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# Modeling radiation induced segregation in Iron-Chromium alloys

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## Abstract

Radiation induced segregation in ferritic Fe-Cr alloys is studied by Atomistic Kinetic Monte Carlo simulations that include diffusion of chemical species by vacancy and interstitial migration, recombination, and elimination at sinks. The parameters of the diffusion model are fitted to DFT calculations. Transport coefficients that control the coupling between diffusion of defects and chemical species are measured in dilute and concentrated alloys. Radiation induced segregation near grain boundaries is directly simulated with this model. We find that the diffusion of vacancies toward sinks leads to a Cr depletion. Meanwhile, the diffusion of self-interstitials causes an enrichment of Cr in the vicinity of sinks. For concentrations lower than 15%Cr, we predict that sinks will be enriched with Cr for temperatures lower than a threshold. When the temperature is above this threshold value, the sinks will be depleted in Cr. These results are compared to previous experimental studies and models. Cases of radiation induced precipitation and radiation accelerated precipitation are considered.

*Keywords:* Fe-Cr alloys; Monte Carlo simulation; Diffusion; Irradiation effect; Segregation

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## 1. Introduction

Ferritic Fe-Cr steels are good candidates as structural materials for the next generation of nuclear power plants (generation IV and fusion reactors) [1, 2]. The addition of Cr prevents corrosion and the Fe-Cr ferritic form is weakly sensitive to the swelling phenomenon. However, the irradiation flux induces an increase of point defect concentrations – vacancies and self-interstitial atoms (I) – that migrate toward sinks where they are eliminated. These defect fluxes may induce a variation in the alloy composition in the vicinity of sinks called Radiation Induced Segregation (RIS) [3]. If this causes a Cr depletion, the alloy can become sensitive to corrosion. On the other hand, if this leads to a Cr enrichment, the local concentration can reach the solubility limit, causing Radiation Induced Precipitation (RIP), which could lead to embrittlement. RIS has been extensively studied in austenitic steels where Cr depletion and Ni enrichment are frequently observed at sinks. These tendencies are relatively well-understood, even if the interstitial contribution is still under discussion [3]. In ferritic steels, the situation is far from being clear: approximately 15 experiments have been reviewed by Lu et al. [4] in very different materials and conditions, showing both depletions and enrichments in the vicinity of sinks. However, it is difficult to draw clear conclusions on how irradiation conditions and materials properties control the tendency towards enrichment or depletion. A systematic study, focusing on industrial steels with Cr content between 8 and 12% has been performed by Was et al. [5]. They observed that for given irradiation conditions, sinks tend to be enriched in Cr at low temperature and to be depleted in Cr at high temperature. Moreover, the Cr enrichment tends to decrease with the alloy Cr content. These tendencies are reproduced with the inverse Kirkendall model of Wharry *et al.* [6] and are attributed to a positive coupling of Cr with self-interstitials (dominant at low temperatures) and a negative coupling with vacancies (dominant at high temperatures). Other factors, such as grain boundary misorientation [7], interactions with C or other impurities [7, 8] may influence the segregation of Cr at sinks.

In the present study, we limit ourselves to the Fe-Cr binary system in order to understand basic mechanisms controlling RIS at the atomic scale. Thermodynamics of Irreversible Processes (TIP) shows that a complete description of RIS requires a full determination of the Onsager coefficients  $L_{ij}$ , or alternatively, of partial diffusion coefficients  $d_{ij}$  [3]. Such a consistent description remains to be established for concentrated Fe-Cr alloys. Existing models are based on Density Functional Theory (DFT) calculations and multi-frequency models that are only valid in the dilute limit [9, 10], or have been extended to concentrated alloys using additional approximations [9, 5, 6]. Others use Molecular Dynamics (MD) simulations that rely on empirical potentials and only determine the self-interstitial contribution [11, 12].

We present here a multiscale approach of RIS, starting from DFT calculations of the point defect migration energies. A diffusion model describing the variation of point defect properties with local composition is developed. Atomistic Kinetic Monte Carlo (AKMC) simulations are performed in order to (i) determine the  $L_{ij}$  coefficients and predict the RIS tendencies; and (ii) model the evolution of point defect and Cr concentration profiles under irradiation in the vicinity of a grain boundary (GB). AKMC simulations include the effect of non-homogeneous concentration fields and account for the stochastic nature of point defect migration. It also enables the simulation of RIP, when the RIS leads to a strong enrichment of Cr near GBs and therefore to nucleation of  $\alpha'$  precipitates.

In section II we present a reminder of RIS principles in the framework of TIP. In section III, the diffusion model and the AKMC method are introduced. The fitting of parameters to DFT calculations is detailed and relevant point defects properties are discussed. In section IV, the point defect tracer diffusion coefficients and Onsager coefficients are analyzed. The effect of composition and temperature on these Onsager coefficients is studied. Simulations of RIS and RIP near grain boundaries are also shown. We discuss these results by comparing them to previous models and experiments. We conclude by commenting on the limitations of our model, possible improvements and perspectives.

## 2. Thermodynamics of Irreversible Processes and Radiation Induced Segregation

RIS is due to fluxes of vacancies ( $J_V$ ) and self-interstitials ( $J_I$ ) towards  
65 point defect sinks that, in an A-B alloy, induce fluxes of chemical species ( $J_A$   
and  $J_B$ ). TIP describes the fluxes  $J$  as linear combinations of thermodynamic  
driving forces, i.e. chemical potential gradients [3]:

$$J_\alpha = -\sum_\beta L_{\alpha\beta} X_\beta \quad (1)$$

with  $X_\beta = \nabla\mu_\beta/(k_B T)$ .  $L_{\alpha\beta}$  are the Onsager coefficients,  $\mu_\beta$  the chemical  
potentials,  $k_B$  the Boltzmann constant and  $T$  the temperature.

