Across-scale self-healing mechanism for radiation damage in nano-crystal tungsten

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Outline

- **Background**

SIA, SIA_n, V, GB

- **Results**

--Fundamental interaction of the interstitial, vacancy with the GB;

--Interstitial clusters behavior near the GB:

segregation, reflection and dynamic emission;

--A general insight into the interstitial emission near a defect sink;

--Evaluation of the radiation response of the GB under a fusion environment.

- **Summary**

--Self-healing prospect for radiation damage in nano-crystal W.

Background: radiation effects in NCs

- The defect accumulation rate:

  NC Au >PC Au at 15K,

  NC Au<<PC Au at 300K.

- **NC Au** recovers more quickly than **PC Au**.

Y. Chimi et al. J. Nucl. Mater. 297, 355 (2001)

- The effect of the grain size on the density of defects: there exists a defect-free zone.

  ZrO2: 15nm, **Pd**: 30nm.T=300K

M. Rose et al. Nucl. Instr. Meth. B 127, 119 (1997)

Nano-crystals often exhibit radiation tolerance, which depends on temperature, grain size and radiation dose.

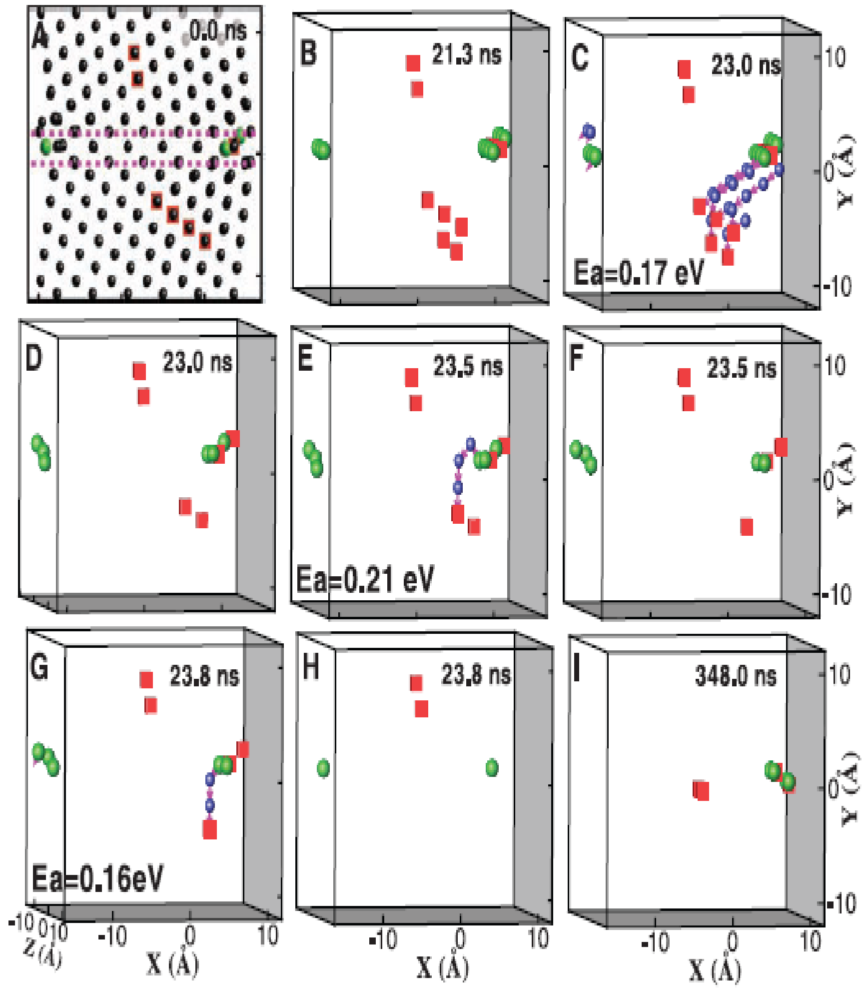
Background: self-healing mechanisms in NCs

♦ Complex self-healing mechanisms

1. Interstitial emission:

➢Upon irradiation, interstitials are loaded into the boundary, which then acts as a source, emitting interstitials to annihilate vacancies in the bulk.

➢This unexpected recombination mechanism has a much lower energy barrier than conventional vacancy diffusion and is efficient for annihilating immobile vacancies in the nearby bulk, resulting in self-healing of the radiation-induced damage.

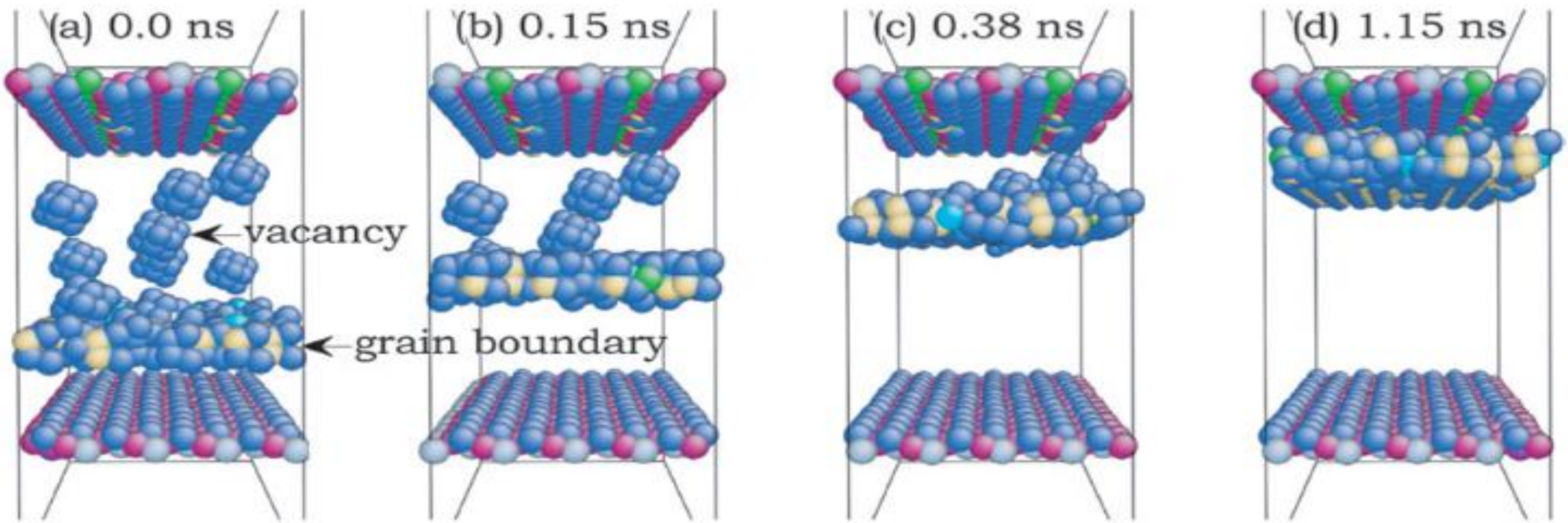


X.-M. Bai *et al*, Science, **327** (2010) 1631

Background: self-healing mechanisms in NCs

2. GB motion

Coupled GB motion, in some cases enhanced by interstitial loading, can lead to a radiation-damage healing mechanism, in which a large stress activates coupled GB motion, and the GB sweeps up the defects, such as voids and vacancies, as it passes through the material.

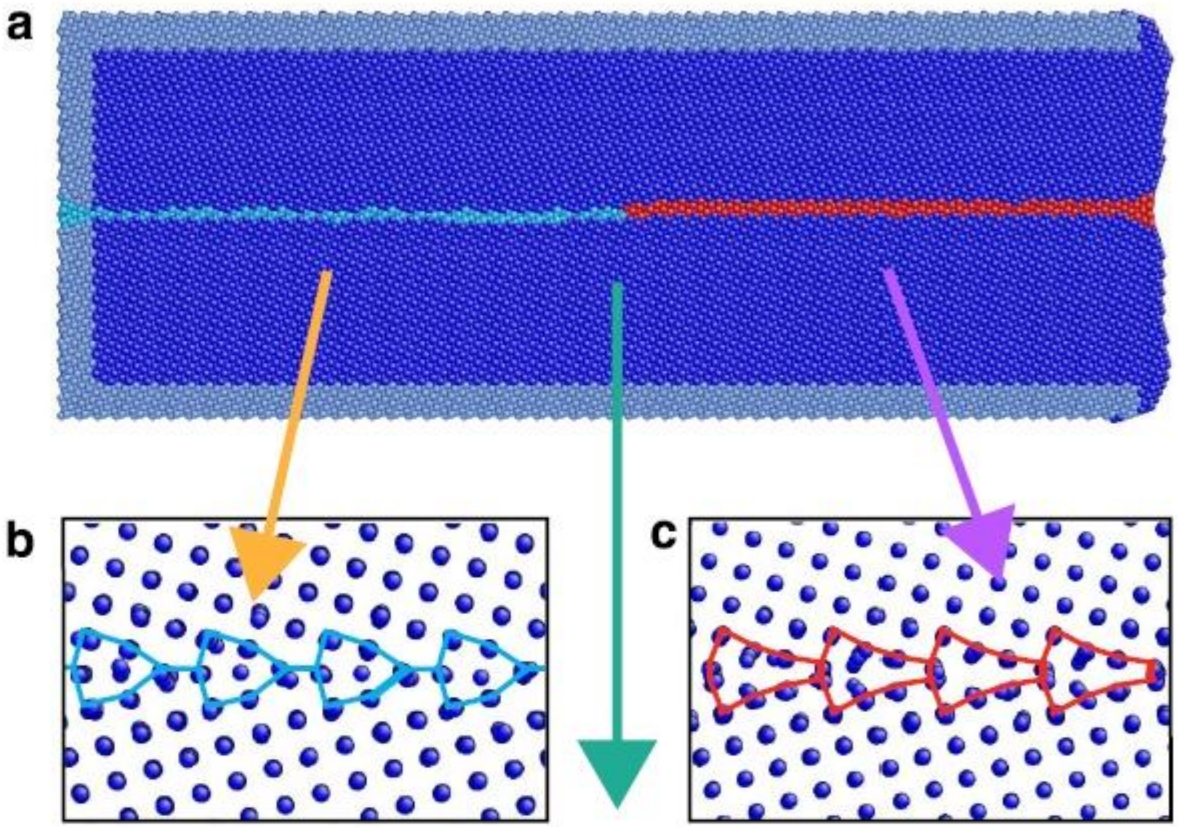


V. Borovikov *et al,* Nucl. Fusion **53** (2013) 063001

Background: self-healing mechanisms in NCs

3. GB phase transition

Owing to the presence of multiple metastable phases, grain boundaries can absorb significant amounts of point defects created inside the material by processes such as irradiation.



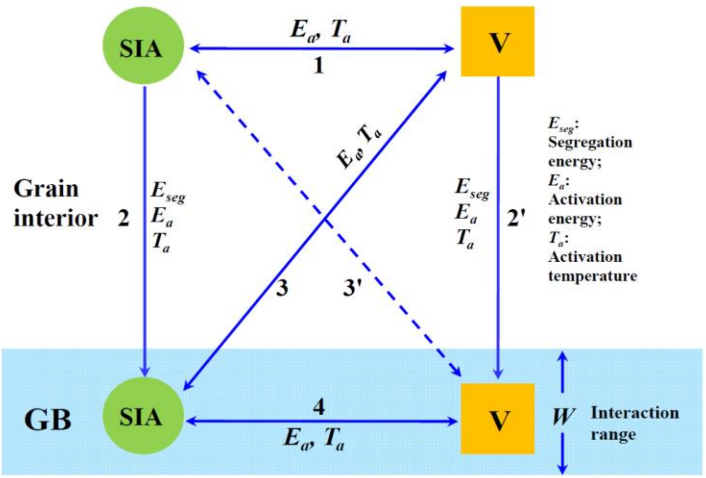
T. Frolov, *et al*. Nat. Commun. 4 (2013) 1899.

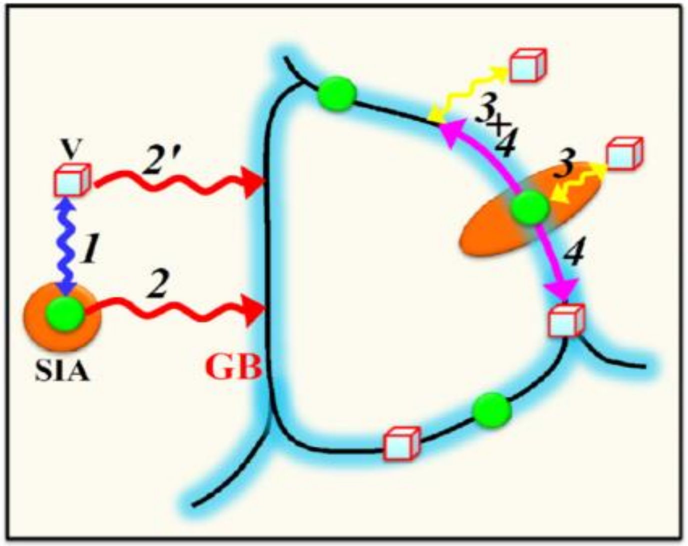
Background: self-healing mechanisms in NCs

4. Coupled interstitial motion along the GB and vacancy segregation

➢The self-healing capability of nano-crystalline iron is closely related to the coupling of the individual fundamental segregation and annihilation processes of vacancies and interstitials near the GB.

➢Although the interstitial is tightly bound to the GB after segregation, it efficiently removes the vacancies near the GB while moving along the GB, with the low-barrier region extending into the neighborhood of the GB and even into the grain interior.

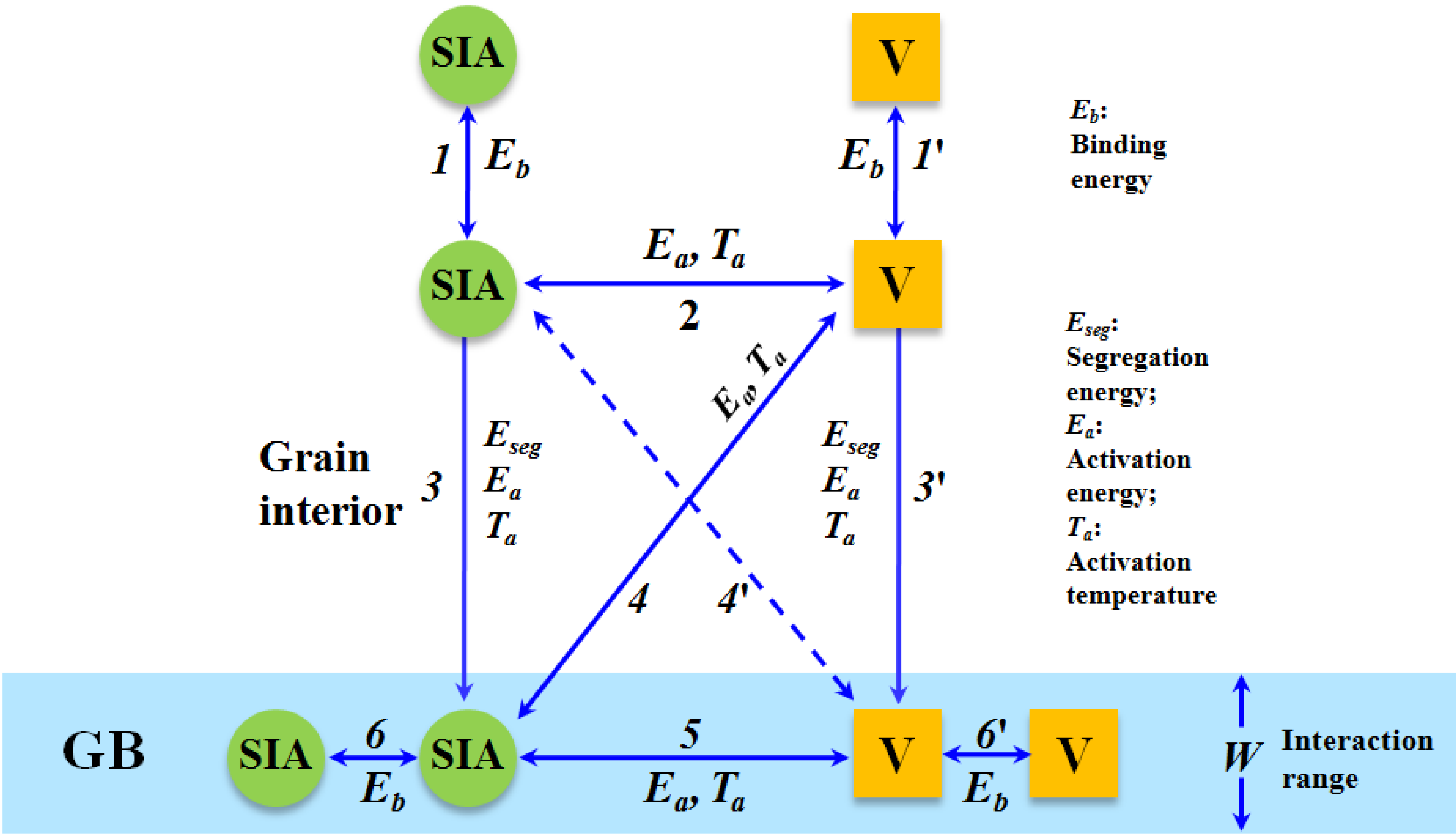




X. Li , *et al*. Acta Materialia 109 (2016) 115-127

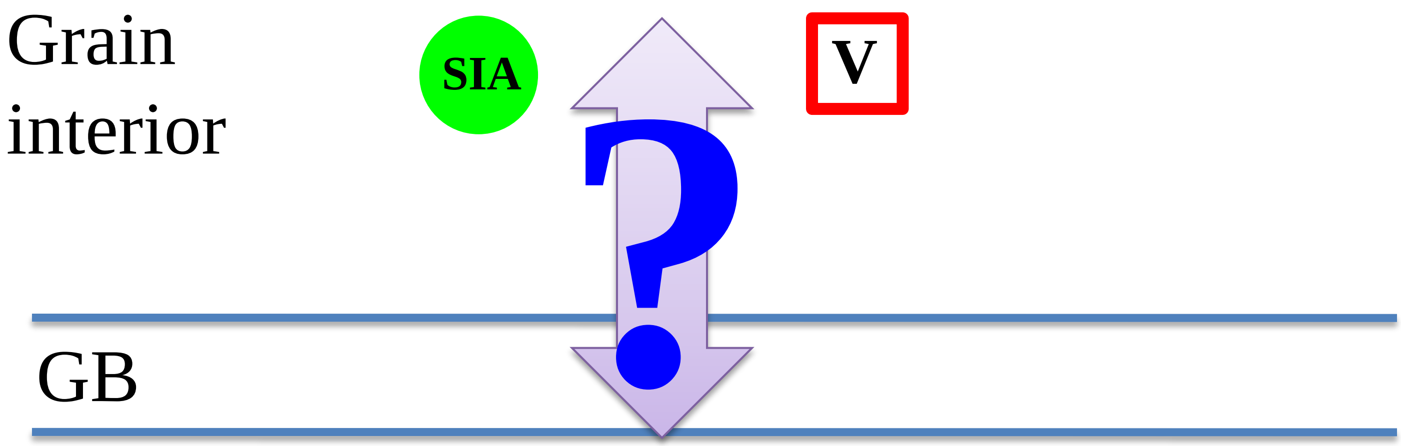
In irradiated nano-crystals

Actually, there are a large number of competitive processes involved in damage evolution, including diffusion, segregation, annihilation, clustering, emission of the interstitial (SIA), vacancy (V) and their clusters.



