a number of fcc metals, identifying metals in which this transformation may be more likely. Finally, we discuss the implications of this mechanism.

These simulations were primarily done with parallel-replica dynamics (PRD) [11]. With PRD, given $M$ processors, a speedup over MD of up to a factor of $M$ is possible. Here, we used $M = 39$ and obtained speedups between 23 and 31. PRD requires that transitions between states be detected. We defined transitions to occur whenever any atom, upon minimization (which we did every 5 ps), moved more than 0.2 nm from its previous position. PRD also requires that, upon entering a new state, replicas of the system be dephased to randomize their initial conditions; we used a dephasing time of 5 ps. To account for correlated dynamical events, when a processor detects a transition, the system on that processor is evolved forward in time by a correlation time (3.5 ps here). The temperature was maintained with a Langevin thermostat with a coupling constant of $10^{11}$/s. In our MD simulations, we used the same temperature control as in the PRD simulations. Snapshots of trajectories were saved every 0.5 ps. Nudged elastic band [12] calculations were done between the snapshots to build minimum energy paths (MEPs) and identify saddle point energies between minima. To describe the Cu-Cu interaction, we used the embedded atom method (EAM) [13] with the parameters given in Ref. [11]. Vacancy voids containing $n$ vacancies were initially formed by removing an atom and its $n - 1$ nearest neighbors.

Using PRD, we simulated the behavior of voids in Cu containing 20 and 45 vacancies on the microsecond time scale. For clusters containing 20 vacancies, we used cells containing 500 atoms before the vacancies were introduced. In introducing vacancies, atoms were removed

 

entirely, as opposed to being placed elsewhere in the cell. Calculations involving 45 vacancies were done with cells that originally had 4000 atoms. To test whether the 500-atom cells are too small, we performed one simulation of a 20-vacancy void in a cell with 4000 atoms and saw behavior similar to what we report below.

The energetic stability of a void or an SFT depends on its size. There are ''magic numbers'' for both voids and SFTs that are lower in energy than other sizes. We define a ''magic'' void structure as having perfect shells of atoms removed; for SFTs, removing a perfect triangle of vacancies in a {111} plane results in a magic SFT. In the case of voids, the first three magic sizes are $n = 13$, 19, and 43, while perfect SFT sizes are 3, 6, 10, 15, 21, 28, 36, and 45. Voids with other vacancy counts result in nonequiaxed voids. Thus, a cluster of 20 vacancies contains one too many vacancies for an equiaxed void size and one too few for a perfect SFT.

We performed PRD at constant volume on a 20-vacancy void. The one extra vacancy on the void surface is observed to be quite mobile at moderate temperatures. In one particular simulation at 400 K, surface vacancies (the extra vacancy plus nearby vacancies in the void) executed 728 hops, at which point the extra vacancy reached an octahedral vertex on the void surface, as illustrated in the inset of Fig. 1. This phase of the evolution of the void, in which the vacancy diffused until it found the vertex configuration, lasted for about 1.35 $\mu$s.

Once in this configuration, the extra vacancy can hop around the vertex to symmetrically equivalent structures.

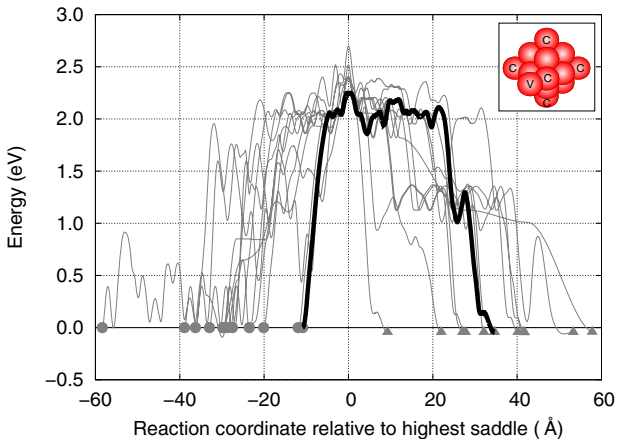


FIG. 1 (color online). Inset: The 20-vacancy void in Cu. In this display convention, red (or gray) spheres are vacancies. Notice the extra vacancy (labeled V) near one of the vertex sites (labeled C). Main figure: MEPs for the transformation of a 20-vacancy void to an SFT from 12 different MD simulations. The path in bold is analyzed in detail in the text; the others are shown for comparison. The hyperdistance of the reaction coordinate is the sum of the scalar distance all atoms move from one image to the next and has been shifted so that the highest energy saddle of each path is at 0. The circles and triangles represent the beginning and the end of each path.