70 In steady state, under the conditions where there is no precipitation and  
 $L_{\alpha\beta}$  coefficients are independent of the local composition, the gradient of B and  
V near a sink are related by:

$$\nabla C_B = -\frac{L_{AI}L_{AV}}{C_V(L_{AI}D_B + L_{BI}D_A)} \left( \frac{L_{BV}}{L_{AV}} - \frac{L_{BI}}{L_{AI}} \right) \nabla C_V \quad (2)$$

where  $D_A$  and  $D_B$  are intrinsic diffusion coefficients. This profile may also  
be expressed in term of partial diffusion coefficients:  $d_{\alpha V} = L_{\alpha V}/C_\alpha C_V$  and  
75  $d_{\alpha I} = L_{\alpha I}/C_\alpha C_I$  [13, 14].

The sign of the  $L_{\alpha\beta}$  coefficients corresponds to the direction of couplings. For  
example, in the A-B alloy if  $L_{BV} > 0$  fluxes of B and V are in the same direction  
and if  $L_{BV} < 0$  they are in opposite directions. In simple cases, general rules of  
concentration variations can be derived from point defect diffusion coefficients.  
80 RIS is thus often analyzed in terms of Inverse Kirkendall effect: for the vacancies,  
if B is the fast diffusing species (ie  $D_B > D_A$ ), a depletion of B at sinks is  
expected (note that it is only true when  $L_{BV} < 0$ ); for interstitials, if B is the  
fast diffusion species, an enrichment of B is expected ( $L_{BI}$  is always positive) [3].  
On the other hand, in the case of significant attraction between solute atoms and  
85 vacancies,  $L_{BV}$  may be positive, leading to solute atoms dragged by vacancies  
and a solute enrichment at sinks (this is called the drag effect). Beyond such

interpretations, one must know the full set of  $L_{ij}$  coefficients in Eq. 2 and how they depend on temperature and concentration in order to determine the RIS profiles.

90 The  $L_{ij}$  coefficients are very difficult to extract from diffusion experiments but they can be in principle easily deduced from atomic scale simulations. This requires: (i) a good description of jump frequencies and their variation with respect to the local environment and (ii) a good method to compute the  $L_{ij}$  coefficients from the jump frequencies. For the second point, two strategies are  
95 possible:

1. A numerical determination of the  $L_{ij}$  (or  $d_{ij}$ ) coefficients by MD or AKMC simulations. MD simulations with an empirical potential have been used by Terentyev, Pechenkin et al. [11, 12] for the coefficients of self-interstitials. Here we use AKMC simulations to directly measure the  $L_{ij}$  coefficients of  
100 both vacancies and self-interstitials.
2. An analytical calculation of the  $L_{ij}$  coefficients (or alternatively, of the partial diffusion coefficients) from point defects jump frequencies, using multi-frequency diffusion models valid for dilute systems. This approach has been applied to Fe-Cr alloys by Choudhury et al. [9] and by Was,  
105 Wharry et al. [5, 6]. Those diffusion models were limited to short-range interacting alloys and the contribution to the  $L_{ij}$  coefficients of some vacancy jumps beyond the first nearest neighbor sites of the solute atom had to be neglected. Recently, long-range interaction models of the  $L_{ij}$  coefficients have been developed [15, 16]). In concentrated alloys, due to the  
110 high complexity, approximate mean field methods are used to determine the  $L_{ij}$  coefficients [3].

### 3. Diffusion model and AKMC simulations

#### 3.1. Diffusion model and effective pair interactions

The calculation of point defects jump frequencies is based on a rigid lattice model using effective pair interactions hereafter referred to as the “AKMC  
115

model”. We start from a previous version [17] that only includes vacancy diffusion. It assumes that the free enthalpy of a given atomic configuration can be written as a sum of effective pair interactions on a rigid bcc lattice.

Such “broken bond” models with constant pair interactions are widely used in AKMC simulations to model diffusive phase transformations in alloys [18, 19, 20, 21]. However, Fe-Cr alloys have a special thermodynamic behaviour, with strong vibrational and magnetic contributions. The latter are especially important: they lead to a change in the sign of the alloy mixing energy around 10 at.% Cr. In ref [17], magnetic and vibrational contributions are taken into account by introducing a temperature dependence on all interactions and by making Fe-Cr interactions on lattice sites dependent on local concentration (see Refs. [22, 17]). This model generates solubility limits in good agreement with recently updated Fe-Cr phase diagrams [23, 24], showing an asymmetrical miscibility gap (see fig. 1 in Ref [17]). It gives diffusion coefficients and kinetics of precipitation in good agreement with experimental data, in the range of temperatures and compositions considered here (300-950 K and up to 20% of Cr).

1

In the present study, the diffusion of self-interstitials is modeled in a similar manner. As we will see in the next section, dumbbells with a  $\langle 110 \rangle$  orientation have the most stable interstitial configuration in Fe and dilute Fe-Cr alloys. We therefore only consider this configuration. The migration occurs through the Johnson mechanism [25]: a jump of the dumbbell towards a nearest-neighbor atom, with a rotation of  $60^\circ$ . Two types of nearest neighbor sites can be distinguished : four sites in tension (T) and four sites in compression (C) [26]. Self-interstitial atoms can only jump to compression sites.

The jump frequency for an exchange between an atom  $A$  (= Fe, Cr) and a self-interstitial  $I$  is given by  $\Gamma_{AI} = \nu \exp(-\Delta G_{AI}^{mig}/k_B T)$ , where  $\nu = 10^{13} \text{s}^{-1}$  is

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<sup>1</sup>In Fe-Cr solid solutions, the ferro-to-paramagnetic transition leads to an increase of the diffusion coefficients that can be modeled by a correction of the vacancy migration barriers [17]. It is shown to significantly accelerate the precipitation kinetics in alloys with high Cr contents (above typically 25%). As we limit our study to concentrations lower than  $\sim 15\%$ , such effects are not included in the present model.



the Debye frequency and  $\Delta G_{AI}^{mig}$  the migration barrier :

$$\Delta G_{AI}^{mig} = \Sigma_j \tilde{g}_{AIj} - \Sigma_{k,n} g_{Ak}^{(n)} - \Sigma_l g_{Il} - g_{Ii} - \Sigma_{pq,n} \Delta g_{pq}^{(n)} \quad (3)$$

where the first term on the right hand side corresponds to interactions created  
 145 by the atom of the interstitial jumping at the saddle point ( $\Sigma_j \tilde{g}_{AIj}$ ). The  
 second and third terms correspond to broken interactions around the targeted  
 atom  $A$  and around the interstitial.  $g_{Ii}$  is the interaction broken within the  
 dumbbell and the last term corresponds to  $pq$  bounds that are not broken but  
 experience a change in their local concentration and consequently a change in  
 150 their interactions [17].