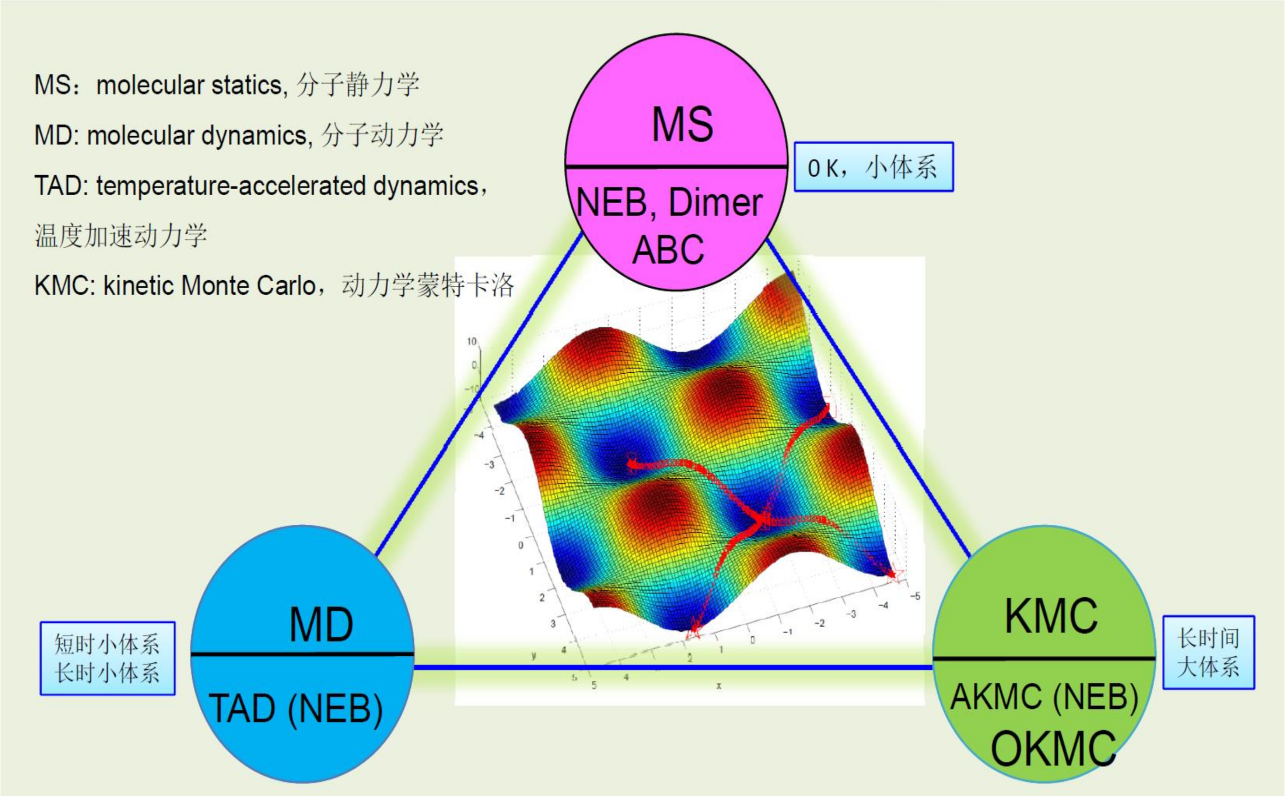
In irradiated nano-crystal W

W as a plasma facing material, will subjected to 14 MeV neutron irradiation, and a high density of low-energy H/He. Radiation defects are created in the material. These defects not only affect the mechanical property of W, but also introduce trapping sites for H/He ions. Suppressing of the displacement damage in W by introducing defect sinks into W is of great engineering significance.



Compared with other metallic systems, how the radiation-created interstitial, vacancy interact with the GB is not well understood. The interaction inherently occurs at multiple time and length scales, spanning from ps and nm to year and meter.

Simulation techniques at different scales



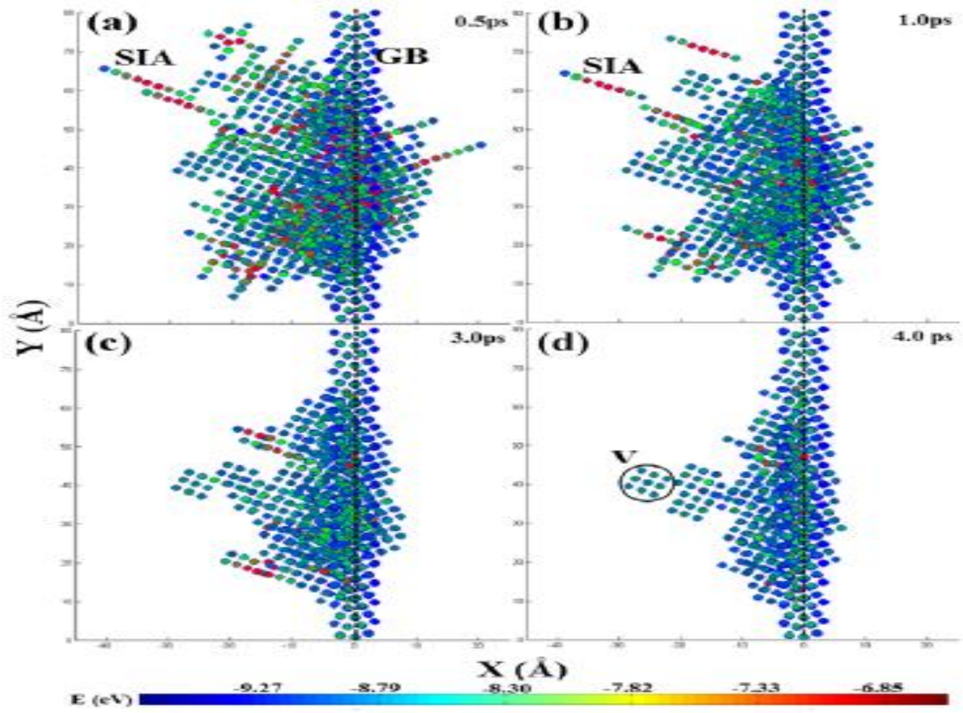
To reveal the interaction of the defects with the boundary, sometimes, the simulation techniques at different scales have to be combined, e.g., molecular statics, molecular dynamics, and Kinetic Monte Carlo methods. In recent five years, we have implemented these methods, and also developed some new calculation methods, which were employed sequentially to investigate the interstitial and vacancy behavior in nano-crystals W and Fe. Generally, parts of these methods are combined to give an across-scale insight into the radiation damage healing process in nano-crystal tungsten.

Results:

1. Fundamental interaction of the interstitial and vacancy with the grain boundary

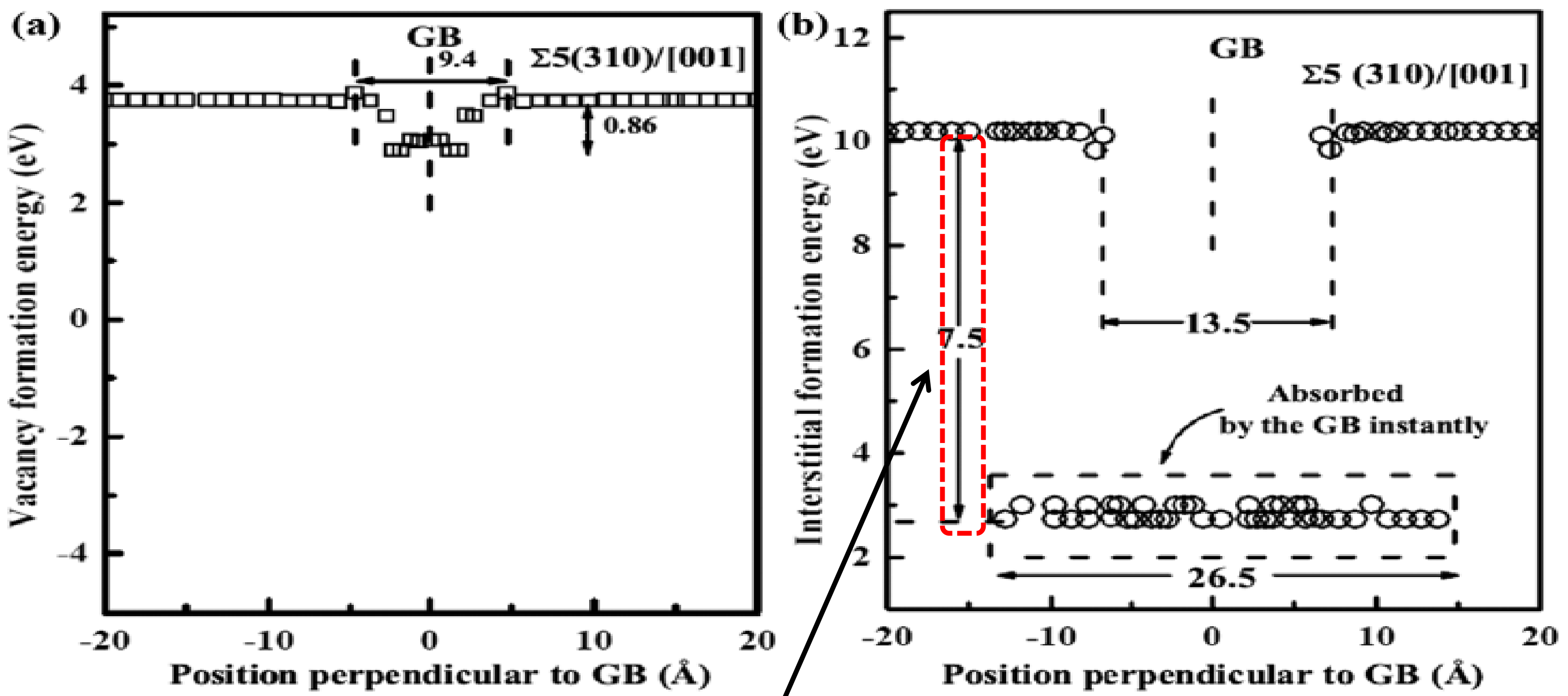
Results: Primary radiation damage near the GB

We started with the simulation of displacement cascades near a 5(3 1 0)/[0 0 1] symmetric tilt GB in bcc W at 600 K.
The cascade was initiated by a 6 keV PKA.



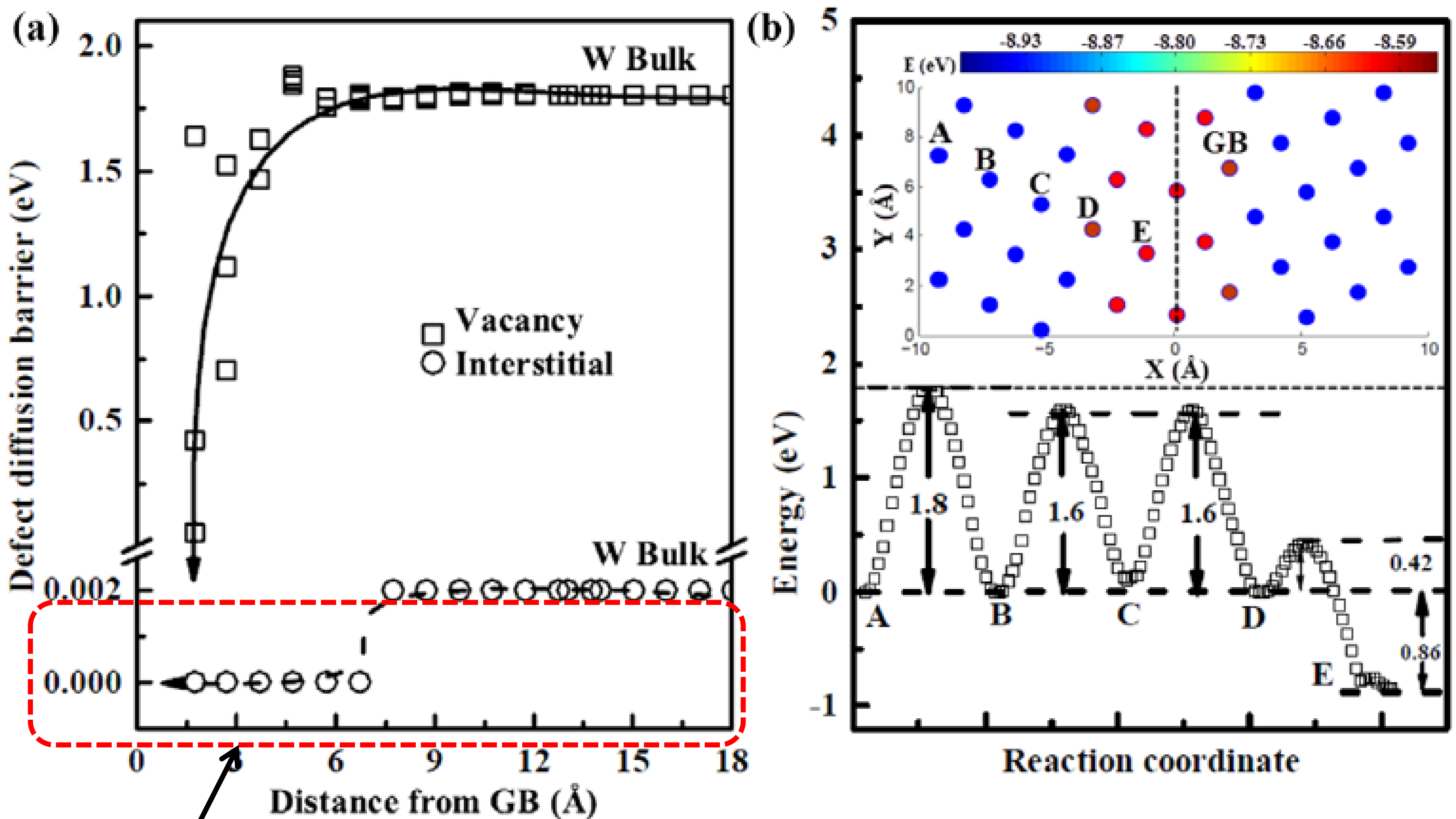
During a time period of 50 ps, it was found the GB preferentially absorbed interstitials, while vacancies remained immobile. Some di- and tri- vacancy were also produced near the GB.