Eventually the void undergoes an interesting transformation: as the vacancy executes a hop around the vertex, the corresponding moving Cu atom enters the void, attracting atoms on opposing void surfaces and triggering the transformation of the void into an SFT. The details of the transformation depend on the specific conditions of the simulation. As shown in Fig. 1, twelve different MD simulations initiated from the state in the inset led to 12 different pathways. The paths shown are the MEPs found from snapshots from the MD; repeated segments were removed so that only distinct states that are absolutely necessary for the transformation to occur are shown. For the 20-vacancy case, the SFT has a lower energy than the void by 0.04 eV.

The transformation from void to SFT has a very high potential energy barrier $\Delta E$ between 2.25 and 2.70 eV. At $T = 400$ K, assuming an Arrhenius form for the rate [$k = \nu \exp(-\Delta E/k_B T)$, where $k_B$ is the Boltzmann constant] and a standard prefactor $\nu = 10^{13}/\mathrm{s}$, it would take $10^6$ years for this event to occur. In contrast, we observed times of first passage ($\tau = 1/k$) between 1 and 15 ns, implying a much greater prefactor. Estimating the prefactor from the bold path in Fig. 1, with $\tau = 5.9$ ns and $\Delta E = 2.25$ eV, we find $\nu = 4 \times 10^{36}/\mathrm{s}$, a factor of $10^{25}$ higher than the standard value. One possible explanation for this high prefactor is that there is a huge number of pathways with a standard prefactor (rather than a small number of pathways with huge prefactors). However, we can rule this out by estimating the rate, and prefactor, for one particular pathway using harmonic transition state theory, which gives the above pure Arrhenius form. In this approach, the Vineyard prefactor [14] is computed as the product of the normal-mode frequencies at the minimum divided by the product of the nonimaginary frequencies at the saddle point. This gives a prefactor of $\nu = 5 \times 10^{42}/\mathrm{s}$, which, although differing somewhat from the $4 \times 10^{36}/\mathrm{s}$ value estimated from MD, is indeed extremely high. These prefactors are higher, by more than 20 orders of magnitude, than any prefactor we have calculated, or are aware of, for processes in metallic systems, indicating that something unusual is happening.

This extremely high prefactor implies the transition state has much higher entropy than the void state. Our simulations were performed at fixed cell dimensions. In the initial void state, the material can be partitioned into two regions: region I has the atomic density $\rho$ of Cu and region II, containing the void, has $\rho \sim 0$. As the system approaches the SFT state, atoms fill the void, increasing the volume of region I at the expense of region II and pulling the system into tension; the system is now composed of only one region, which has increased its volume, and this change in volume dramatically affects the entropy. The rate prefactor $\nu$ can be written as $\nu_0 \exp(\Delta S/k_B)$ where $\nu_0$ is the frequency at the minimum along the reaction coordinate ($\sim 10^{13}/\mathrm{s}$) and $\Delta S$ is the entropy increase in going from the basin to the transition region due to the softening of all the other vibrational modes. The relationship for the entropy change $\Delta S$ for a volume change $\Delta V$ in an isothermal

system is approximately $\Delta S = \alpha B \Delta V$ [15], where $\alpha$ is the coefficient of volumetric thermal expansion and $B$ is the bulk modulus. For a rough estimate, we take $\alpha$ and $B$ to be their zero temperature, zero pressure values for this potential ($\alpha = 5.56 \times 10^{-5}$/K and $B = 1.42 \times 10^{12}$ dyn/cm$^2$). Assuming the transformation of a 20-vacancy void increases the effective system volume by 10 $\Omega$ ($\Omega$ = atomic volume = 11.8 Å$^3$) at the transition state, we find $\Delta S = 67.5 k_B$. This increases the prefactor by $\exp(67.5) \sim 10^{29}$ times, roughly consistent with the observed effect. We thus believe this argument captures the essential physics of the origin of the large prefactor.