In a first approximation, the interactions between self-interstitials and atoms  
 in the lattice ( $g_{Il}$ ) are limited to those between first nearest neighbors. The  
 dumbbell composition (Fe-Fe, Fe-Cr or Cr-Cr) is taken into account and specific  
 interactions are introduced to control its formation, binding and migration  
 155 enthalpies. For this, we take into account interactions between the atoms within  
 the dumbbell and distinguish interactions of dumbbell atoms with their neigh-  
 bors on C sites and on T sites. For mixed Fe-Cr dumbbells, the interactions  
 with atoms on C sites depend on the dumbbell direction (see Table 2). The de-  
 tailed balance conditions are verified and symmetrical relations are taken into  
 160 account.

### 3.2. *Ab initio calculations of point defects properties*

#### 3.2.1. *Vacancy properties*

The details of the vacancy properties has been presented in Ref. [17]. We  
 only recall here the results relevant for the analysis of Onsager coefficients.  
 165 Martinez et al. have computed the 10 migration barriers controlling the Fe  
 and Cr tracer diffusion coefficients in Fe (according to Le Claire's model [27]).  
 The results are very similar to those of Choudhury et al. [9] and Messina et  
 al. [16]. These studies show a weak Cr-V interaction and a low migration  
 barrier for the Cr-V exchange (corresponding to the  $W_2$  frequency using the

170 usual LeClaire’s notation) for the Cr-V exchange, in comparison with the other  
vacancy jumps. This results in a rapid diffusion of Cr in Fe (tracer diffusion  
coefficients  $D_{Cr^*} > D_{Fe^*}$ ) [17].

The pair interactions of the AKMC model have been fitted to some of these  
DFT results. In most cases, migration barriers and binding enthalpies generated  
175 by this model are in good agreement with the DFT calculations. The migra-  
tion barriers of jump frequencies  $W_3$  and  $W_4$  are slightly higher than the DFT  
values. Meanwhile, the binding energy between Cr and the vacancy is slightly  
negative (almost zero) in the AKMC model, while it is slightly positive in the  
DFT calculations.  $W_3$  and  $W_4$  jump frequencies may affect the rotation of the  
180 vacancy around solute atoms and therefore the drag effect [15, 10]. In spite of  
these differences, the model gives tracer and interdiffusion coefficients in good  
agreement with experimental data in ferromagnetic alloys [17, 28].

### 3.2.2. *Self-interstitial atoms properties*

Self-interstitial properties have been studied by Olsson et al.[29] in dilute Fe-  
185 Cr alloys using DFT calculations and by Terentyev et al. [11] in concentrated  
Fe-Cr alloys using the 2BM empirical potential.

We present here a DFT study of self-interstitial properties (formation, migra-  
tion and binding energies) in pure metals, dilute and more concentrated Fe-Cr  
alloys, with the objective of fitting the corresponding AKMC parameters.

190 DFT calculations were performed using the PWSCF code [30]. We per-  
formed spin-polarized calculations within the generalized gradient approxima-  
tion (GGA). Accurate projector augmented wave (PAW) potentials were used,  
where the 3d and the 4s electrons were considered as valence electrons. The  
kinetic energy cutoff chosen for the plane-wave basis set was 544 eV. All the  
195 calculations were carried out with 128-atom supercells, using a  $(3 \times 3 \times 3)$ -  
point grid and the Methfessel-Paxton broadening scheme with a 0.3 eV width.  
To calculate the energetics of interstitial atoms, we have adopted a constant  
volume-per-atom approach. For instance, the lattice parameter of a cubic su-  
percell containing  $N$  Fe lattice atoms and one Fe interstitial was rescaled in

200 order to give a total volume equal to the sum of  $N + 1$  times the Fe atomic volume in a defect-free bcc lattice. The atomic positions were fully relaxed with a residual value of less than  $0.04\text{eV}/\text{\AA}$  for each force component of all atoms.

The binding energy of a configuration containing  $n$  point defects noted  $d_i$  is given by:

$$E_b(\text{config}) = \sum_{i=1}^n E(d_i) - E(\text{config}) - (n - 1)E_{ref} \quad (4)$$

205 where  $E_{ref}$  is the total energy of a supercell of pure Fe,  $E(d_i)$  is the total energy of a supercell containing the single defect  $d_i$  and  $E(\text{config})$  is the total energy of the supercell containing all the defects ( $d_i$ ). A positive binding energy refers then to an attractive interaction.

The migration barriers have been determined using the drag method as in 210 our previous work [17].

### *Pure metals.*

Table 1: Self-interstitial atoms formation energies (in eV) in pure Cr, computed in DFT-PAW calculations

configuration	Cr-NM	Cr-AFM
100	6.63	6.84
110	5.58	6.08
111	5.64	6.20
Octahedral	6.76	7.04
Tetrahedral	6.31	6.60

In pure iron, our DFT calculations give a formation enthalpy of 3.96 eV for the  $\langle 110 \rangle$  dumbbell, the most stable orientation in pure iron (in agreement with previous studies [31, 25]). The  $\langle 111 \rangle$  dumbbell has a formation enthalpy 215 of 4.74 eV.

Formation energies of different self-interstitial configurations in pure Cr, with a non-magnetic (NM) or anti-ferromagnetic (AFM) state, are reported in Table 1. Olsson et al. [29] have obtained values slightly smaller but with almost the same relative stability between the different configurations. The magnetic state 220 has a very limited effect on the relative stability of the different configurations.