Results: Formation energy for the vacancy and interstitial near the GB



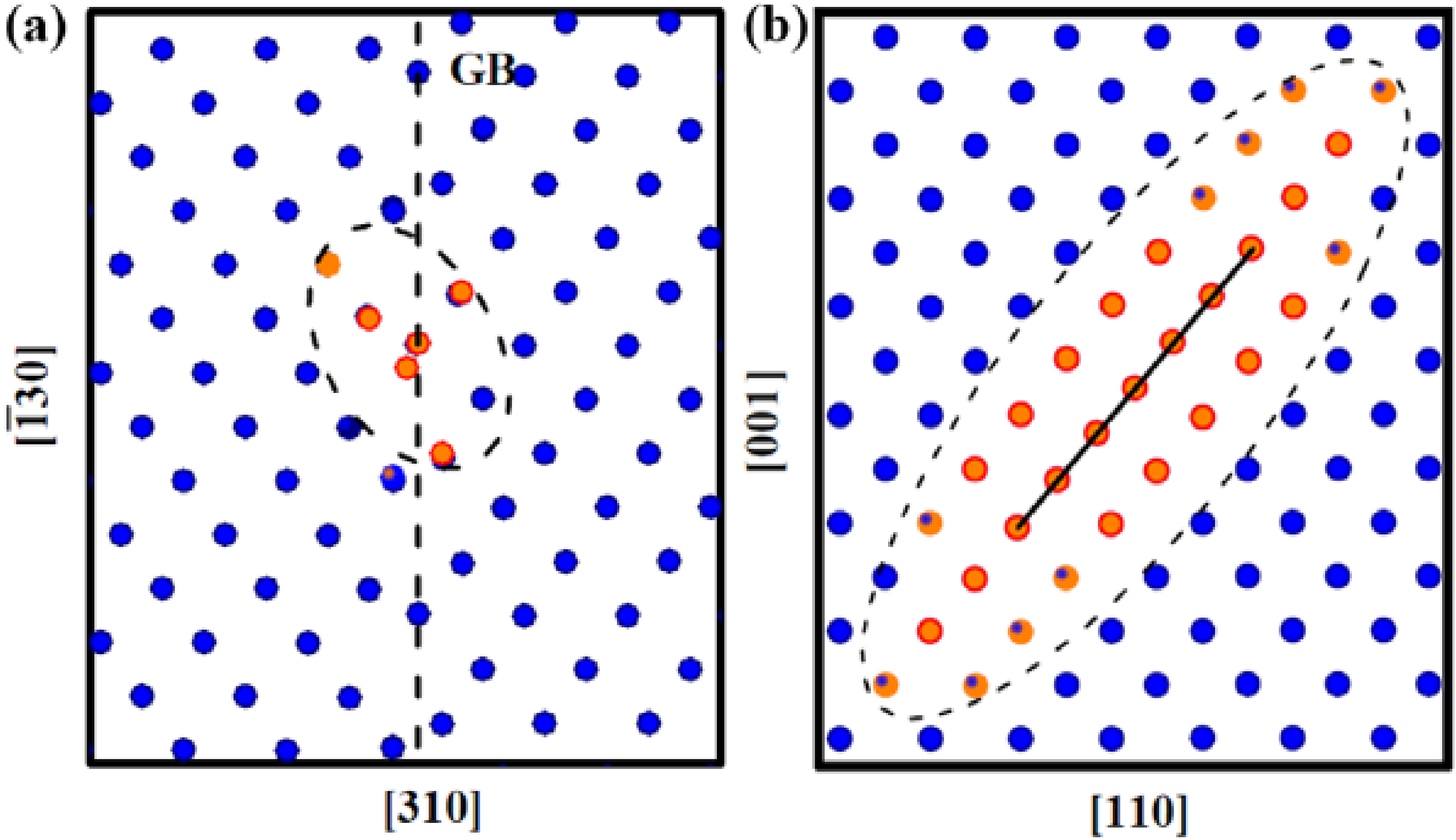
Calculations of defects formation energies show that the SIA is extremely tightly bound to the GB. The binding energy for the vacancy and interstitial is 0.86 versus 7.5 eV, respectively.

Results: Diffusion of the vacancy near the GB



Calculations of diffusion barriers near the GB show that the SIA has extremely high mobility. The vacancy diffusion near the GB is greatly accelerated.

Results: Spontaneous annihilation region at the GB and in the bulk



Similar energetic feature around the interstitial: there forms an spontaneous annihilation region both near the GB and in the bulk.

Results: Basic interaction parameters

	(to characterize the sink for defects)			(to characterize the catalysts for V–SIA annihilation)		
	V_m^{bulk}	V_m^{GB}	SIA_m^{bulk}	SIA_m^{GB}	ann_{V-SIA}^{GB}	$ann_{V-SIA}^{near-GB}$
Barrier (eV)	1.8	0.98	0.002	0	0	0.31
T_a (K)	702	382	1	0	0	121
Range (Å)		9.4		26.5	10	11.6
Fraction (%)		3		8	3	3

The GB enhances diffusion and annihilation of interstitials and vacancies within a limited region. MS calculations provide necessary parameters for high level simulation of damage evolution at long time scale.

X. Li et al., Nuclear Fusion (2013), 53, 123014

X. Li et al., Journal of Nuclear Materials (2014), 444, 229–236

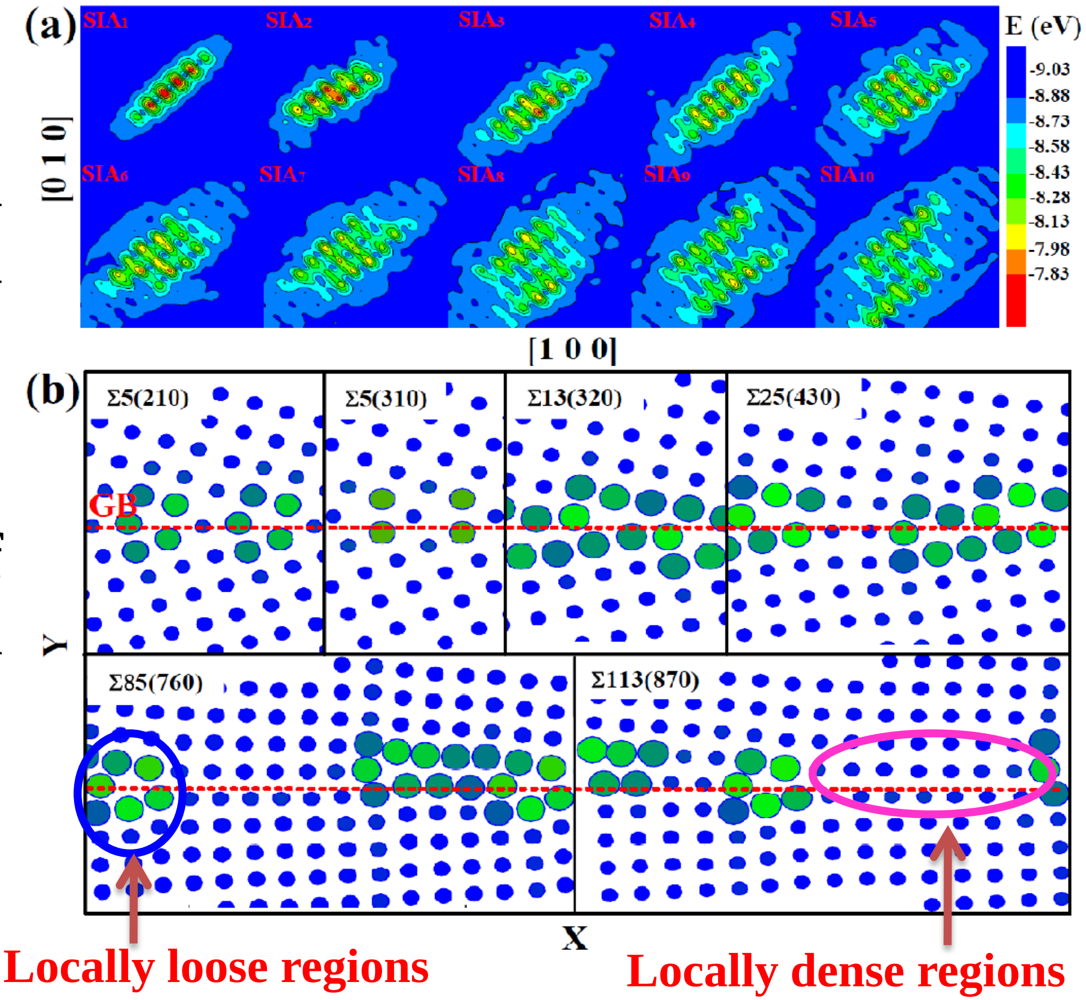
2. Interstitial clusters behavior near the grain boundary:

I. Segregation and reflection

Atomic structures of the SIA_n and GBs

- The bulk SIA-cluster in W is composed of parallel <111> crowdions.

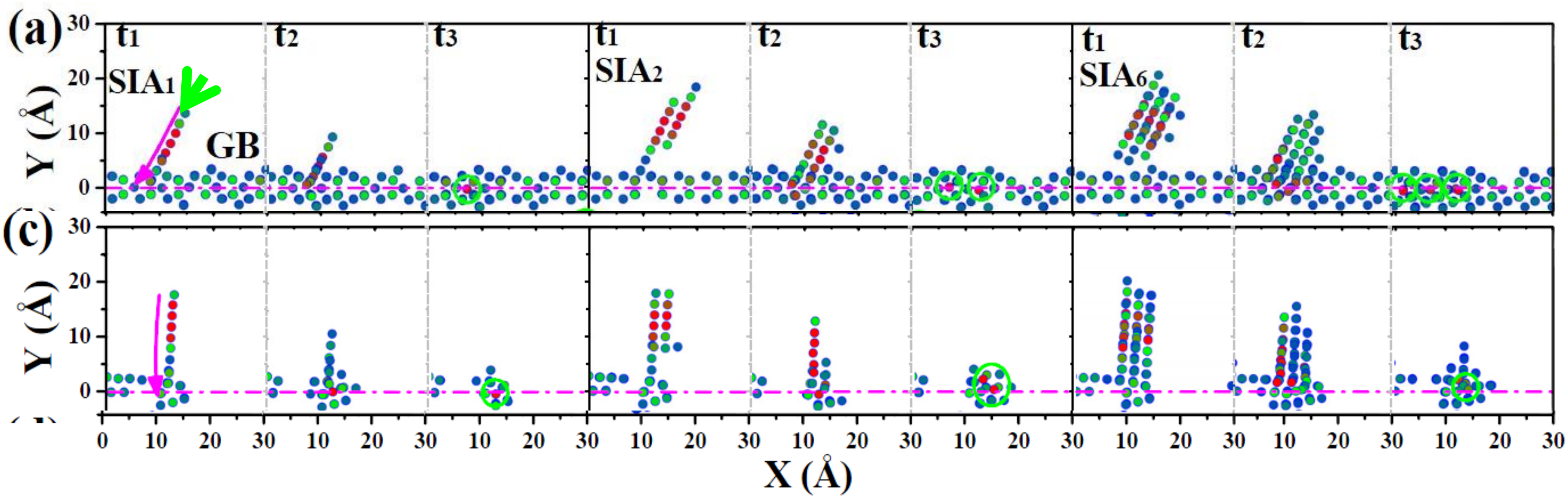
- The GB is composed of the locally loose region and also dense region.



Then, how does the local GB structures affect the SIA-cluster behavior nearby and the annihilation mechanism ?

Results: Segregation

Pure Σ5

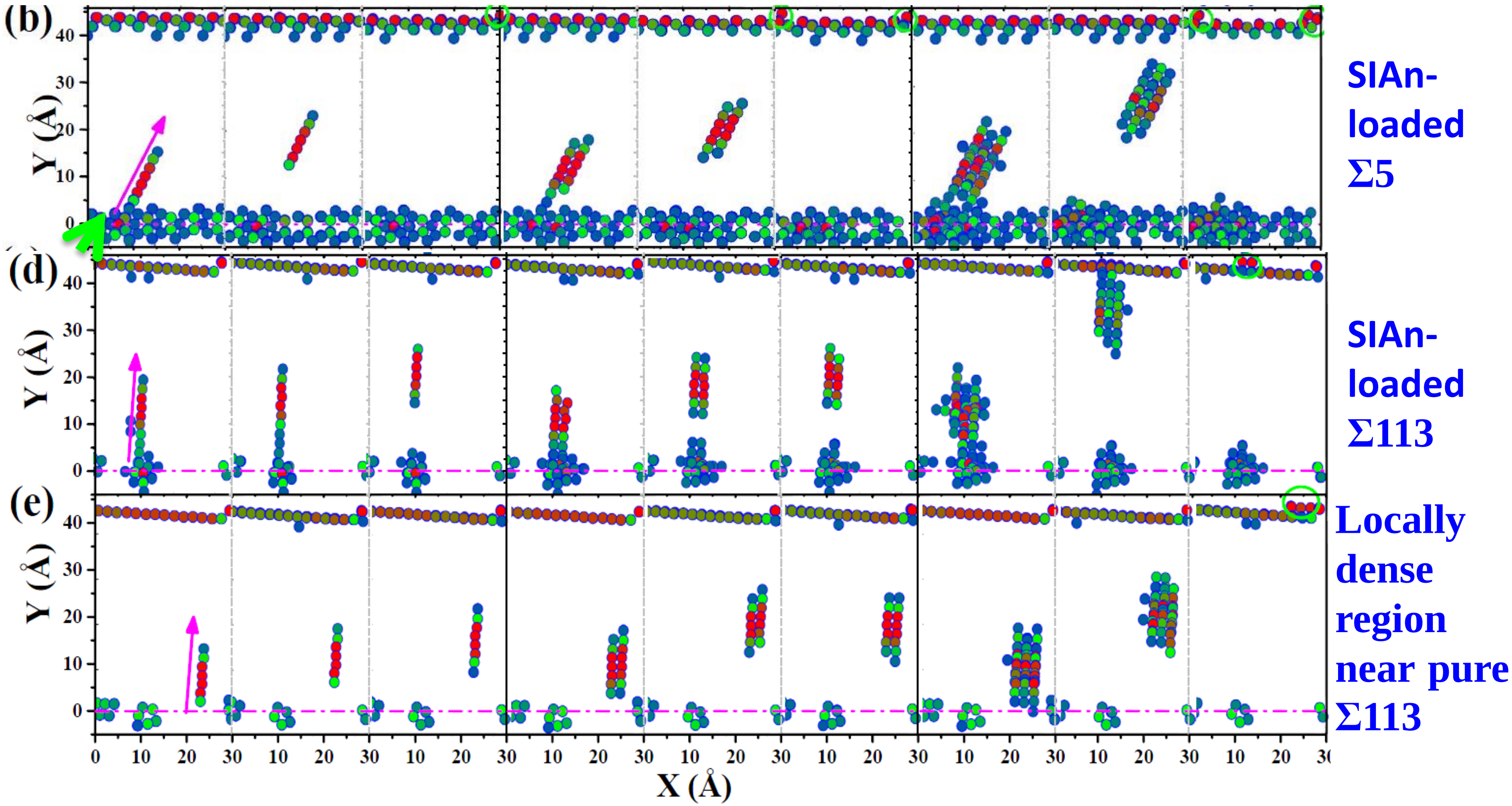


Locally loose region near pure Σ113

- ✓**A SIA$_n$ was intentionally put at several typical sites about 10 Å away from the GB.**

- ✓**Near the locally loose region, both the single SIA and SIA-cluster were always observed to move towards the GB via replacement-atom sequences during multiple runs of MD simulations. Therefore, the locally loose GB region acts as a sink for interstitial and clusters.**

Results: Reflection



Near the locally dense region, the SIA cluster was observed to be rebounded back into the grain interior in MD simulations of SIAn behavior near the GB. This motion was termed as the interstitial reflection by the GB.

Results: Reflection

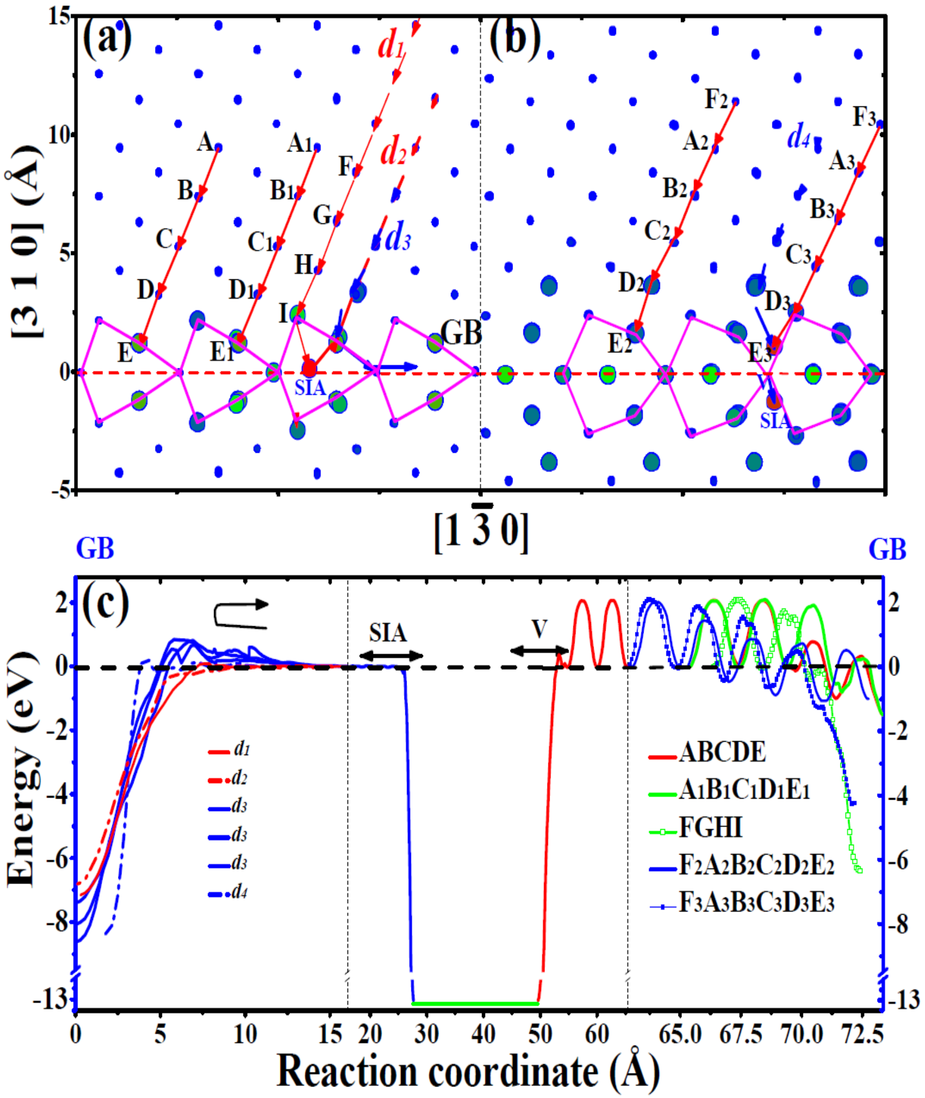
✓We speculated that the locally loose region either could not accommodate excess SIAs, consequently scattering them into the neighboring vacant region or even reflecting them back into the grain interior.