The transition from the 20-vacancy void to an SFT is triggered by one atom entering the void and attracting atoms on opposing surfaces. For this size void, the moving atom and the opposite void surface are closer than the potential cutoff and begin interacting as soon as the atom enters the void. To see whether the transformation would occur even when atoms cannot directly interact across the void, we examined a void containing 45 vacancies, where the distances between opposite sides are larger than the potential cutoff. After 0.25 $\mu$s at 475 K, this void also transforms to an SFT. The MEP for the observed process is shown in Fig. 2. The effective potential energy barrier is again very large, over 4 eV, and the transformation is again driven by a large entropy increase. In this example, the transformation is not complete, as a 9-vacancy void remains trapped in the SFT interior [Figs. 3(a) and 3(b)].

We note that, for both 20- and the 45-vacancy voids, the rate limiting step for the transformation is not necessarily the highest potential energy barrier. For the 45-vacancy void, we have estimated a harmonic free energy by calculating the Vineyard rate $k$ for saddle points along the pathway relative to the initial minimum and converting it to a free energy $\Delta A$ via the relationship $k = \nu \exp(-\Delta A / k_B T)$, assuming $\nu = 10^{13}$/s. These $\Delta A$ are shown in Fig. 2 as the open circles. We find that, rather than the highest barrier of 4.0 eV, an earlier barrier with a height of 2.74 eV is the rate limiting step. This suggests that scaling the volume-based entropy factor presented above to larger void sizes would probably require that $\Delta V$ be a nonlinear function of the void size.

The void-to-SFT transformation consists of both a volume and a shape change of the vacancy cluster. In the PRD simulations, the cell volume was held constant at the bulk Cu volume, neglecting any energy changes associated with volume relaxation and residual strain in the system. However, for an isothermal system, there is a well-known result [16–18] relating the change in Gibbs free energy at constant pressure to the change in Helmholtz free energy at constant volume for the same process, $\Delta G_p \approx \Delta A_v$. This expression is not expected to be highly accurate for the void-to-SFT process, both because the volume and pressure changes are substantial and because the empty volume of the void introduces uncertainty into the constant-volume condition. To the extent it is approximately true, though, it implies the rate for this process under constant pressure conditions would be similar to that observed here under constant volume. While the barrier would be reduced under constant pressure, the prefactor would reduce as well. Indeed, in estimating these effects for zero pressure and temperature, conditions which result in the greatest relaxations compared to our simulations, we find that, for the bold path in Fig. 1, the barrier is reduced from 2.25 to 1.15 eV while the Vineyard prefactor is reduced from $10^{42}$ to about $10^{22}$/s, still very high.

A remaining question concerns whether Cu is special or if these transformations also occur in other fcc metals. Figure 4 shows the energetic stability of voids versus SFTs for several fcc metals as a function of cluster size, calculated using EAM potentials [19]. The results for Cu are in the intermediate range for these metals. Thus, we might expect that direct void-to-SFT transformation would occur more rapidly in Pd than in Cu, while the rate of

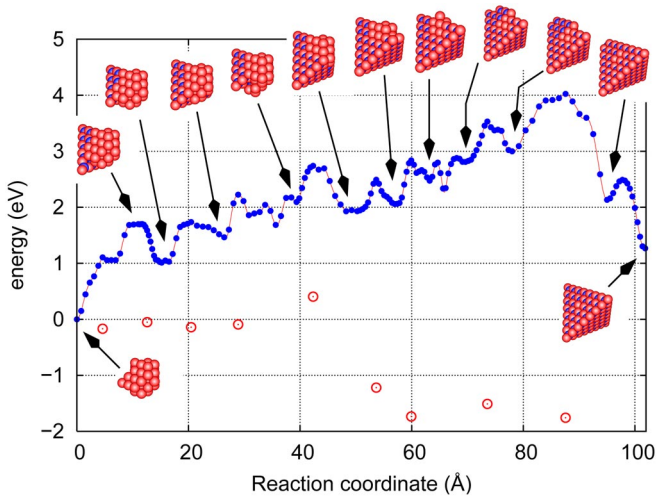


FIG. 2 (color online). MEP for the constant-volume transformation of a 45-vacancy void to an SFT. The inset figures are minima from the parallel-replica simulation showing the structure of the vacancy cluster as the transformation evolves [red (or gray) spheres are vacancies and blue (or dark gray) spheres interstitials, relative to an initial fcc reference structure]. The open circles are estimates of the free energy along the path.

