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Creeping Motion of Self Interstitial Atom Clusters in Tungsten

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The formation and motion features of self interstitial atom (SIA) clusters in tungsten are studied by molecular dynamics (MD) simulations. The static calculations show that the SIA clusters are stable with binding energy over 2 eV. The SIA clusters exhibit a fast one dimensional (1D) motion along ⟨111⟩. Through analysis of the change of relative distance between SIAs, we find that SIAs jump in small displacements we call creeping motion, which is a new collective diffusion process different from that of iron. The potential energy surface of SIAs implicates that the creeping motion is due to the strong interaction between SIAs. These imply that several diffusion mechanism for SIA clusters can operate in BCC metals and could help us explore deep insight into the performance of materials under irradiation.

Body-centered cubic (BCC) metals, such as iron and tungsten which have been widely applied in the nuclear industry, are studied extensively during the past decades[1–3]. The microstructure evolution of material under irradiation is always a major concern depending on the structure and mobility of self-interstitial atom (SIA) defect(s)[4,5]. Single SIA in BCC metals could have various configurations[6]. There is a special configuration called crowdion originally proposed by Paneth which describes a linear compression region induced by a SIA[7]. Crowdion has some peculiar characteristics, for example, crowdion can move rapidly along the closed packed direction ⟨111⟩ with very low activation energy[7,8].

When a SIA cluster is made up of two or more ⟨111⟩ SIAs, it can be regarded as a bundle of crowdions[9]. The SIA clusters also show some peculiar characteristics like the single crowdion. Similar to the fast motion of crowdions along ⟨111⟩, SIA clusters in Fe also exhibit one dimensional (1D) fast migration along ⟨111⟩ direction indicated by molecular dynamics (MD) simulations[9–13], which has been confirmed by the experiment of Fe under electron irradiation[14]. The migration barrier corresponding to this 1D motion is very low and always in the magnitude of tens of meV. A main character of SIA cluster motion is that the migration barrier is nearly independent of the size of cluster[10,12,13]. Osetsky et al. have shown that the SIA cluster is a set of crowdions with their individual centers in a flexible configuration, which means that the movement of one crowdion along ⟨111⟩ only weakly change the SIA cluster's energy[12]. This diffusion mechanism also explains that why individual crowdion jumps away about 2Δ to 4Δ (for BCC structure $\Delta = \sqrt{3}a_0/2$, a_0 is the lattice constant.) from the mass center of cluster[12]. A question arises: is this picture universal for other BCC metals, taking W as an example. In another aspect, the multistring Frenkel-Kontorova (FK) model developed by Dudarev and coworkers[15–17] is a coarse-grained model based on that crowdions are synchronized. The temporal fluctuation of crowdion around the mass center is ignored in the FK model. In this paper, we focus on the motion style of small SIA clusters (N-SIA clusters within the range of $2 \leq N \leq 7$) in W using MD simulation, especially on the fluctuation of crowdions in one SIA cluster. Our results show that the crowdions in W are tightly bound together and drag each other in small steps along ⟨111⟩ during their motion. The reason is that the potential energy of SIA clusters strongly depends on the relative distance between the SIAs.

Methods

All atomistic simulation results are obtained with MD++ code[21] using a Finnis-Sinclair (FS)[22] type potential modified by Ackland and Thetford[23], which is widely used in the simulation of W, including cascades[18], dislocation motion[19], dislocation-vacancy interaction[20], etc. In addition, the results of the formation energy and vibration spectrum of crowdion calculated using Ackland-Thetford[23] and Derlet-Nguyen-Manh-Dudarev[8] potentials show a similar trend[24]. The simulation box for perfect crystal contains 6, 4 and 12 unit cells along the $[1\bar{1}0]$, $[11\bar{2}]$ and [111] direction, respectively. The stacking sequence of {111} plane of body-centered cubic (BCC) structure is ABCABC $\cdots$. We build a N-SIA cluster by first choosing N nearest neighbor atoms belonging to three adjacent {111} planes and then replace each of them by two

atoms along [111] direction, which is the same way as in Fe by Osetsky et al. in Ref. 9. Detailed MD simulation processes can be found elsewhere[24].

Generally, the position of SIA is used to monitor the motion of SIA and often obtained by Wigner-Seitz (WS) cell method[25], where the motion of SIA can be regarded as a series of discrete jumps. For bcc structure, the crystal can be represented as an ensemble of atomic strings parallel to the [111] direction. If we adopt the relative distance between mass center (RDMC) of two neighboring atomic strings containing one SIA respectively to describe the motion of SIA, the RDMC will change continuously. The connection between the two methods is that when one SIA jumps Δ from its neighboring SIAs, the RDMC between them increases/decreases 0.058Δ (=0.016 nm). For tungsten Δ = 0.2741 nm if we choose a_0 = 0.31652 nm[22]. Hereafter, we use jump and move to describe the discrete and continuum diffusion processes respectively.