✓To support the above speculation, more MD simulations were designed and performed. First, the locally loose region was artificially loaded with the SIA_n. Then, it was more frequent to observe the reflection of the newly produced SIA_n. The newly created SIA_n was reflected back into the bulk as a whole rather than dissociation.

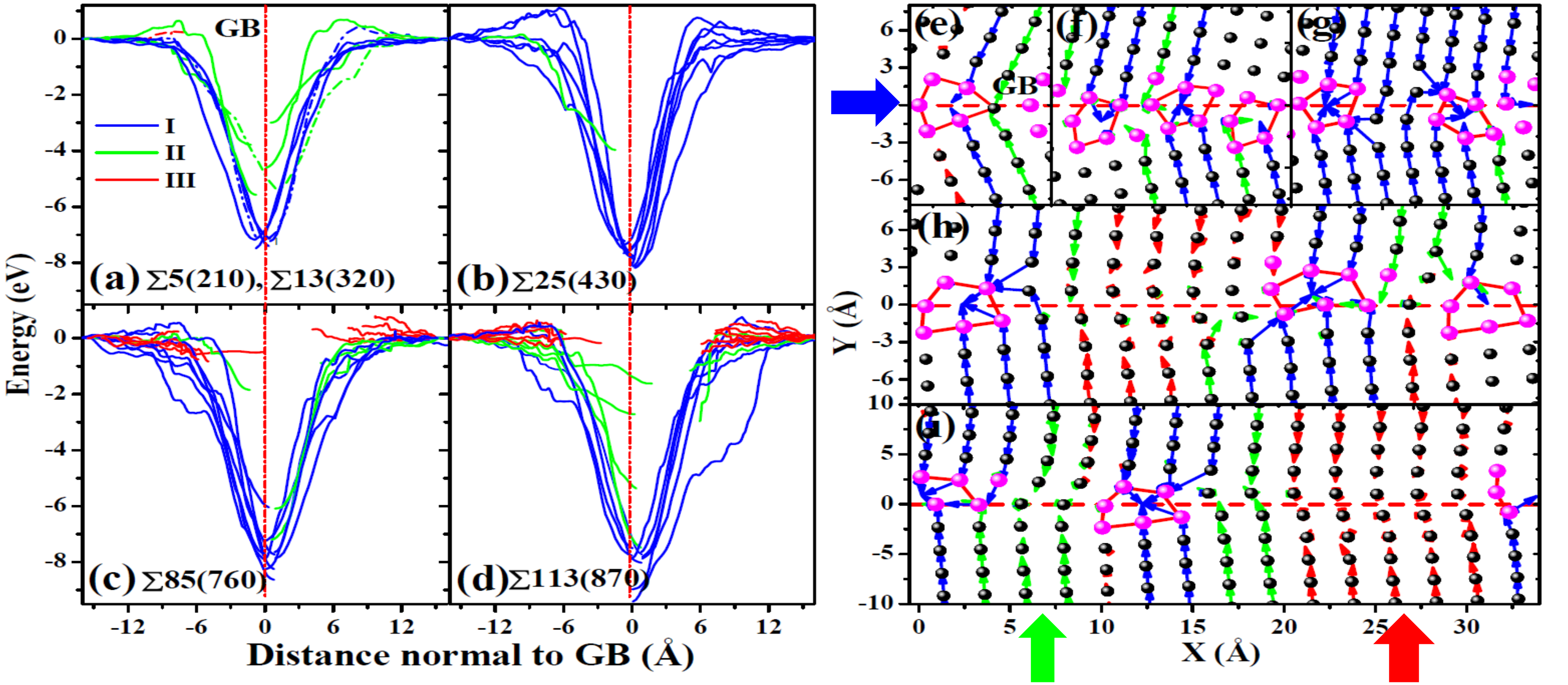
Results: Energy landscape for single SIA near Σ5

✓**To understand the trapping and reflection of the SIA_n by the GB, the kinetics of the SIA near the GB were investigated.**

✓**Near the locally pure GB, a descent energy landscape was obtained (Fig. (c)), e.g., along paths d_1 and d_2 (Fig. (a)). It suggested an energetically and kinetically favorable trend for the SIA to be trapped by the GB. The prediction was consistent with the aforementioned current observations in MD simulations and in other studies.**

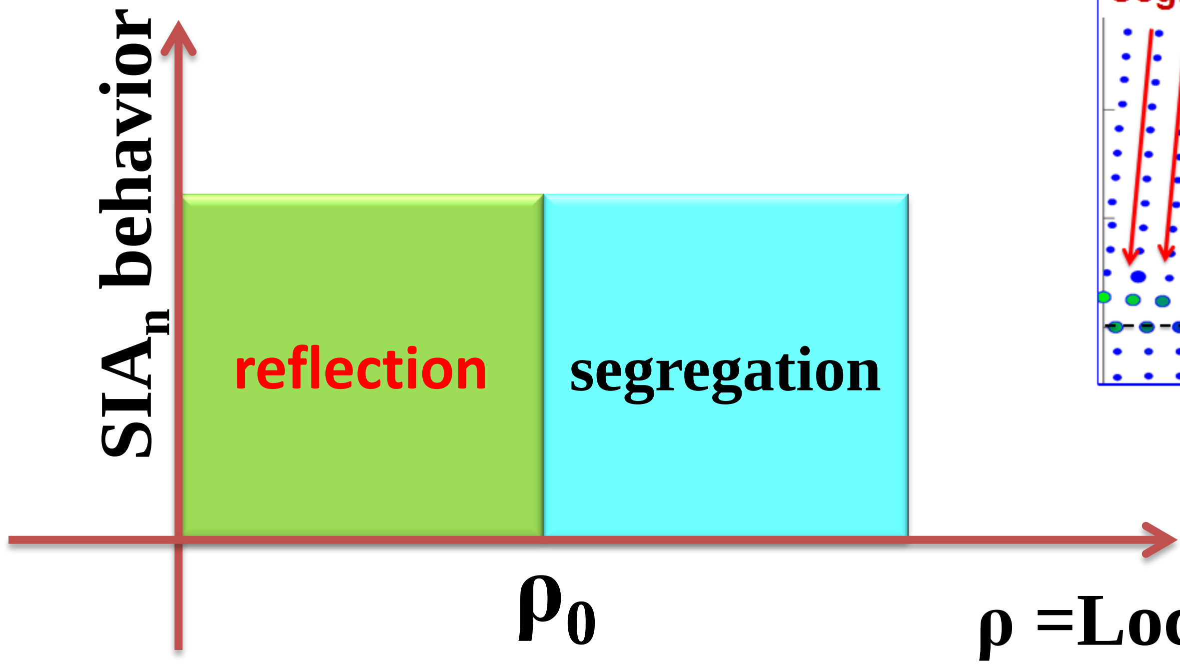


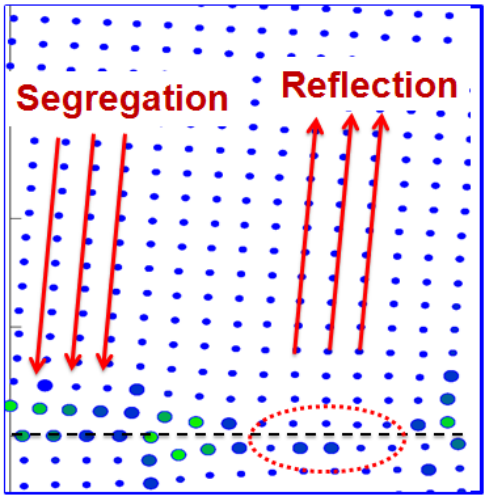
Results: Energy landscape for single SIA near other GBs



- ✓ **We further calculated the SIA energy landscape near other GBs;**
- ✓ **Three types of the SIA energy landscapes are obtained: downhill (I); uphill & downhill (II); nearly uphill (III).**
- ✓ **This is closely related to local GB structures. The SIA tends to reside at a local loose region barrier-freely or overcoming a barrier while the absorption is prohibited near a tight region.**

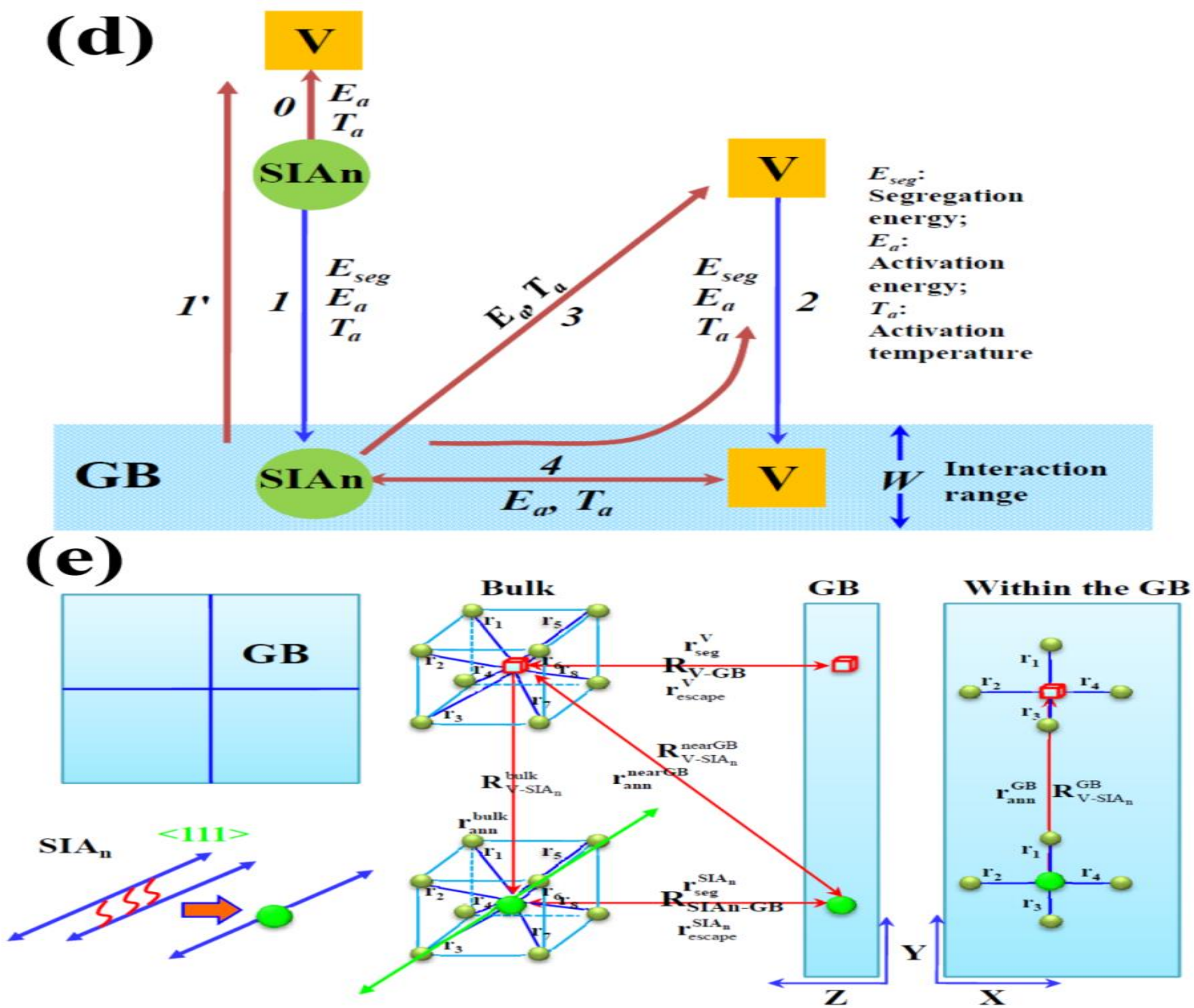
Results: Reflection





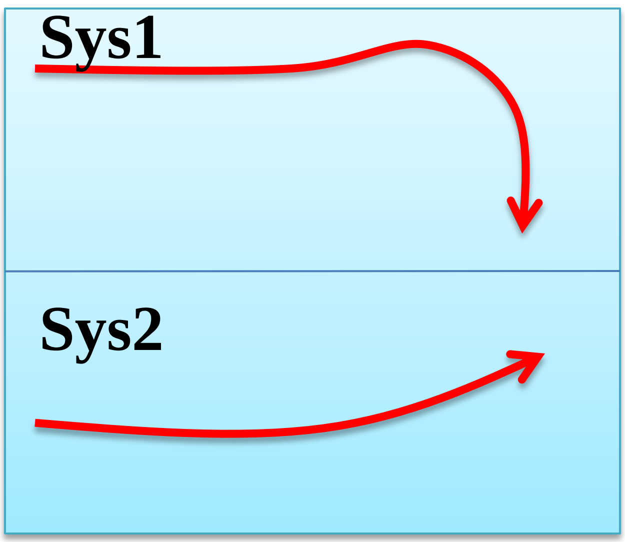
✓ **Therefore, a more general conclusion is: for the interstitial and interstitial cluster of parallel <1 1 1> crowdions, their behavior near the GB, segregation or reflection, is determined by the local GB density. As the density is below a certain value, the corresponding region will reflect interstitials. Otherwise, the region acts a sink for interstitials.**

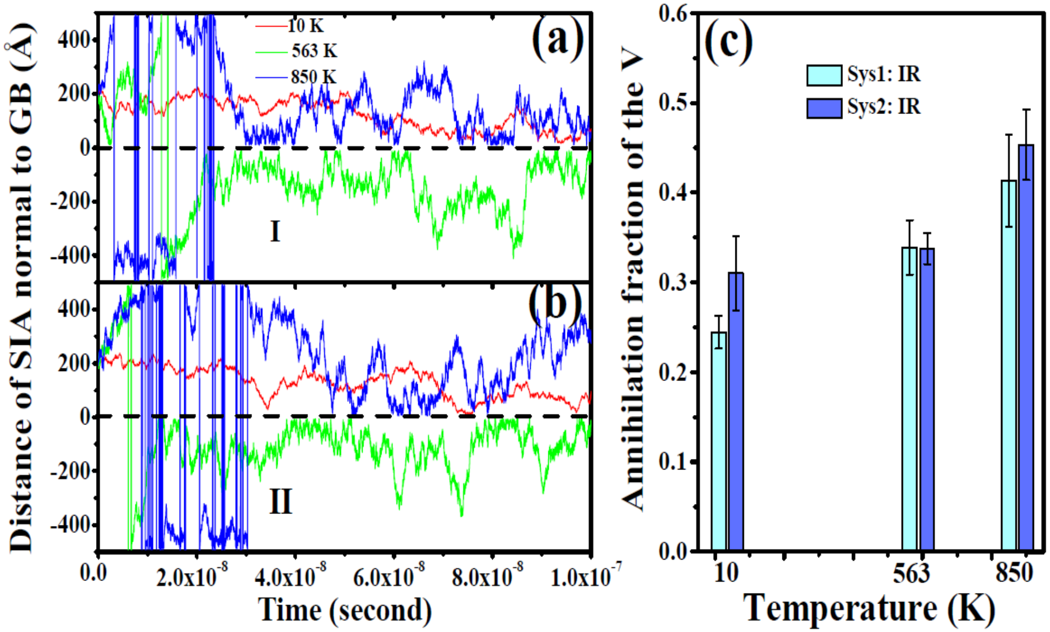
Results: OKMC model for evaluating the effect of IR on SIA_n-V annihilation



- ✓ **To evaluate the effect of the interstitial reflection on the annihilation capacity, we performed OKMC simulations.**

Results: Effect of IR on SIA_n-V annihilation





- ✓ **We designed two types of the SIA energy landscape. One is climbing and then descent; the other one is just climbing.**
- ✓ **The annihilation of bulk vacancies was enhanced due to the reflection of an interstitial-cluster of parallel <1 1 1> crowdions by the GB.**