The  $\langle 110 \rangle$  configuration is the most stable one in each case, but the formation energy of  $\langle 111 \rangle$  is very close. The formation energies of the  $\langle 100 \rangle$  dumbbell, octahedral and the tetrahedral configurations are significantly higher.

*Binding energies in Fe-Cr alloys.*

225 Binding energies have been calculated for 52 configurations involving a  $\langle 110 \rangle$  dumbbell in Fe, with up to four Cr atoms in first and second nearest neighbor positions. Table 2 presents a selection of binding energies computed in DFT and with our AKMC model. Fig. 1 summarizes the comparison between the DFT calculations and the AKMC model for all configurations. A few binding  
230 energies between Fe atoms and  $\langle 110 \rangle$  dumbbells in Cr, and between Cr and  $\langle 111 \rangle$  dumbbells in Fe are also given on Table. 2.

In the 52 configurations of Fig. 1 the  $\langle 110 \rangle$  dumbbell is more stable than the  $\langle 111 \rangle$ , except for two cases. In these two cases, the  $\langle 111 \rangle$  configuration is an energy slightly lower than the  $\langle 110 \rangle$  configuration, but is still negative with a  
235 strongly negative energies (respectively -0.63 and -0.80 eV) and therefore have negligible probabilities of occurrence.

The mixed interstitial (line 1 in Table 2) is stable in pure Fe, with a positive binding energy (+0.022 eV). The interactions between a Fe-Fe  $\langle 110 \rangle$  dumbbell and a Cr atom on tension site (line 2) are repulsive (-0.038 eV). The ones with  
240 a Cr atom on a compression site (line 3) are attractive (+0.016 eV).

Cr-Cr dumbbells are strongly repulsive in pure iron (line 11, -0.554 eV) and more generally in all the dilute Fe-Cr configurations that we have considered. The binding energy of a mixed interstitial with a Cr atom on a tension site is negative (line 7) whereas the one with a Cr atom on a compression site  
245 depends on the position of the Cr atom within the dumbbell (lines 8 and 9). Configurations with more Cr atoms (e.g. lines 10, 11 and 12) usually have very negative binding energies. This results from the magnetic frustration occurring between Cr neighbors in Fe. These frustrations explain the ordering tendency of dilute Fe-Cr alloys [32]. However, some configurations with two or more Cr  
250 atoms have positive binding energies (especially with Cr on compression sites,

e.g. on lines 4, 6, 9) and may tend to decrease the mobility of dumbbells.

In pure Cr, the mixed and Fe-Fe  $\langle 110 \rangle$  dumbbells (lines 13 and 14) are very attractive, with high binding energies respectively close to 1 and 2 eV.

In general, our results are similar to the previous DFT results of Olsson et al. [29]. The results obtained by Terentyev et al. [11] with the 2BM potential tend to overestimate the attraction between  $\langle 110 \rangle$  dumbbells and Cr atoms compared to DFT calculations. As mentioned in [11], the binding energies between  $\langle 111 \rangle$  dumbbells and Cr atoms are positive (lines 15 and 16), but they are lower than the difference between the formation energies of  $\langle 111 \rangle$  and  $\langle 110 \rangle$  dumbbells in pure Fe (approximately 0.8 eV): these  $\langle 111 \rangle$  configurations are therefore not probable and should not be able to trap the self-interstitials.

The binding energies of the AKMC model are usually in good agreement with the corresponding DFT values (Fig. 1), especially for configurations involving only 1 or 2 Cr atoms. In the case of configurations including 3 and 4 Cr atoms, the AKMC model reproduces the general trend, i.e. strongly negative binding energies.

### 3.2.3. Migration energies in Fe-Cr alloys

DFT calculations of migration barriers between configurations involving one  $\langle 110 \rangle$  dumbbell and between 1 and 4 Cr atoms are given in Fig. 2.

The present calculations give a migration energy of 0.34 eV for the  $\langle 110 \rangle$  dumbbell in pure iron, in agreement with previous studies [25, 26, 9]. In alloys, our DFT study shows that this mechanism is associated with the lowest migration energy of the  $\langle 110 \rangle$  dumbbell. The mixed interstitial has a migration barrier significantly lower than the Fe-Fe dumbbell in pure iron: 0.23 instead of 0.34 eV. The migration barriers of the Cr-Cr dumbbells are even lower ( $\sim 0.05$  eV) but configurations involved in these processes are very repulsive ( $E_b \ll 0$ ).

In configurations with one Cr atom, the migration barriers are close to those of Choudhury et al. [9] and Olsson et al. [26]. Choudhury et al. [9] have also computed migration barriers for self-interstitials jumps without rotation. Their migration barriers are systematically higher when compared to the Johnson

mechanism, which further validates our choice of migration mechanism.

For migration barriers with 1 or 2 Cr atoms, the AKMC model is in good agreement with the DFT calculations (Fig. 2). For higher Cr concentrations, the discrepancy can be as high as 0.4 eV. However, they correspond to configurations with negative binding energies, i.e. low probabilities. A better agreement could be obtained by introducing pair interactions between dumbbells and atoms at positions further than first nearest neighbors and a composition dependence to the saddle-point pair interactions. However, as this would slow down the AKMC code, we prefer to leave this improvement for a future study.

Finally, the attempt frequency of vacancy jumps is assumed to be  $\nu_0 = 10^{13} \text{ s}^{-1}$  and the migration barriers include a migration entropy of  $2.1 k_B$  [17]. The migration entropy of interstitials has never been experimentally measured. For the sake of simplicity, it has been chosen here to take the same value as the vacancies.

To summarize, key self-interstitials properties revealed by DFT calculations and reproduced by the AKMC model are: the moderate attraction between interstitials and Cr atoms in dilute Fe, the stability of mixed interstitials in dilute Fe and the rapid migration of the mixed interstitial.

### 3.3. AKMC simulations

Two kinds of AKMC simulations have been performed: measurements of transport coefficients and simulations of RIS near a grain boundary.