Results and Discussion

The stability of SIA clusters is revealed by the binding energy of SIA clusters, E_b, which is defined as[26]

$$E_b(N) = E_f(N-1) + E_f(1) - E_f(N) \quad (1)$$

where $E_f(N)$, $E_f(N-1)$, $E_f(1)$ are the formation energies of SIA cluster with N SIAs, $N-1$ SIAs and single SIA respectively. The minimum energy states of clusters are obtained by using simulated annealing method[27] in conjunction with steepest descent relaxation. Table II shows the formation energies and binding energies of SIA clusters concerned in this work. The binding energies are all over 2 eV, which suggests that the N-SIA ($2 \le N \le 7$) clusters are very stable. Actually, during the simulation time (3 ns) at 900 K, all the SIA clusters neither dissociate nor change their motion direction. For Fe, one SIA in a cluster can jump away about 2Δ to 4Δ from its neighboring SIAs and the energy change is small[12]. In order to verify whether this diffusion mechanism is applicable for SIA clusters in W, we analyze the evolution of RDMC between two SIAs in one cluster which fluctuates around an average value during the simulation.

The average value of RDMC, ⟨RDMC⟩, can be regarded as the most probable distance between two neighboring SIAs at specific temperature. It can not be used to describe the relative movement of SIAs nor the absolute value of RDMC. The deviation relative to the average value d = RDMC − ⟨RDMC⟩ is a proper quantity reflecting the relative movement of SIAs. Obviously, when SIA jumps Δ, d will be ±0.058Δ (±means different jump direction). Fig. 1 shows the evolution of d of 2-SIA cluster at 300 K. From this figure, only one data point exceeds the black dashed line, implying that the SIA jumps Δ away from its neighboring SIAs only once. Actually there are several points exceeding the black dashed line and no points exceeding two times ±0.058Δ during the whole simulation time (3 ns), which indicates that the jump distance between SIAs does not reach 2Δ. This tendency can also be seen from the small value of variance of RDMC of 1.8×10^{-5} at 300 K as listed in Table I.

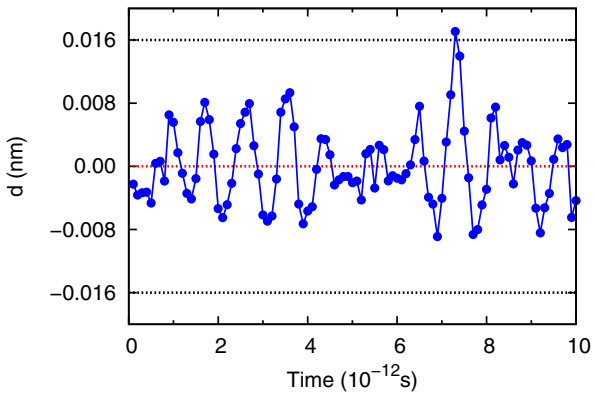

Figure 1 | Evolution of d = RDMC − ⟨RDMC⟩ between two SIAs of a 2-SIA cluster at 300 K. The black dashed line with the value of d = ±0.058Δ (±0.016 nm) corresponds to that one SIA jumps Δ individually.

Table I | Average and variance of RDMC for 2-SIA cluster at different temperatures

Temperature (K)	Average (nm)	Variance
300	0.110	1.8×10^{-5}
600	0.111	3.8×10^{-5}
900	0.111	5.6×10^{-5}

The RDMCs of a 2-SIA cluster at 600 K and 900 K are similar to the case of 300 K, which are listed in Table I. The variance of RDMC does not change much as the temperature increases, which implies that the atomic motion process does not change with temperature. Through analyzing the RDMCs of other size cluster, we find that the tendency of RDMCs is the same as that of 2-SIA cluster and we could safely infer that all SIA clusters have similar motion style to the 2-SIA cluster. We call this motion style "creeping motion", that is, the SIA cluster jumps to the next stable configuration by a successive small steps of constituent SIAs along ⟨111⟩. This motion picture is different from the case of Fe where the crowdions can jump independently over a range from 2Δ to 4Δ obtained by Osetsky et al.[12]. They found that the interaction energy between the crowdion and its neighboring crowdions is weakly dependent on their relative distance along the crowdion line[12]. The creeping motion in our case suggests that there is a strong interaction between crowdions. We ascribe the different motion picture of SIAs to the different interactions in Fe and W.