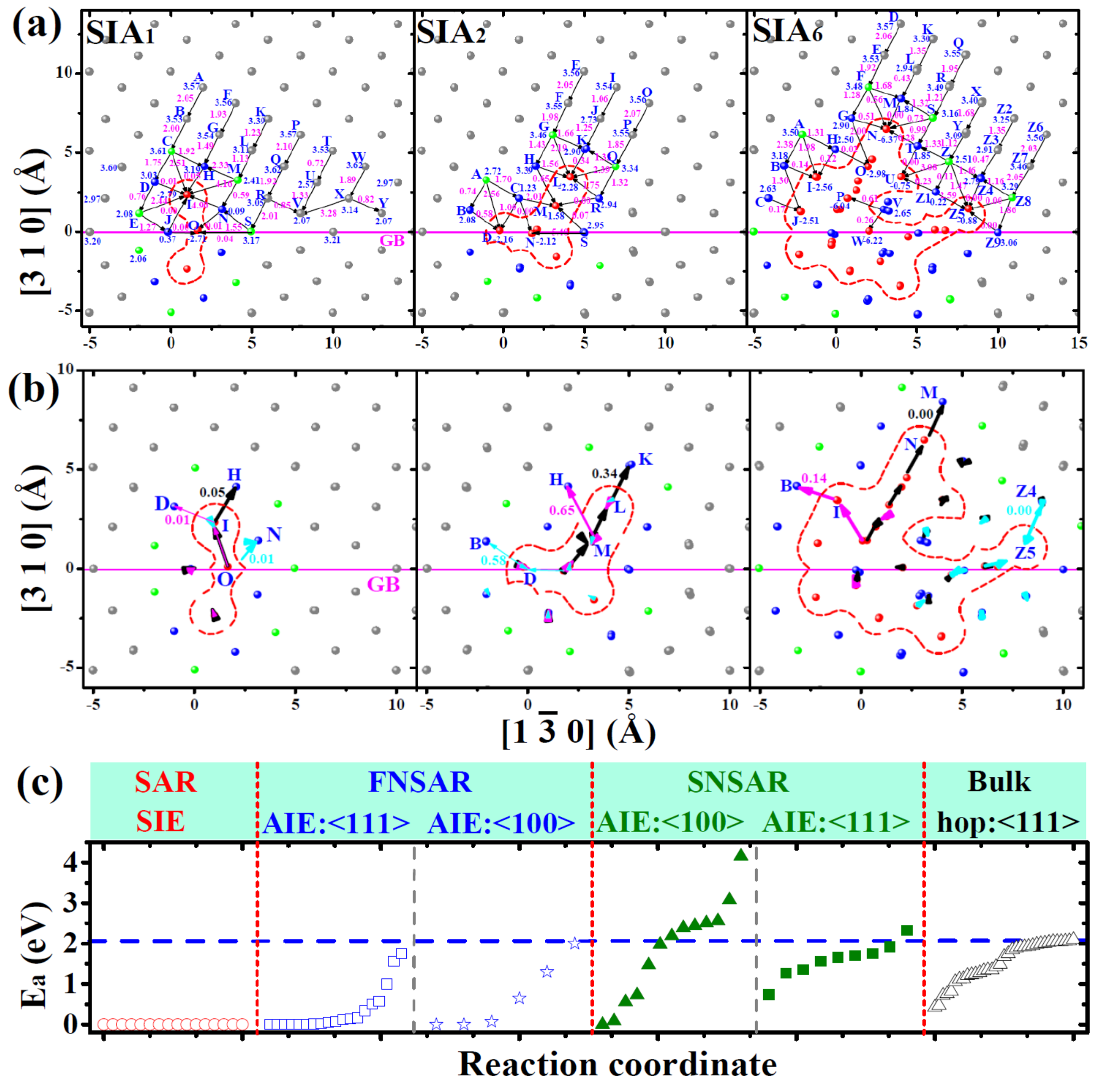
2. Interstitial clusters behavior near the grain boundary:

II. Dynamic interstitial emission

Results: Static SIA$_n$-V interaction

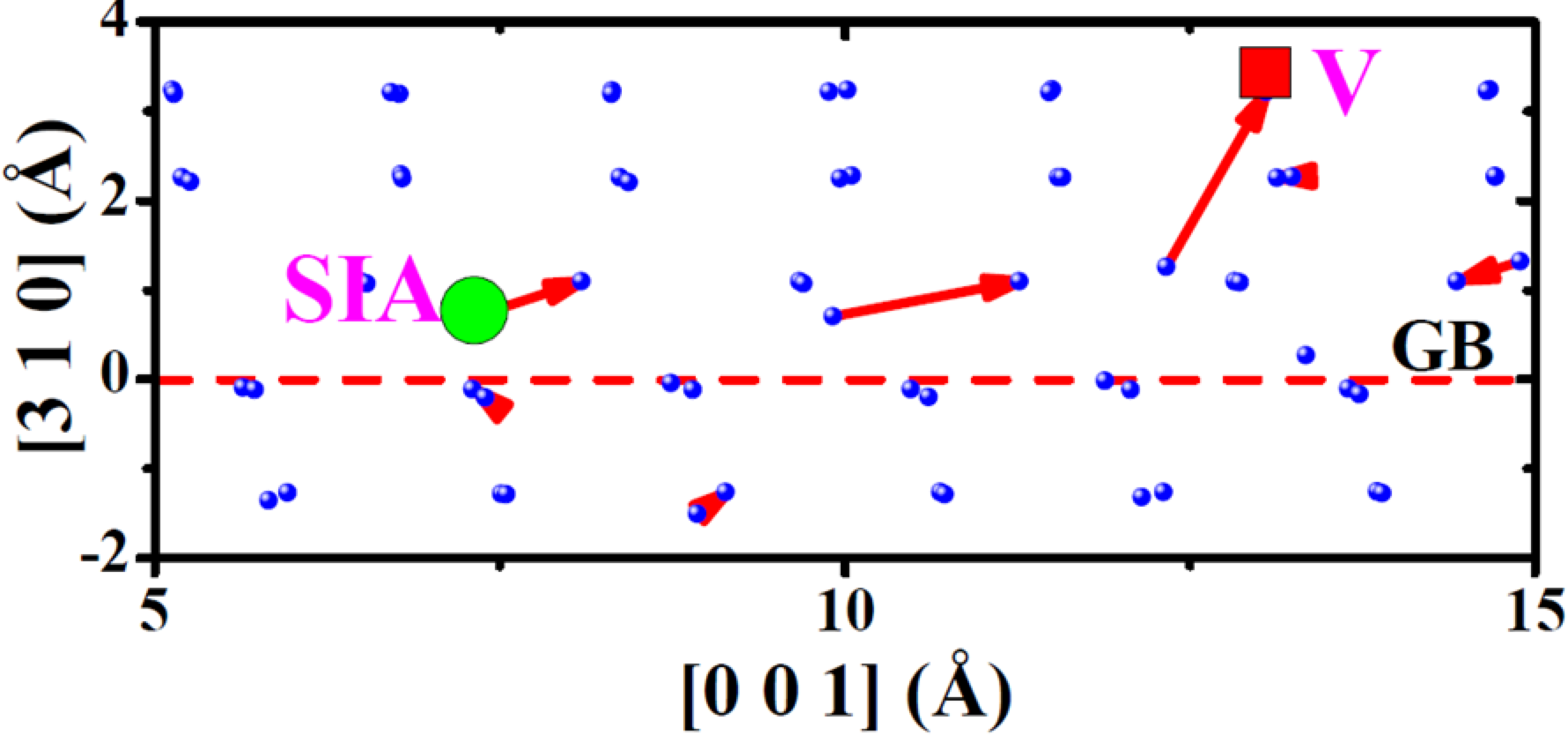
✓We first investigated the static interaction of small interstitial clusters (SIA$_n$) with the vacancy (V) near the GB.

✓We calculated the location and diffusion of a V around a SIA$_n$. **The reduced vacancy formation energy (Evf) around a SIA$_n$ indicated the enhanced occupancy of the V nearby the SIA$_n$. A spontaneous annihilation region formed around a SIA$_n$ (“SAR”). Meanwhile, the annihilation mechanism could be termed as spontaneous interstitial emission ("SIE”).**



✓**The V near the first and second nearest neighbors of the SAR (“FNSAR”, “SNSAR”) could also recombine with a SIA in the SIA$_n$ at a low barrier via activated IE (“AIE”). Out of these regions, the diffusion of the V via conventional hop was also accelerated.**

Results: Dynamic SIA_n-V interaction near the GB



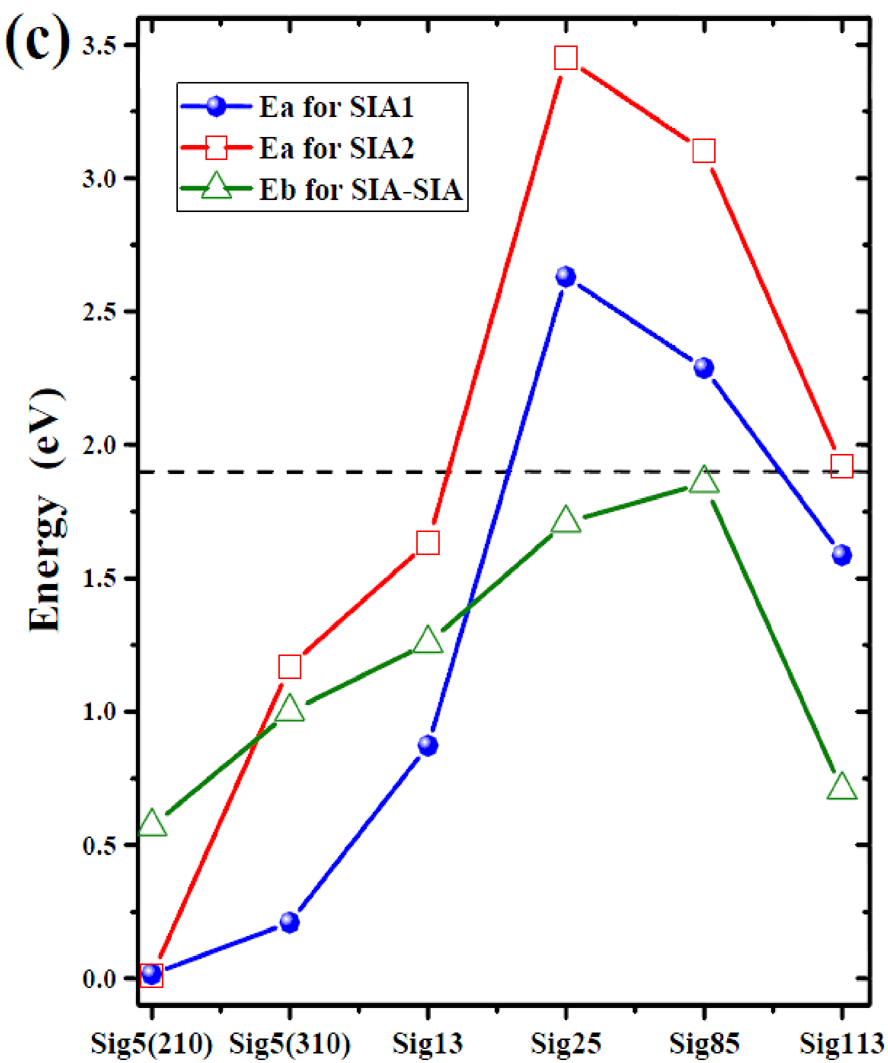
By performing MD simulations of the interstitial (SIA) and vacancy (V) behavior near a Σ5(310) grain boundary (GB) in tungsten, we found the SIA first moved along the GB and then recombined with a V near the GB. Such mechanism should depend on the diffusion property of the SIA along the GB.

Results: Diffusion of SIA_n along the GB

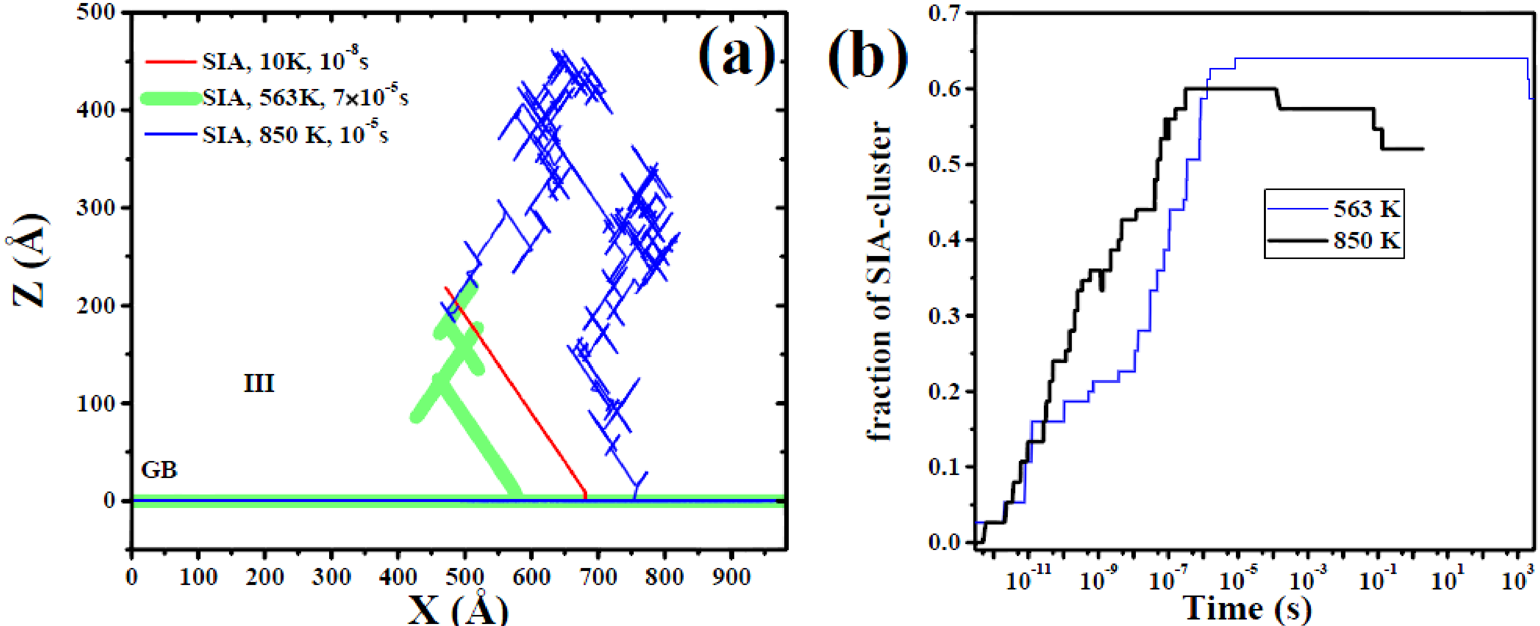
✓Therefore, we calculated the diffusion of the single SIA and di-SIA along more GBs.

✓We found both the diffusion energy barrier and the binding energy depend on the GB structure.

✓The diffusion energy barrier for the SIA is smaller compared with that for the V diffusion in the bulk except in GBs of Σ25 and Σ85. The binding energy is over 0.6 eV. Thus **multiple SIAs at the GB can be clustered. Compared with the single SIA, the mobility of the SIA_2 is lower**, which is, however, comparable to that for the V except in GBs of Σ25 and Σ85.



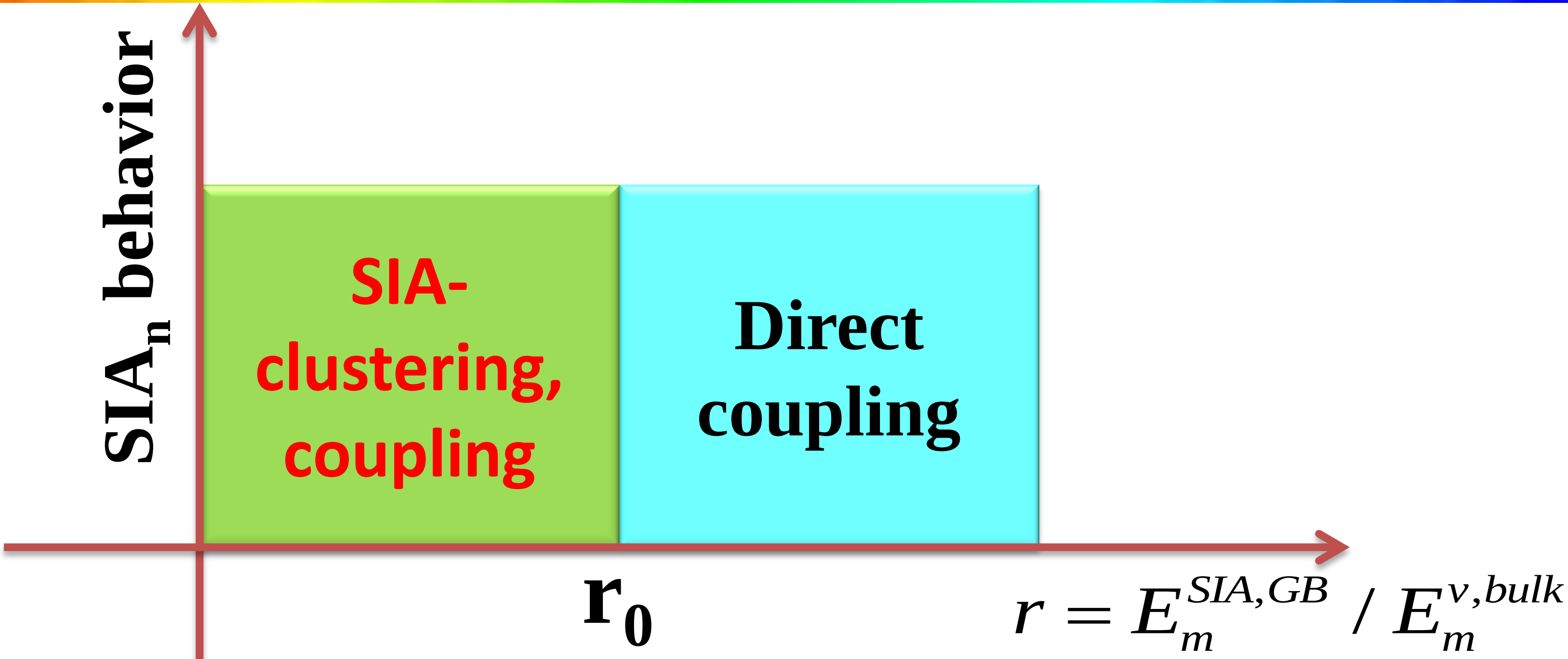
Results: Dynamic SIA_n-V annihilation prospect



✓The dynamic annihilation prospect at several typical experimental temperature values was then investigated by the OKMC method. The focus was on the long-ranged diffusion of the defects and the collective/coupled motion of defects at the GB and near the GB.