For the first ones, one point defect (V or I) is introduced in a simulation box with  $N = 4096$  bcc sites, periodic boundary conditions and up to 15% of Cr. The jump frequencies are computed with our diffusion model and a residence time algorithm (RTA) is used to choose the jumps and to increment the time [33]. Tracer diffusion coefficients of point defects  $d = I, V$  and  $L_{ij}$  coefficients are computed with generalized Einstein's relations [34]:

$$D_d = \frac{\langle \Delta r_d^2 \rangle}{6t} \quad (5)$$

and

$$L_{ij} = \frac{1}{6V_{tot}k_B T} \frac{\langle \Delta R_i \Delta R_j \rangle}{t}, \quad (6)$$

where  $\Delta r_d$  is the average displacement of defect  $d$  during time  $t$ .  $\Delta R_i$  is the total displacement of species or defect  $i$  during time  $t$  and  $V_{tot}$  is the total volume of the system. To obtain sufficient statistics, average values are calculated on  $10^5$  series of  $10^5$  Monte Carlo steps. Measurements are performed in homogeneous solid solutions, i.e. outside the miscibility gap or slightly inside – but in the latter case checking that  $\alpha'$  precipitation does not occur during the measurements.

Simulations of RIS at grain boundaries are performed in samples with  $N = 512 \times 64 \times 64$  bcc sites, with a GB located in the middle of the long dimension. These simulations take into account the following events [35, 36]:

- the creation of Frenkel pairs (I-V) with a production rate  $K_0$ . I-V pairs are created randomly within the simulation box, along sequences of 10 displacements in  $\langle 111 \rangle$  directions. This mechanism corresponds to electron rather than neutron or heavy ion irradiation.
- the migration of I and V, according to the diffusion model,
- the recombination of I and V pairs below a recombination radius  $R_c$  of 4 nearest neighbors.
- the annihilation of I and V when they jump on a GB. Within our rigid approach, the GB is simply modeled as a planar perfect sink.

## 4. Results

### 4.1. Point defect tracer diffusion coefficients

We present first diffusion coefficients of point defects which determine the steady state point defect concentration under irradiation. The tracer diffusion coefficients of one vacancy and one interstitial in alloys at nominal concentrations up to 15%Cr and at temperatures between 300 K and 1500 K are presented in Figures 3. The vacancy diffusion coefficients slightly increase with the Cr concentration, due to the low Cr-V exchange barrier in Fe.

335 Self-interstitial diffusion coefficients are higher (up to 5 orders of magnitude  
at 300 K) than the vacancy diffusion coefficients. It has to be noted that a  
change of interstitial migration entropy in the energetic model would change  
the I diffusion coefficients. The effect of Cr concentration on the I diffusion  
coefficient depends on temperature. At temperatures lower than the threshold  
340 value  $T_s \sim 600$  K, the addition of Cr induces an acceleration of self-interstitial  
diffusion. At  $T > T_s$  the inverse tendency is observed.

The increase of the interstitial diffusion coefficient with concentration at low  
temperature is due to the stability and the low migration barrier of the mixed  
dumbbell. The influence of Cr concentration on self-interstitial diffusion at high  
345 temperature can be explained by the dissociation of the mixed interstitials and  
the trapping of I on Cr atoms. These results are in qualitative agreement with  
the MD simulations of Terentyev, Pechenkin et al., using the 2BM empirical  
potential [11, 12]. A fit of the self-interstitial diffusion coefficients by an Arrhe-  
nius law:  $D_I = D_I^0 \exp(-\Delta H_I^{mig}/(k_b T))$  gives  $H_I^{mig} = 0.34, 0.29, 0.27, 0.25$  eV  
350 for 0.25, 5, 10 and 15%Cr respectively, close to the values of Terentyev et al.  
(Table 2 in ref. [11]). However, in their MD simulations, the threshold temper-  
ature is lower ( $T_s \sim 400$  K). This may be related to the overestimation of the  
I-Cr attraction by the 2BM potential, as the trapping effect becomes dominant  
at lower temperatures.

#### 355 4.2. Onsager coefficients

We have measured that for concentrations ranging from 0.25 to 15 %Cr  
and temperatures between 300 and 1500 K, the  $L_{FeI}$  and  $L_{CrI}$  coefficients are  
positive and the  $L_{FeV}$  and  $L_{CrV}$  coefficients are negative. Fe and Cr atoms  
diffuse thus in the opposite direction than vacancies and in the same direction  
360 as interstitials.

In the dilute limit, one observes the theoretical result  $L_{FeV}/L_{FeFe} = -1$ .  
The  $L_{CrV}/L_{CrCr}$  ratio is close to  $-2$  which indicates a strong negative coupling  
between vacancies and Cr atoms displacements, as could be expected from the  
small migration barrier  $\Delta H_2$  for the Cr-V exchange in Fe and from the absence



365 of drag effect. This ratio is lower than in the studies of Choudhury et al. [9] and  
 Messina et al. [16] that give a value close to  $-1$  in the dilute limit (one Cr atom).  
 The results of Messina et al. suggest a vacancy drag effect (i.e. that  $L_{CrV}$   
 becomes positive) at very low temperatures (below 300 K). These discrepancies  
 are due to the overestimation by the AKMC model (see 3.2.1) of the migration  
 370 barriers,  $\Delta H_3$  and  $\Delta H_4$ , that control the rotation of the vacancy around the  
 Cr atoms [15, 16]. This illustrates how sensitive the Onsager coefficients, and  
 therefore the RIS phenomena, are to small differences in the migration barriers.

Intrinsic diffusion coefficients  $D_{Fe}$  and  $D_{Cr}$  coefficients are positive outside  
 of the miscibility gap. Therefore:

$$-\frac{L_{FeI}L_{FeV}}{C_V(L_{FeI}D_{Cr} + L_{CrI}D_{Fe})} > 0.$$

375 and the segregation tendency (enrichment or depletion) depends on the sign of  
 $(L_{CrV}/L_{FeV}) - (L_{CrI}/L_{FeI})$  according to Eq. 2. These ratios are shown in  
 Fig. 4, for different compositions and temperatures.  $L_{CrI}/L_{FeI} > C_{Cr}/C_{Fe}$ ,  
 indicating a preferential transport of Cr by self-interstitials which implies a  
 systematic tendency for enrichment of Cr near the point defect sinks by self-  
 interstitial diffusion.  $L_{CrV}/L_{FeV} > C_{Cr}/C_{Fe}$  also indicates a preferential trans-  
 380 port of Cr by vacancies which implies a systematic tendency for depletion of Cr  
 near the point defect sinks by vacancy diffusion.