The interaction between crowdions in one SIA cluster can be revealed by the potential energy surface (PES) as a function of d. Generally, the probability density function $P(d)$ of finding system with d between SIAs is related with the Landau free energy $F(d)$ by[28]

$$F(d) = -k_B T \ln P(d) \quad (2)$$

where k_B is the Boltzmann's constant and T is the absolute temperature. Then the free energy difference between $F(d)$ and $F(0)$ can be described by

$$\Delta F = F(d) - F(0) = k_B T \ln \frac{P(0)}{P(d)}. \quad (3)$$

The above formula provides us a method to estimate the free energy difference if we know the probability density function $P(d)$ which can be readily obtained from the results of MD simulations. $F(0)$ is a reference point and we choose $F(0) = 0$. Fig. 2 shows the $P(d)$ as a function of d and it can be fitted well by a Gaussian type function $P(d) = A\exp\left(-\frac{d^2}{2\sigma^2}\right)$. Taking this into Eq. 3 we can obtain $\Delta F = k_B T \frac{d^2}{2\sigma^2}$ as shown in Fig. 2. For solids under low temperature, we can make an approximation like $\Delta F = \Delta U + T\Delta S \approx \Delta U$, where $\Delta U = U(d) - U(0)$ is the potential energy change due to the variation of d. For the migration entropy of SIA is only several k_B, we can safely ignore the contribution of migration entropy to the free energy difference[29]. Consequently, we could find that the potential energy increases rapidly as a parabolic function of d. From this strong interaction between SIAs, we could infer that when one crowdion jumps

Table II | Formation and binding energy of SIA clusters

N	$E_f(N)$ (eV)	$E_b(N)$ (eV)
2	15.439	2.311
3	21.020	3.294
4	25.772	4.123
5	30.508	4.139
6	34.994	4.389
7	37.709	6.160

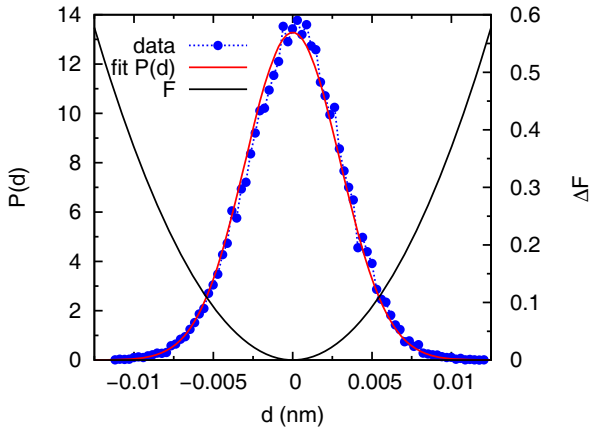

Figure 2 | Probability density function $P(d)$ as a function of d = RDMC − ⟨RDMC⟩ at 300 K of 2-SIA cluster. Data points are obtained from the MD simulations. The fitting function is $P(d) = A exp\left(-\frac{d^2}{2\sigma^2}\right)$ with A = 13.282 and $\sigma = 2.99 \times 10^{-3}$ nm. The right y axis shows the free energy difference $\Delta F = k_B T \frac{d^2}{2\sigma^2}$.

away, its neighboring crowdions follow it tightly to keep the d at a small value to minimize the interaction energy. Since the relative distance between crowdions can not be very large, the jump distance made by one crowdion can not be large either. In order to describe the motion quantitatively, we make an estimation of the jump length in discrete diffusion hops. As an approximation, we assume the movement of crowdion is like an oscillator vibration under the harmonic potential $U(d) = \frac{1}{2}Kd^2$. Comparing this with the expression of ΔF above, we obtain $K = k_B T/\sigma^2$. According to the equipartition theorem[30], the energy of an oscillator is $k_B T$, which is related to the amplitude d_A by the equation $\frac{1}{2}Kd_A^2 = k_B T$. Then we obtain the amplitude $d_A = \sqrt{2}\sigma \approx 0.004$ nm corresponding to the SIA jump about $\Delta/4$ in discrete motion picture which is a reasonable estimation of the upper limit of SIA jump length.

Conclusion

The formation and motion of N-SIA ($2 \le N \le 7$) clusters are simulated within MD approach. Our results show that the SIA clusters are very stable with binding energy over 2 eV and exhibit a 1D fast motion along ⟨111⟩ during the whole simulation process (3 ns). The diffusion process of SIA clusters is characterized by a creeping motion, i.e., when one crowdion jumps a small distance then simultaneously its neighboring crowdions jump a small distance in coordinated fashion. The whole cluster jump to the next stable configuration by a series of small distance jumps with an upper limit about $\Delta/4$ in comparing with that the crowdion in Fe can jump about 2Δ to 4Δ away from neighboring crowdions. This new diffusion mechanism is resulted from the strong interaction between crowdions in W. More detailed studies of SIA clusters are needed to check whether the picture is suitable for other BCC metals, such as V, Mo etc. The effects of this motion style on the atom transport, jump frequency and migration barrier of SIA clusters in W will be performed in the near future.

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Author contributions

W.H.Z., C.G.Z. and Z.Z. conceived the research. W.H.Z. carried out the calculations and wrote main manuscript. Y.G.L. and Z.Z. reviewed the manuscript.

Additional information

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