✓As the diffusion energy barrier of the SIA along the GB ($E_a^{SIA,GB}$) is very high (e.g. in GBs of Σ25 and Σ85), the SIA is not activated at the GB at the temperature of interest e.g. 10, 563 and 850 K. In this case, the SIA is pined at the GB after segregation from the bulk. Then, the bulk V either hops towards the GB once activated or remains immobile in the bulk as it is not activated. In this case, the annihilation of the V with the SIA is described by their static interaction.

Results: Dynamic SIA_n-V annihilation

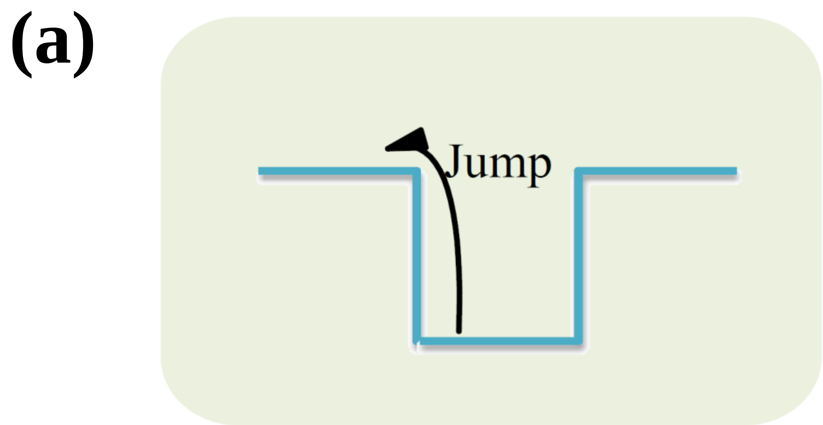


✓ **Therefore, a more general conclusion is: the annihilation mechanism at the GB is determined by the relative value of the interstitial diffusion energy barrier along the GB and that for the bulk vacancy diffusion. As the ratio is below a certain value, the interstitial segregated to the GB moves along the GB, gets clustered therein, and then annihilates the vacancy via the coupled motion of the cluster along the GB and the motion of the vacancy towards the GB. Otherwise, the annihilation proceeds via the coupled motion of the interstitial along the GB and the segregation of the vacancy nearby.**

Li, et al., Nuclear Fusion (2017, revised. **Acta Materialia**, (2016), 109, 115-127

3. A general insight into the interstitial emission near a defect sink

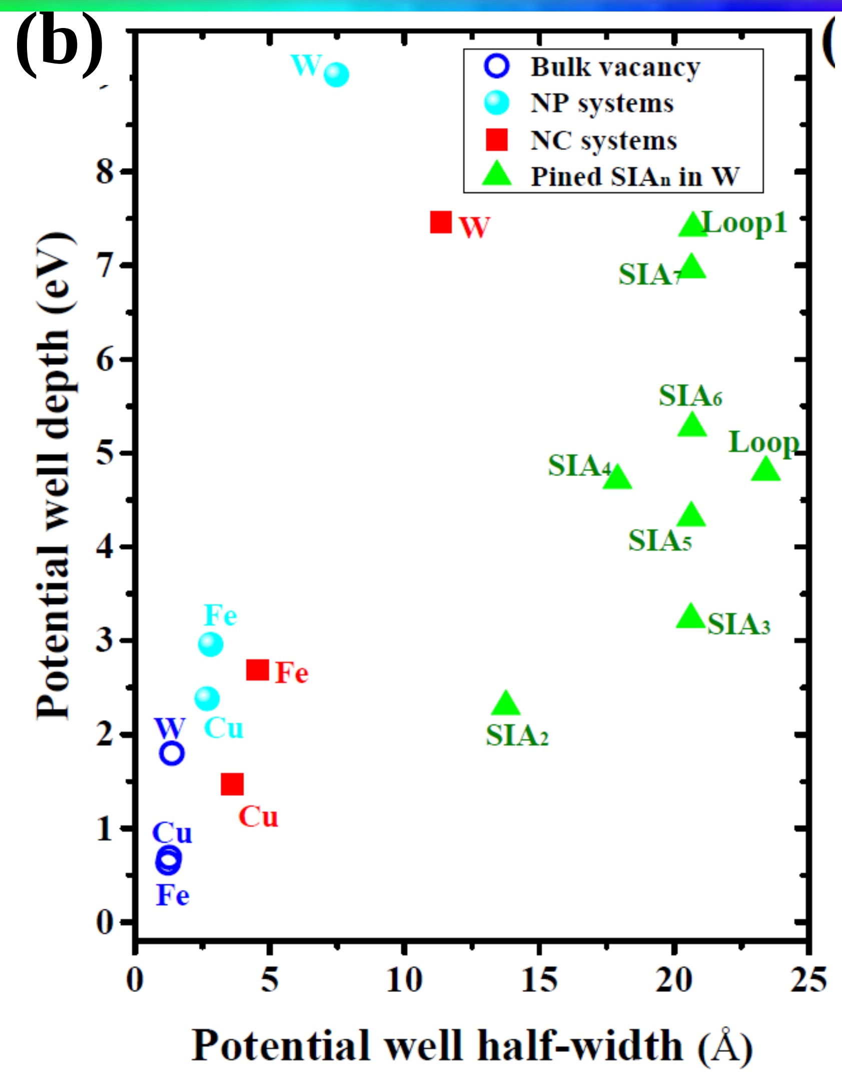
Results: Squared potential well for the SIA



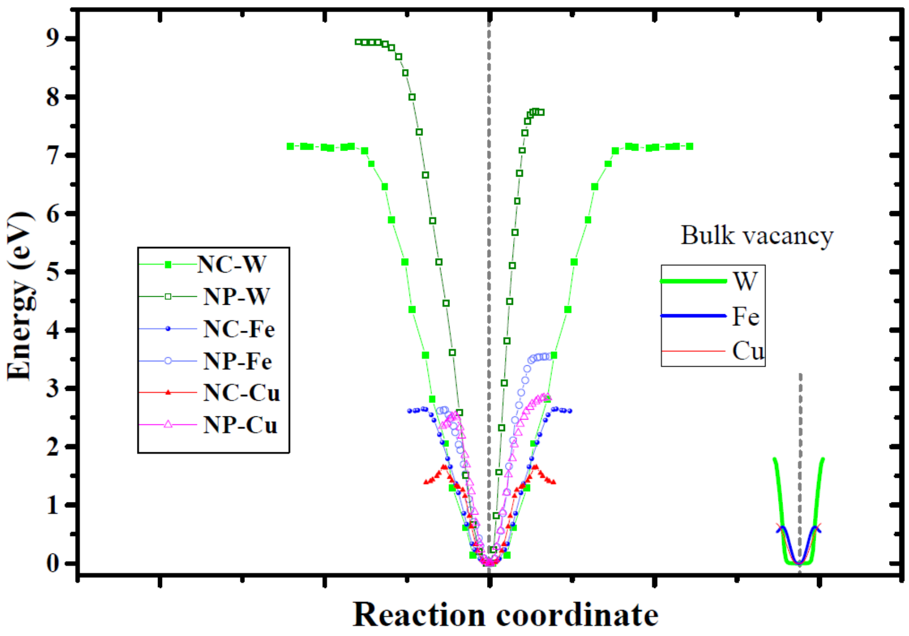
✓Generally as we say a defect sink binds tightly with an interstitial, leading to the difficulty in the emission of the interstitial out of the sink, we have intuitively considered the potential-well at a sink as a squared one.

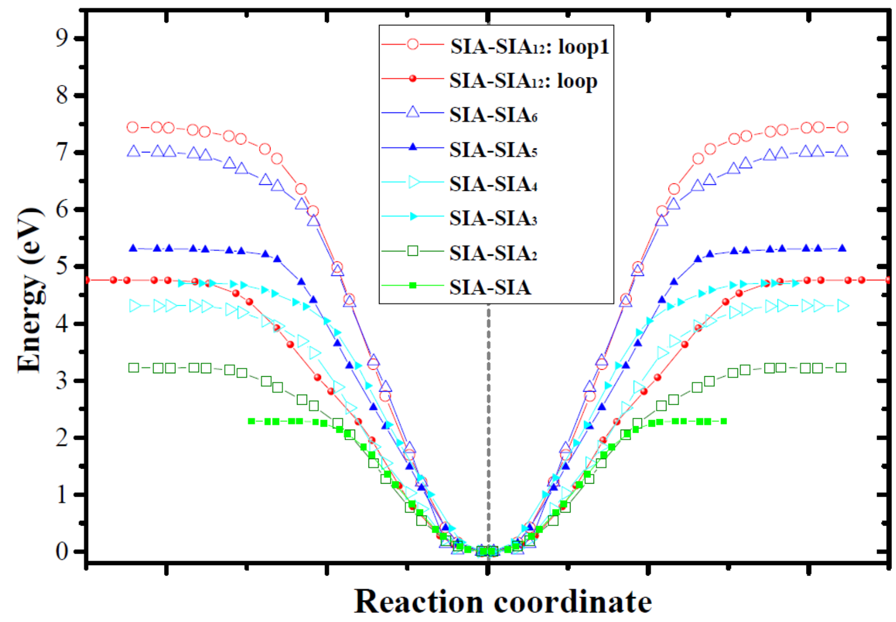
✓We considered three types of defect sinks, the SIA-GB, SIA-surface, SIA-SIA_n .

✓We calculated the depth (binding energy) and the potential-well half-width (a half of the SIA-sink interaction range). The two parameters severely depend on the system.



Results: Potential well for the SIA

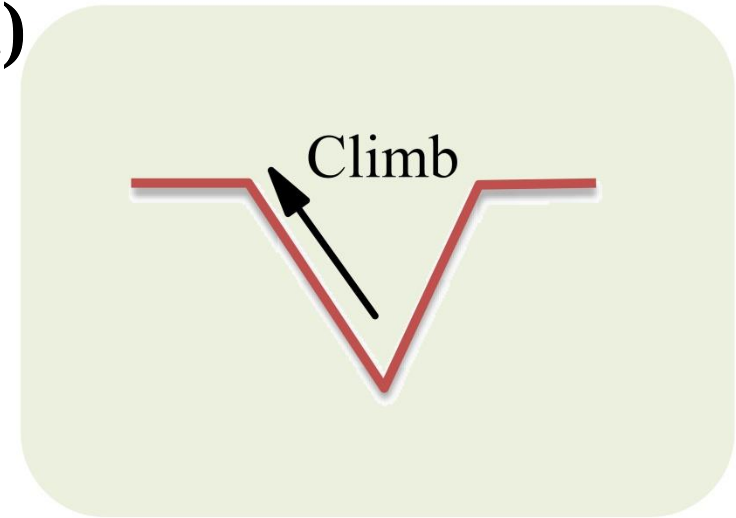




✓**By forcing an interstitial into the GB/surface/SIA$_n$, we calculated the potential-well of an interstitial near these defect sinks.**

Results: Triangled potential well for the SIA

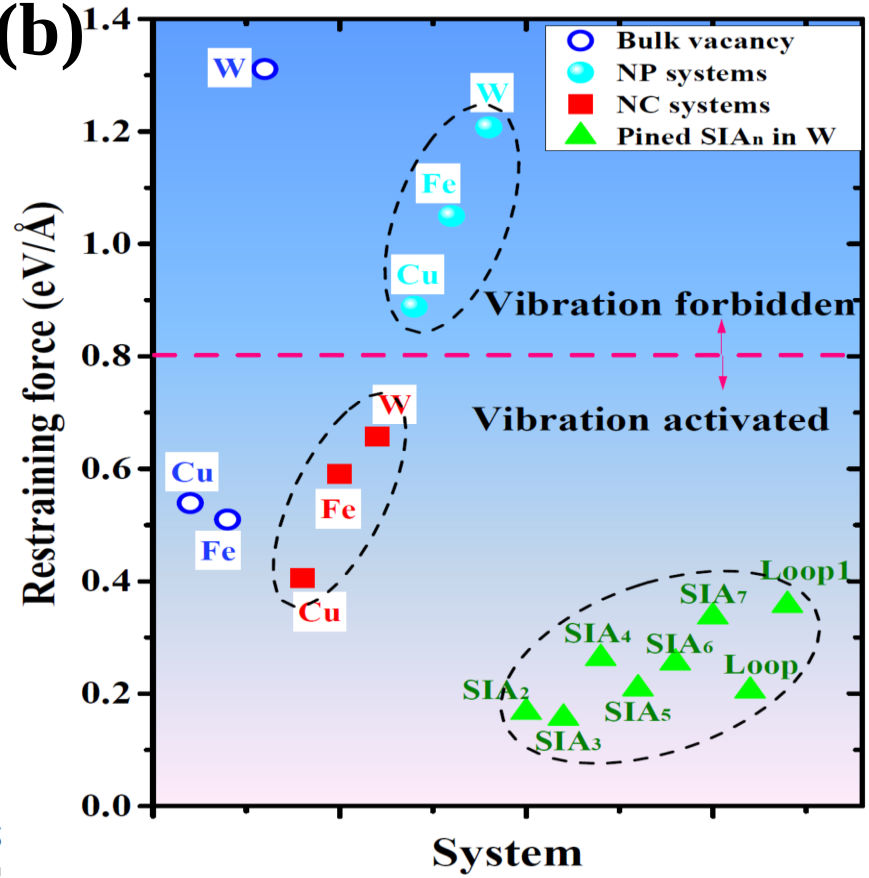
(a)



✓We found the potential-well exhibited a triangle shape. The potential well was thus approximated by a triangled one.

✓Based on this concept, the slop of the well acts as a common indicator for measuring the difficulty for an interstitial emission from a sink. The slop has a physical meaning of the energy barrier that an interstitial overcomes as migrating over the distance of one Å.