The  $L_{CrI}/L_{FeI}$  and  $L_{CrV}/L_{FeV}$  ratio both decrease with temperature, but  
 not at the same rate. The interstitial contribution is dominant ( $L_{CrI}/L_{FeI} >$   
 385  $L_{CrV}/L_{FeV}$ ) below a threshold temperature while the vacancy contribution pre-  
 dominates above that temperature. Between 5 and 15%Cr the alloy should tend  
 to be enriched in Cr in the vicinity of point defect sinks at low temperature and  
 to be depleted at high temperature. One should notice that both contribu-  
 tions are quite close, especially at high temperature (Fig. 4). The temperature  
 390 threshold depends on the alloys composition: it increases between 0.25 and 5%  
 Cr, then decreases between 5 and 15% (in the Fe-15%Cr alloy, the  $\alpha'$  precip-  
 itation occurs rapidly below 600 K, preventing measurement of the Onsager

coefficients, but the threshold value can be roughly estimated to be 400-500 K by extrapolation). These two features are in qualitative agreement with the experimental observations and simulations of Wharry et al. [6] performed in  
 395 alloys with concentrations between 8 and 12%Cr.

For self-interstitials, these results can be compared with the MD study by Pechenkin et al. [12], performed in a similar range of concentrations. They give a ratio of partial diffusion coefficients  $d_{CrI}/d_{FeI}$  decreasing from  $\sim 3.7$  to  $\sim 2.2$  in  
 400 Fe-5%Cr between 600 and 1000 K, and from  $\sim 1.8$  to  $\sim 1.2$  in Fe-10%Cr. With  $d_{CrI}/d_{FeI} = (C_{Fe}L_{CrI})/(C_{Cr}L_{FeI})$ , our AKMC simulations give higher ratios and higher variations: from  $\sim 8$  to  $\sim 3$  in both alloys. Penchenkin et al. [12] have measured the *tracer* diffusion coefficients of Fe and Cr by self-interstitial diffusion in Fe-Cr alloys through MD simulations and have derived an estimation  
 405 of the *partial* diffusion coefficients based on the Manning's approximation. It is thus difficult to determine if the discrepancy comes from this approximation or from differences in the self-interstitials jump frequencies. Nevertheless, the present study confirms the main conclusions of these approaches, without relying on similar approximations.

#### 410 4.3. Radiation induced segregation at grain boundaries

AKMC simulations of RIS near point defect sinks have been performed to check the predictions deduced from the measurements of the  $L_{ij}$  coefficients. Contrary to Eq. 2 they take into account the variation of transport coefficients with the solute concentration in the vicinity of the sink. Moreover, they can  
 415 model precipitation as well as segregation phenomena. We first present steady state concentration profiles when no precipitation is observed and a kinetic study of RIS and then analysis of precipitation in undersaturated and oversaturated alloys. In these simulations, Cr segregation profiles across the grain boundary are characterized by the concentration on the sink plane ( $C_{Cr}^{GB}$ ) and by the total  
 420 quantity of Cr segregated ( $S_{Cr}^{tot} = \int (\frac{C_{Cr}}{C_{Fe}}(x) - \frac{C_{Cr}^0}{C_{Fe}^0})dx$  where  $x$  is the direction perpendicular to the sink and  $C_{Cr/Fe}^0$  is the Cr/Fe concentration in the bulk) [37].

Simulations have been performed for alloy compositions from 1 to 15%Cr, at 650 K and 950 K. Simulations at 650 K were performed with a flux of  $10^{-6}$  dpa.s<sup>-1</sup> and the one at 950K with a flux of  $10^{-3}$  dpa.s<sup>-1</sup>.

Point defects and Cr concentration profiles obtained in simulations at 10%Cr and at the two temperatures are reported in Fig. 5. Steady state point defect concentrations far from sinks are given by:

$$C_V = -\frac{K_I}{2R} + \sqrt{\frac{K_I^2}{4R^2} + \frac{K_0 K_I}{R K_V}} \quad (7)$$

$$C_I = -\frac{K_V}{2R} + \sqrt{\frac{K_V^2}{4R^2} + \frac{K_0 K_V}{R K_I}} \quad (8)$$

with  $K_I = k_{Is} D_I$ ,  $K_V = k_{Vs} D_V$ , where  $k_{Is}$  and  $k_{Vs}$  terms are the sink strengths for point defects elimination [38],  $R = 4\pi R_c (D_I + D_V) / \Omega$  with  $R_c$  the critical distance of recombination,  $K_0$  the point defect production rate and  $\Omega$  the alloy atomic volume. These equations predict concentrations of vacancies and self-interstitials respectively of  $1.5 \times 10^{-11}$  and  $2 \times 10^{-13}$  at 650 K. At 950 K, these concentrations change to  $4.5 \times 10^{-10}$  and  $4.5 \times 10^{-11}$ . Our simulations show a fairly good agreement with these values. As interstitials diffuse faster than vacancies (see Fig. 3), they reach the GB more rapidly and their concentration in the bulk is lower (Fig. 5) : at steady state  $C_I D_I = C_V D_V$ .

At 950 K one observes a depletion of Cr near the GB (see Fig. 5 as an example) for all compositions. At 650K, the observed evolutions depend on the alloy concentration. At 1%Cr, we observe no evolution of the alloy composition at sinks. At 5 and 10%Cr, the GB tends to be enriched in Cr with a larger concentration increase for the alloy at 5%Cr ( $C_{Cr}^{GB}$  goes from 5% to 11%) than for the one at 10%Cr ( $C_{Cr}^{GB}$  goes from 10% to 13%). This RIS behavior is in agreement with the  $L_{ij}$  measurements summarized in Fig. 4.