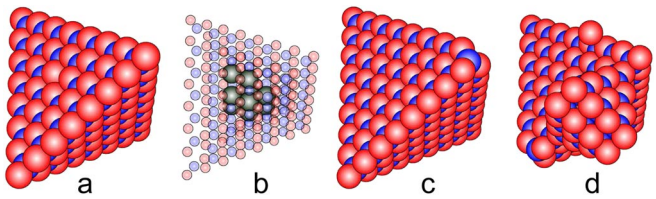


FIG. 3 (color online). SFT structures resulting from the transformation of a 45-vacancy void. (a) is the SFT from the pathway shown in Fig. 2, which still contains a small void of 9 vacancies, shown in (b) by the larger dark spheres. (c) is a nearly perfect SFT formed at $T = 500$ K (one vacancy is trapped in the interior). (d) is from a $T = 600$ K simulation; the void transforms into two smaller SFTs sharing an edge.

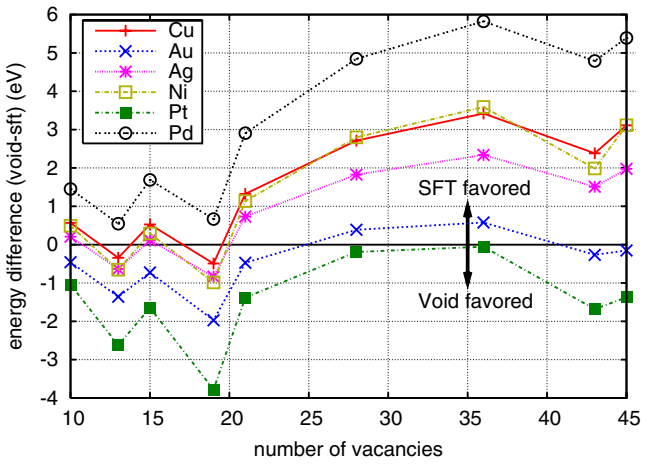


FIG. 4 (color online). Stability of voids relative to SFTs as a function of vacancy cluster size for a number of fcc metals, calculated with EAM potentials. Except for small magic void sizes, SFTs are strongly preferred in Pd, Ni, Cu, and Ag. Voids are favored at small cluster size for Au and especially Pt.

transformation is similar in Cu, Ag, and Ni. For Au and Pt, voids are energetically favored over a wide range of cluster sizes. The rate of transformation ought to be slowest in Pt, making it the preferred material in which to look for this mechanism. The results in Fig. 4 are only for the energetic, as opposed to the free energetic, stability of voids relative to SFTs and do not compare the stability of SFTs to other vacancy cluster types. Even so, we expect that they are an indicator of the relative tendency for voids, if present, to transform to SFTs.

We have seen that the transformation of voids can lead to a variety of complex structures. In addition to the small void trapped in the SFT interior [Figs. 3(a) and 3(b)], Figs. 3(c) and 3(d) show structures from simulations at 500 and 600 K. At 500 K, an SFT formed with one vacancy trapped in the interior. At 600 K, two smaller connected SFTs are formed. These imperfections would presumably anneal out at longer times, as a perfect SFT is energetically favored (compare Figs. 2 and 4).

As mentioned, SFTs have been observed in many fcc metals under irradiation [1]. While even small amounts of gas or impurities, particularly He and O, stabilize voids [20], in ultrapure materials, it seems unlikely that voids would grow to sizes at which this mechanism would become important, as SFTs are preferred even at small sizes. However, for some metals, there are cluster sizes for which voids are energetically more stable than SFTs (see Fig. 4). Thus, at low temperatures, voids would be preferred over SFTs. It is possible that, at these low temperatures, voids could grow to sizes such that SFTs are preferred but they are kinetically trapped as voids and unable to transform on experimental time scales. Raising the temperature would then allow the transformation to proceed. Also, a He might itself stabilize void growth over SFT formation. If impurity gases could then be removed, the void-to-SFT transformation should occur. Thus, there are at least these two experimental conditions under which this mechanism might be crucial for understanding the evolution of the material.

We have demonstrated an unexpected evolutionary pathway for vacancy clusters through transformation to SFTs. While void formation can lead to swelling, the SFT transformation pathway represents an alternative route, opposing swelling effects and increasing the hardness of the material. Therefore, it is important that this mechanism be included in higher-level models of radiation damage. This mechanism also illustrates that even the simplest of materials can exhibit complex behavior that we are just now beginning to understand.

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