(b)



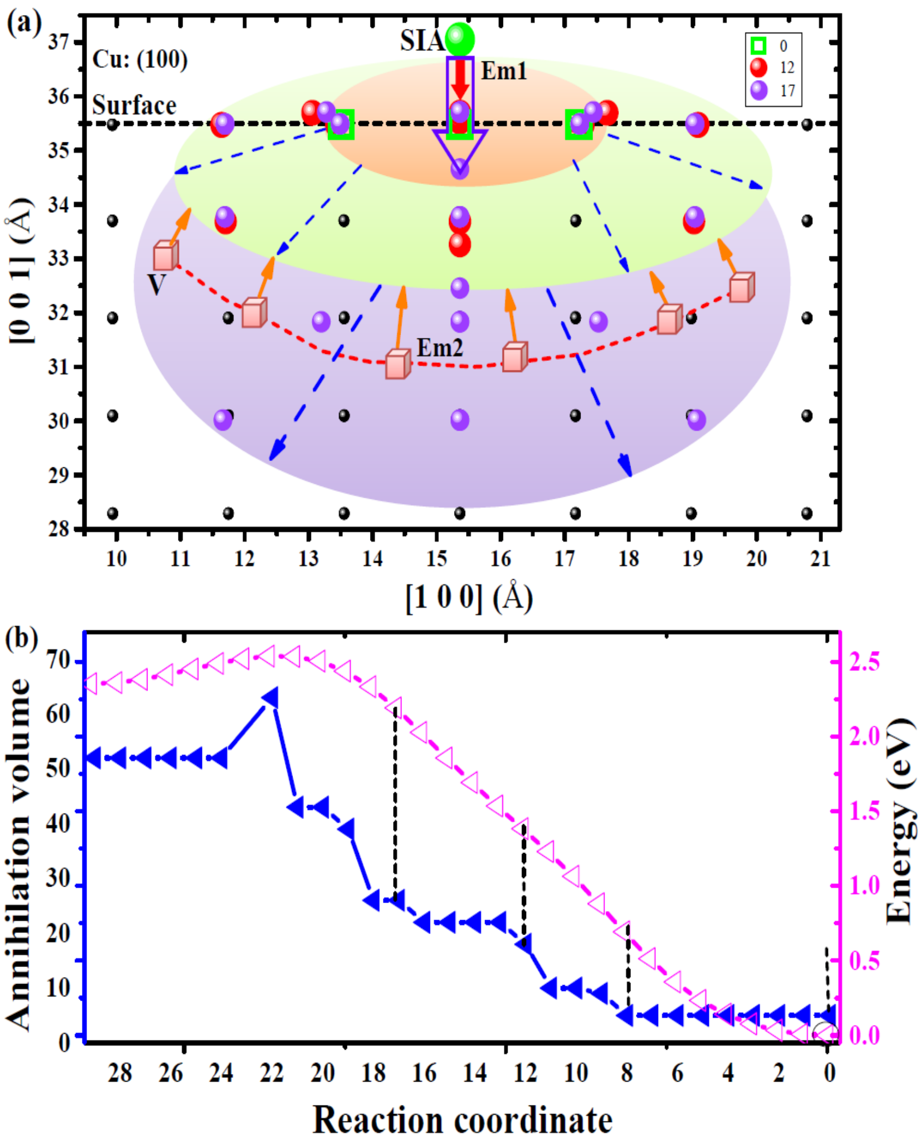
The slop in the nano-porous metals (NPs) is far larger than in nano-crystals and SIA-clusters, indicating that the direct emission in NPs is inhibited, while in other systems, the IE could be activated under a low temperature due to the smaller slop.

Results: New annihilation prospect

✓Based on the triangled potential-well approximation, we got a new annihilation prospect.

✓As the SIA statically locates at a defect sink, there forms a “spontaneous annihilation region”. As the SIA migrates locally along the potential-well, the annihilation region correspondingly propagates or extends towards the region nearby. The vacancy therein is annihilated.

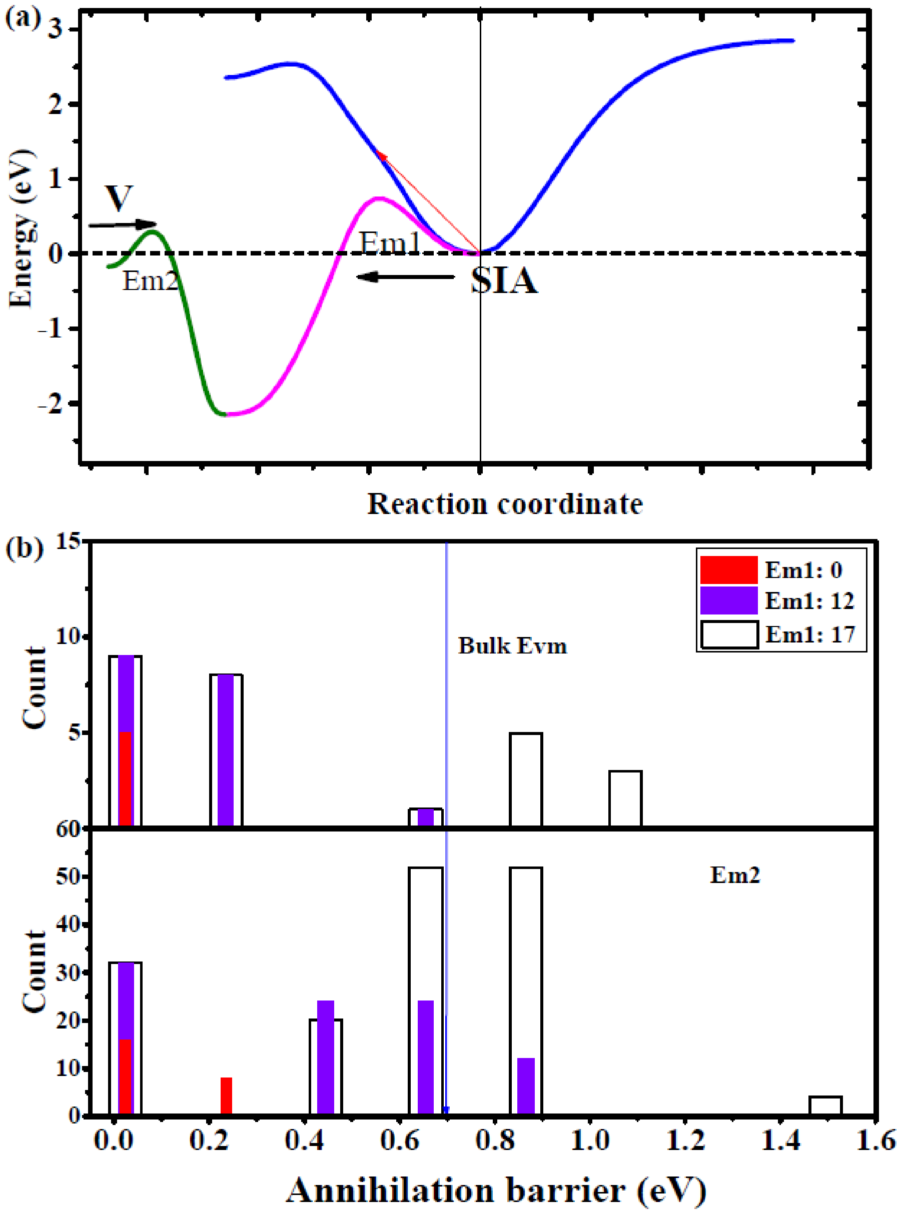
✓In this mechanism, the SIA dose not necessarily migrate through the potential-well at an energy barrier of its binding energy with a defect sink to re-enter the neighboring region and annihilate vacancies therein.



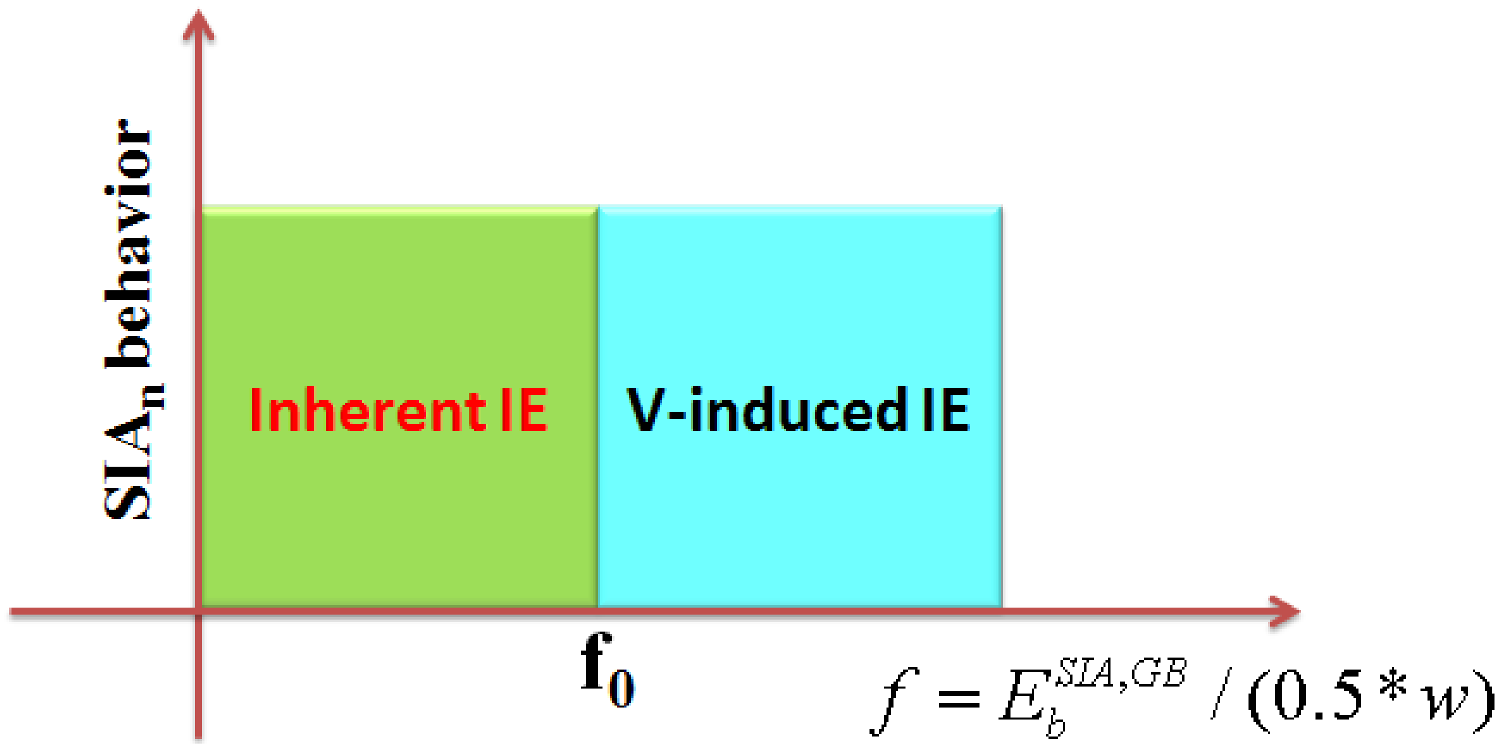
Results: New annihilation prospect

✓**During the extension and propagation of the "spontaneous annihilation region" towards the bulk region nearby, the SIA has to overcome a certain low energy barrier.**

✓**Meanwhile, the vacancy hop around the annihilation region was accelerated.**



Results: New annihilation prospect

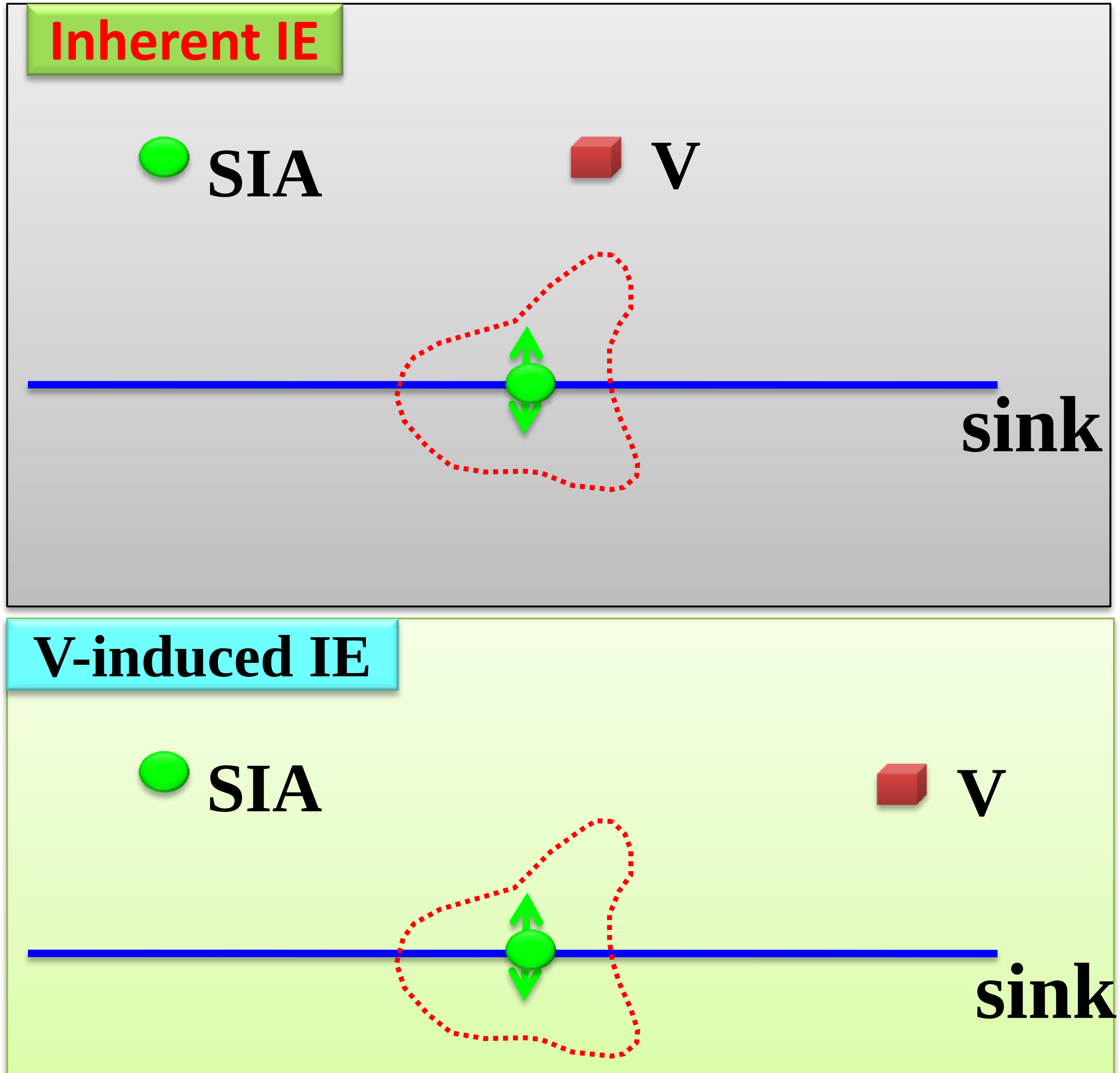


- ✓ **Therefore, a more general conclusion is: the interstitial emission mechanism at a defect sink is determined by the ratio of the interstitial binding energy with the sink to the potential-well half width.**
- ✓ **As the ratio is below a certain value, the annihilation could be induced by a direct interstitial emission. Otherwise, the annihilation has to be started by a vacancy-induced interstitial emission.**

✓The two annihilation mechanisms are illustrated here.

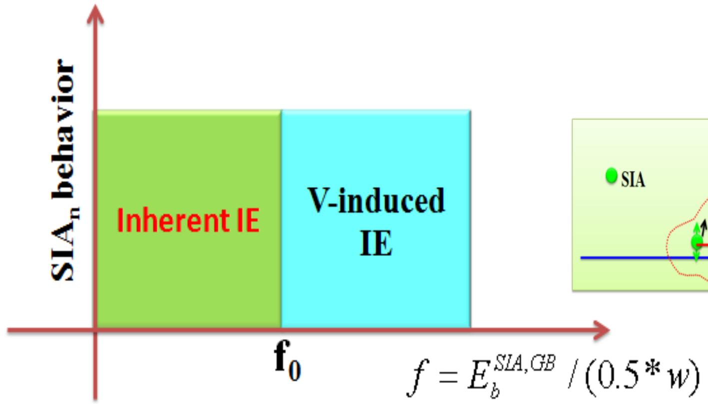
✓Inherent IE:
The SIA migrates locally along the potential-well. The annihilation region correspondingly propagates or extends towards the region nearby. The vacancy therein is annihilated.

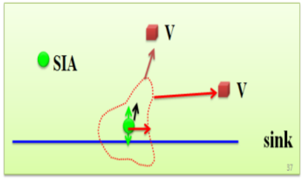
✓V-induced IE:
The V near the SIA reduces the emission energy barrier.