The kinetic evolution of Cr segregation profile according to irradiation dose has been analyzed for the simulation at 10%Cr and 650K using a box of  $256 \times 64 \times 64$  bcc sites (see Fig. 6). We observe that the concentration at sinks reaches a

steady state very fast and that the total quantity of Cr segregated evolves much slower (an exponential fit of these evolutions gives a relaxation dose of 0.023 dpa for  $C_{Cr}^{GB}$  and 0.107 dpa for  $S_{Cr}^{tot}$ ). It has to be noted that the difference in kinetics between  $C_{Cr}^{GB}$  and  $S_{Cr}^{tot}$  observed in our simulations are in agreement with experimental observations in Ni-Cu [39] and Ni-Si [40] alloys. Moreover, by multiplying and dividing the density of sinks by a factor 2, we observe that  $S_{Cr}^{tot}$  decreases with the density of sinks but that  $C_{Cr}^{GB}$  does not evolve much with it. From our best knowledge, kinetic evolutions of concentration profiles at sinks have never been observed in the Fe-Cr alloy at such low doses. Wharry et al. [41] have nevertheless computed with their Inverse Kirkendall model a significant enrichment at sinks at low doses (lower than  $10^{-3}$  dpa) and predict a steady state of Cr enrichment which is reached at 1 dpa or less. However, their measurements on GBs show that concentration profiles keep evolving in doses higher than 1 dpa [41]. This evolution is attributed to microstructural evolutions during irradiation. In particular, the flux of ions induces an evolution of the dislocation loop density which leads to a change of defect concentration and so to an evolution of RIS profiles.

At low temperatures, the Cr enrichment may be sufficient to reach the solubility limit, even if the alloy is undersaturated. In such cases one observes a local Radiation Induced Precipitation near the GB. An example is given in an alloy at 9%Cr and at 563K on Fig. 7. In this case, Eqs. (7) and (8) give the concentrations of vacancies and self-interstitials respectively of  $1.5 \times 10^{-10}$  and  $4.5 \times 10^{-13}$  in agreement with the simulation.

The RIS phenomenon can also be associated with radiation accelerated precipitation. Indeed, at 15%Cr and 650K, the analytic RIS model predicts a depletion of Cr at sinks (see Fig. 4). However, at this composition and temperature, the alloy is in the miscibility gap and decomposes into  $\alpha$  and  $\alpha'$  phases. As shown in Fig. 8, we observe the formation of  $\alpha'$  precipitates and a small depletion of Cr in the vicinity of the sink. This decomposition is accelerated compared to thermal equilibrium as point defect concentrations are increased by irradiation in the bulk. In the GB vicinity, point defect concentrations de-

crease (Fig. 8(a)) and the nucleation, growth and coarsening of  $\alpha'$  precipitates  
480 is much slower than in the bulk: one observes a precipitate free zone around a  
GB. Such precipitate free zones have been experimentally observed by 3D Atom  
Probe during the  $\alpha'$  precipitation near grain boundary in ferritic steels [42].  
In Figs. 7 and 8 we observe some small peaks in self-interstitial concentration  
profiles. These peaks are due to trapping of self-interstitials in configurations  
485 highly concentrated in Cr and at  $\alpha/\alpha'$  interfaces.

## 5. Conclusions

In this study we have analyzed radiation-induced segregation (RIS) in the  
binary bcc Fe-Cr alloy with a new Atomistic Kinetic Monte Carlo model. The  
previous RIS model of Wharry et al. [41] uses partial diffusion coefficients  
490 defined by single effective diffusion barriers for each element-defect exchange  
fitted to a mean of migration barriers in a dilute configuration. This model  
does not exactly take into account the correlations between successive point  
defect jumps. It is nevertheless efficient for Fe-Cr alloys, as diffusion properties  
are quite simple, due to the weak Cr-V interactions. It would probably be less  
495 precise in case of drag effect.

Meanwhile, our model gives a coherent description of jump frequencies and  
transport coefficients in concentrated alloys and has the advantage that it can  
be also used to study radiation-accelerated precipitation (RAP) and radiation-  
induced precipitation (RIP). This model could however still be improved by  
500 correcting the overestimation of the negative coupling between Cr atoms and va-  
cancy diffusion. It is difficult to fully reproduce the evolution of self-interstitial  
migration properties according to the local environment. Improved diffusion  
models with interactions at longer range and/or concentration dependent saddle-  
point interactions would certainly help to reproduce these variations better.

505 Nevertheless we have confirmed qualitative conclusions of previous studies :  
the migration of vacancies toward sinks induces a depletion of Cr in the vicinity  
of sinks. The stability of mixed interstitials and their fast migration induces

a tendency towards Cr enrichment at sinks. Measures of coupling coefficients and simulations of RIS have shown that, for concentrations and temperatures  
510 outside of the miscibility gap, the alloy tends to be enriched in Cr at sinks at temperatures lower than a threshold value and to be depleted in Cr at sinks at higher temperatures. The threshold temperature depends on the bulk concentration in a non-monotonic way.

We however note that the experimental observations in ferritic steels are far  
515 less simple [4] as already noticed in [9]. The main reason is probably that RIS results from a delicate balance between the enrichment due to self-interstitials and the depletion due to the vacancy in these ferritic alloys. The situation is therefore very different from the case of austenitic alloys where the elimination of vacancies and interstitials both contribute to a depletion of Cr and enrichment  
520 of Ni [43, 44]. In ferritic steels, small variations in migration barriers can induce an inversion of tendencies [9]. These variations can be in the order of the uncertainties in DFT calculations (see also Messina et al. [16]), making such multiscale approaches to RIS phenomena especially challenging.

Furthermore, any contribution affecting the migration barriers and the  $L_{ij}$   
525 coefficients could affect the segregation behavior:

- the influence of impurities, e.g. carbon, on the experimental profiles [7, 8] that are not included here. The carbon effect will be integrated in our model in future works.