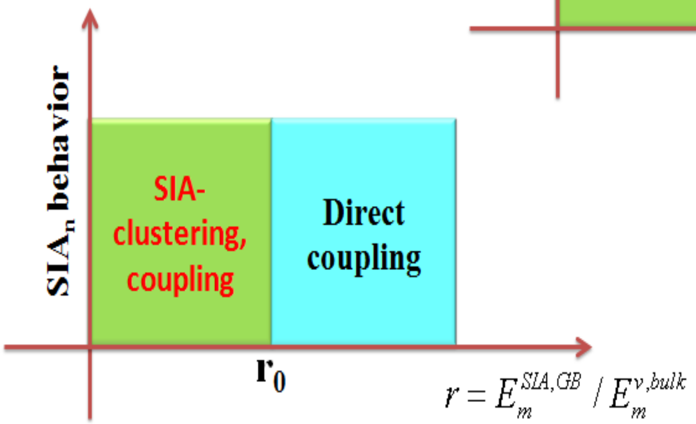


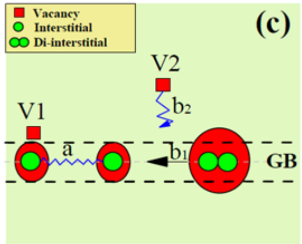
Summary

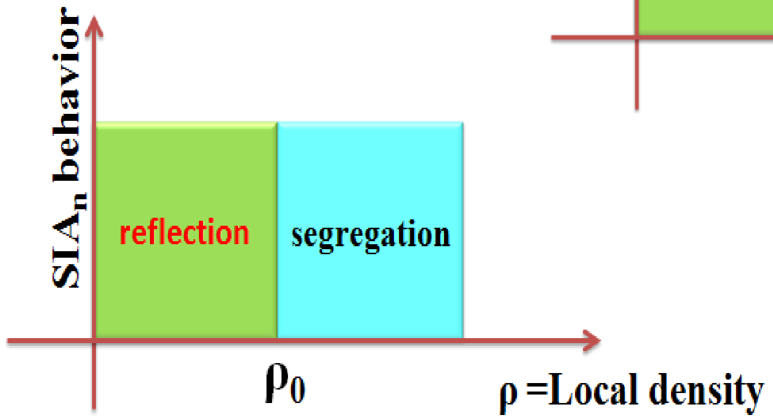
1. **Within different parameter regimes, the SIA$_n$ has a specific behavior and the corresponding annihilation mechanisms.**

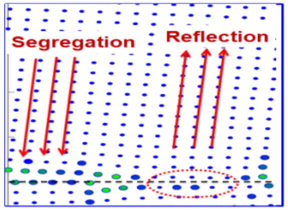


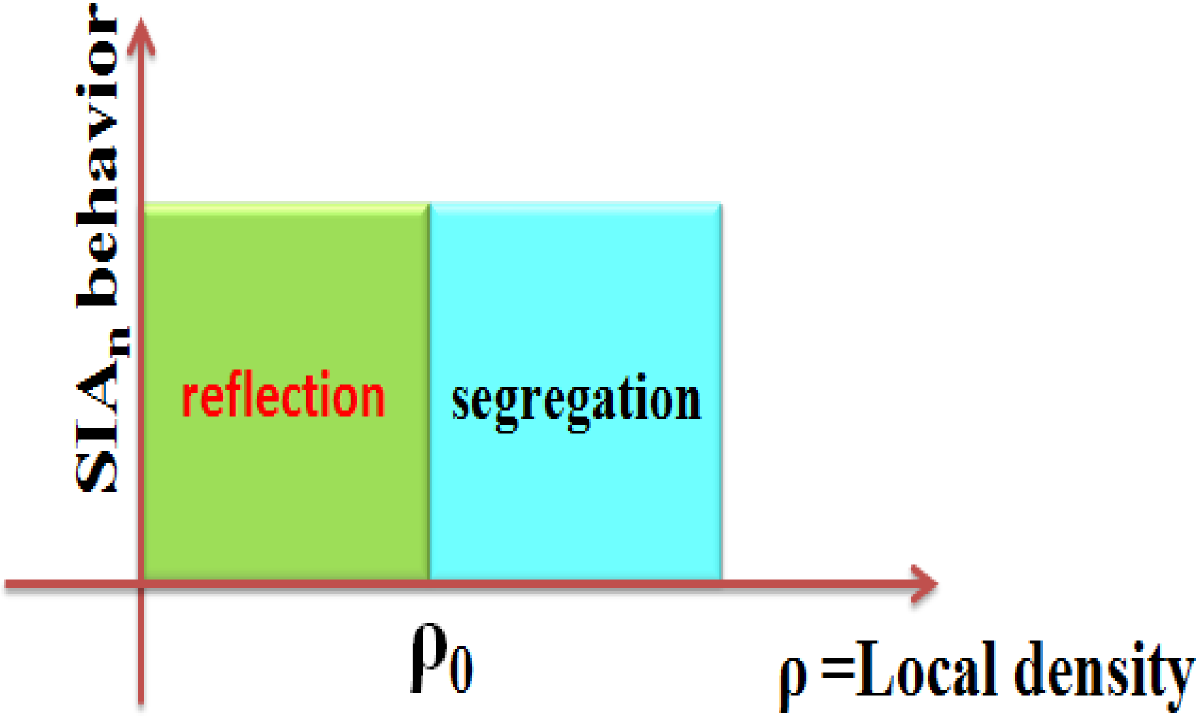


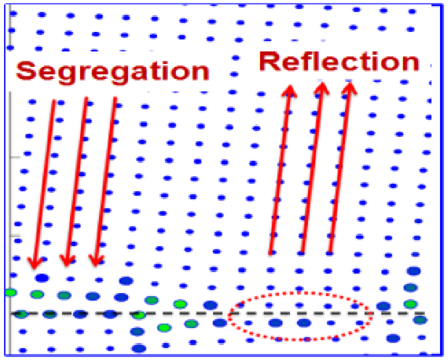




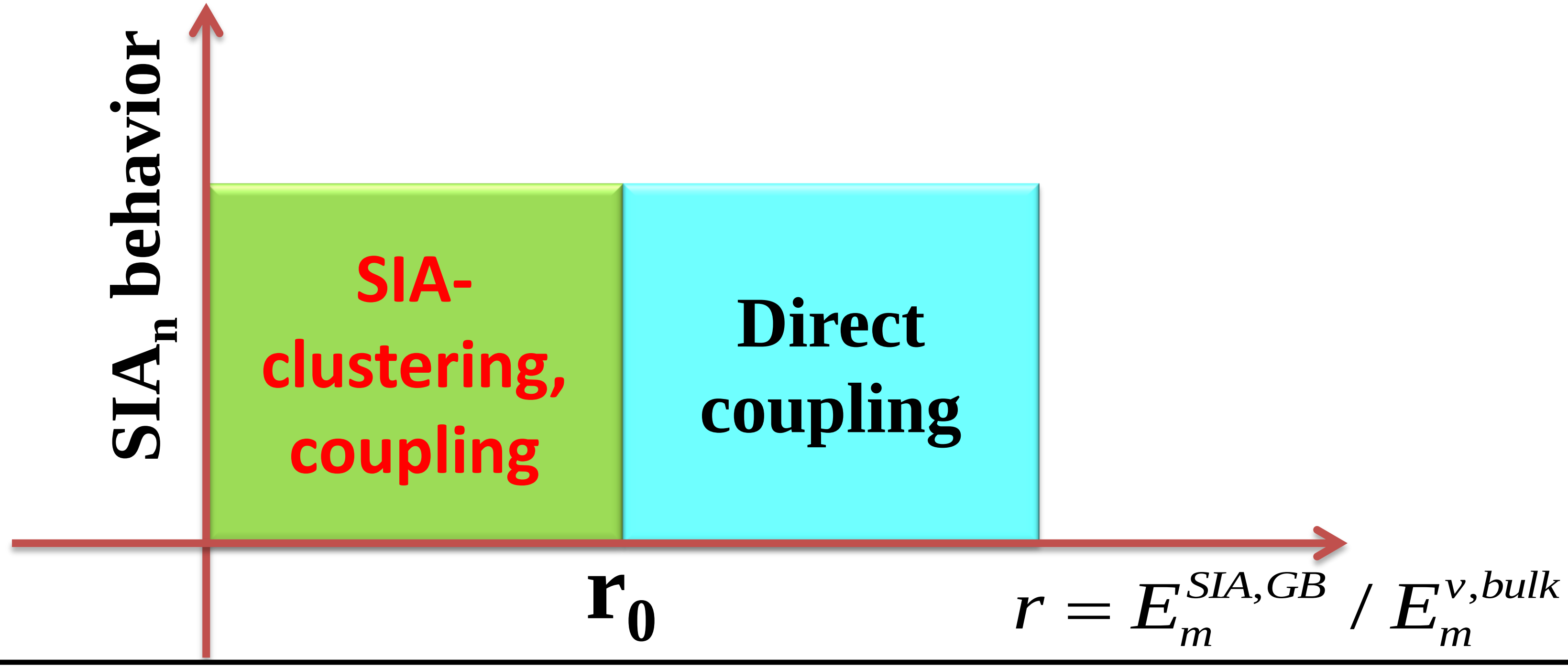




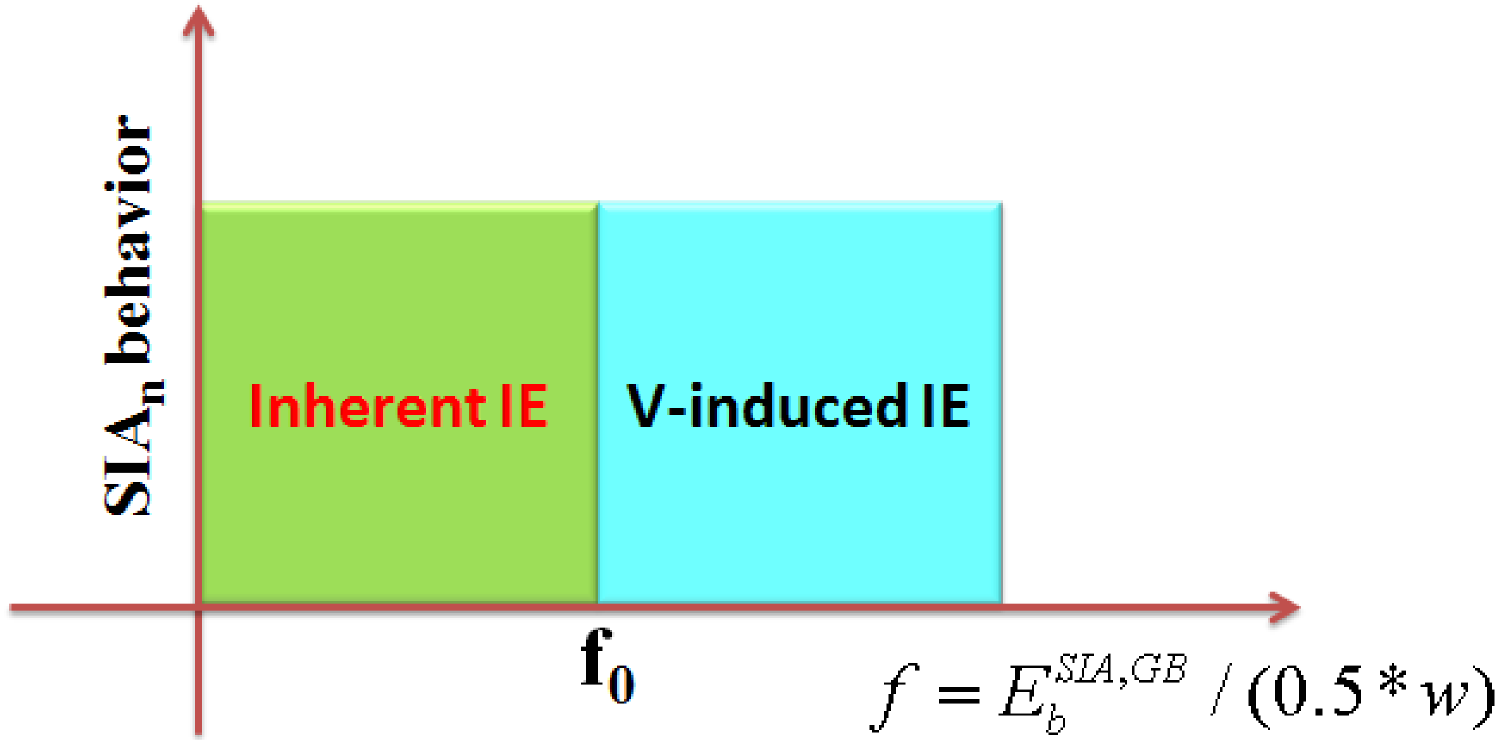




✓ For the interstitial and interstitial cluster of parallel <1 1 1> crowdions, their behavior near the GB, segregation or reflection, is determined by the local GB density. As the density is below a certain value, the corresponding region will reflect interstitials. Otherwise, the region acts a sink for interstitials.



✓ **The annihilation mechanism at the GB is determined by the relative value of the interstitial diffusion energy barrier along the GB and that for the bulk vacancy diffusion. As the ratio is below a certain value, the interstitial segregated to the GB moves along the GB, gets clustered therein, and then annihilates the vacancy via the coupled motion of the cluster along the GB and the motion of the vacancy towards the GB. Otherwise, the annihilation proceeds via the coupled motion of the interstitial along the GB and the segregation of the vacancy nearby.**



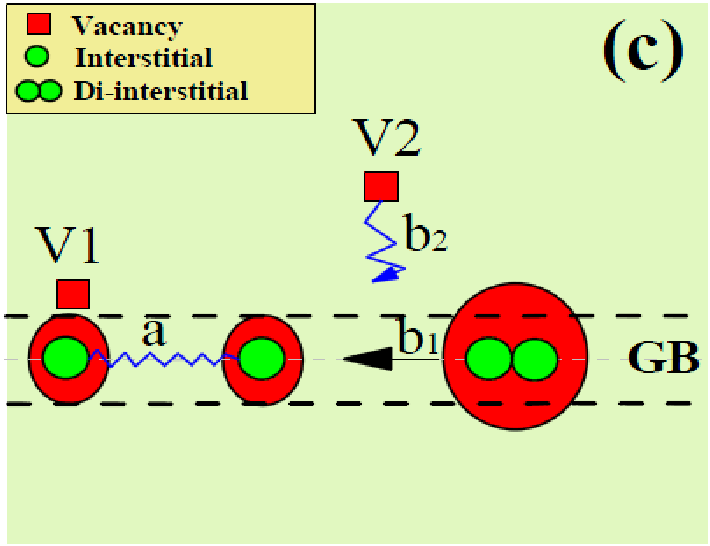
- ✓ **The interstitial emission mechanism at a defect sink is determined by the ratio of the interstitial binding energy with the sink to the potential-well half width.**
- ✓ **As the ratio is below a certain value, the annihilation could be induced by a direct interstitial emission. Otherwise, the annihilation has to be started by a vacancy-induced interstitial emission.**

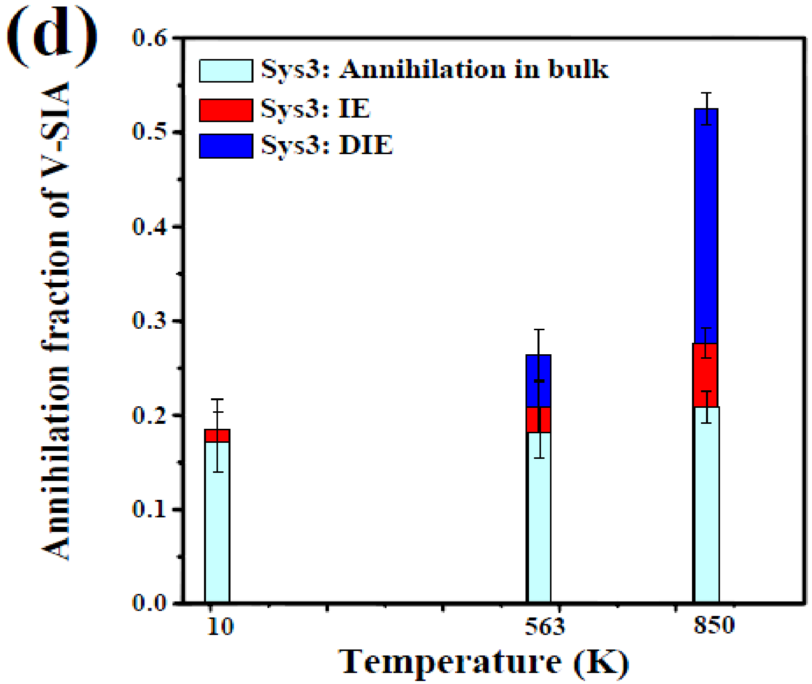
Summary: relevant articles to the presentation

1. X. Li, et al., Annihilating vacancies via dynamic reflection and emission of interstitials in nano-crystal tungsten, **Nucl. Fusion**, 2017 (revised)
2. X. Li, et al., Surface-structure dependence of healing radiation-damage mechanism in nanoporous tungsten, **Nucl. Fusion**, 2017 (under review)
3. X. Li, et al., On the possibility of universal interstitial emission induced annihilation in metallic nanostructures, **J. Nucl. Mater**. 2017 (under review)
4. X. Li, W. Liu, Y. Xu*, C.S. Liu*, B.C. Pan, Y. Liang, Q.F. Fang, J.-L. Chen, G.-N. Luo, G.-H. Lu, Z. Wang, **Acta Mater**, 2016,109: 115-127
5. X. Li, et al., Data Brief 2016, 7:798
6. X. Li, W. Liu, Y. Xu, C.S. Liu*, Q.F. Fang, B.C. Pan, J.-L. Chen, G.-N. Luo, Z. Wang, **J. Nucl. Mater**., 2014,444 : 229-236
7. X. Li, W. Liu, Y. Xu, C.S. Liu*, Q.F. Fang, B.C. Pan, Z. Wang, **J. Nucl. Mater**., 2013, 440 : 250-256
8. X. Li, W. Liu, Y. Xu, C.S. Liu*, Q.F. Fang, B.C. Pan, J.-L. Chen, G.-N. Luo, Z. Wang, **Nucl. Fusion**, 2013, 53 : 123014

Thanks for your attention!

Results: Dynamic SIA_n-V annihilation prospect





✓In some GBs, e.g. Σ5 (2 1 0), Σ5 (2 1 0) and Σ13, $E_a^{SIA,GB}$ is much lower than the bulk value of the V diffusion. Correspondingly, the time of the SIA and V to jump one step differs by at least six orders of magnitude. In this case, the SIA migrates along the GB exceptionally quickly after segregation, while the V remains static in the bulk.

✓Furthermore, the SIA at the GB quickly clustered at the GB. The cluster is mainly di-SIA, which has lower mobility than the single SIA.

✓In the subsequent evolution, the cluster moved along the GB. Simultaneously, the bulk V approached the GB, which was finally annihilated via such coupled process.

✓By comparing the annihilation fraction before and after the dynamic mechanism was incorporated into the model, we found the mechanism enhances the annihilation of the V.