- the influence of equilibrium segregation tendencies, that may reinforce or  
530 oppose the radiation induced ones, and will strongly depend on the interaction between Cr atoms and various point defects sinks.

- long range elastic interactions between sinks (e.g. dislocations) and solute atoms.

These contributions may be introduced in AKMC simulations and give fur-  
535 ther insights into the mechanisms controlling RIS in ferritic steels.

The results presented in this paper may suggest that systematic experimental studies of RIS in pure binary Fe-Cr alloys (especially with minimum C content) depending on Cr content outside of the miscibility gap would help

to better understand couplings between defects and chemical species evolutions  
with Cr content. Moreover, most of RIS profiles have been observed at 1 dpa  
540 and higher doses. To separate short term evolution (the segregation observed  
for a given density of point defect sinks), from later evolution due to microstruc-  
tural changes, alloys could be analyzed at low doses (below 1 dpa, or even 0.1  
dpa). By comparison with ion or neutron irradiations that lead to the creation  
545 of high densities of small dislocation loops in displacement cascades, electron  
irradiation would probably delay the evolution of the sink density. This may  
also help to separate the evolution at low and high doses.

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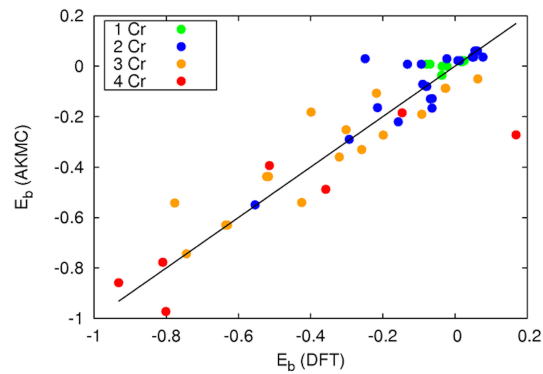


Figure 1: Binding energies between one  $\langle 110 \rangle$  dumbbell and Cr atoms in Fe. Comparison between the AKMC model and the DFT calculations.

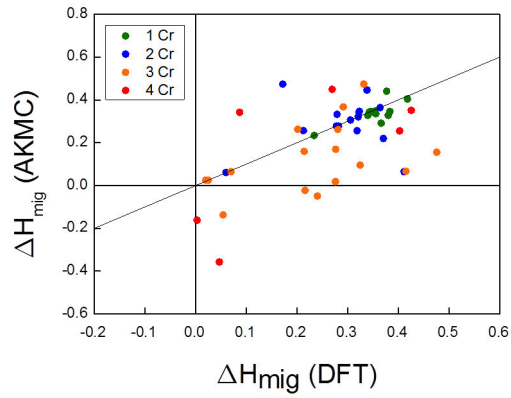


Figure 2: Migration energies of a  $\langle 110 \rangle$  dumbbell, with up to four Cr neighbors in Fe. Comparison between the AKMC model and the DFT calculations.

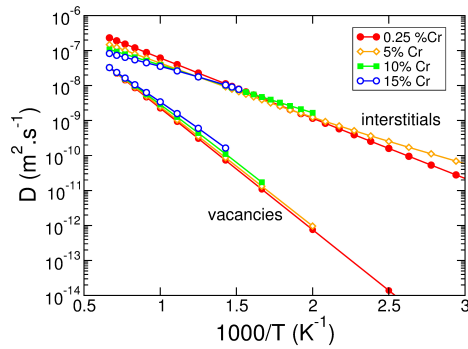


Figure 3: Vacancy and interstitial tracer diffusion coefficients in Fe-Cr alloys at various nominal compositions. AKMC simulations  $10^5 \times 10^5$  MCS in stable and metastable solutions

















SIA configuration	DFT-PAW (this study)	DFT-PAW <sup>a</sup>	2BM-EP <sup>b</sup>	AKMC (this study)
<110> dumbbells in Fe				
1 	+0.022	+0.024	+0.14	+0.022
2 	-0.038	-0.065	+0.16	-0.036
3 	+0.016	+0.05	+0.11	+0.018
4 	+0.078	+0.154	-0.19	+0.012
5 	-0.063	-0.041	-0.05	-0.166
6 	+0.048			+0.036
7 	-0.078	-0.023	+0.13	-0.080
8 	-0.293	-0.209	-0.07	-0.290
9 	+0.055	+0.154	+0.04	+0.060
10 	-0.612			-0.713
11 	-0.554	-0.425	-0.29	-0.550
12 	-0.744			-0.744
<110> dumbbells in Cr (NM)				
13 	+0.920			+1.002
14 	+2.106			+1.164
<111> dumbbells in Fe				
15 	+0.353	+0.373	+0.40	
16 	+0.207	+0.223	-0.02	

Table 2: Binding energies of various configurations obtained in our DFT calculations and AKMC model. Cr atoms are in a dark color and Fe atoms are in white. Values in eV

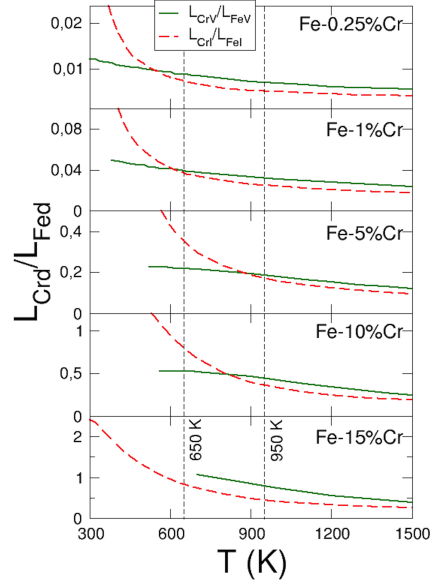


Figure 4: evolution of  $L_{CrI}/L_{FeI}$  and  $L_{CrV}/L_{FeV}$  with  $T$  for different alloy compositions. AKMC measurements:  $10^5 \times 10^5$  MCS, in stable and metastable solid solutions.

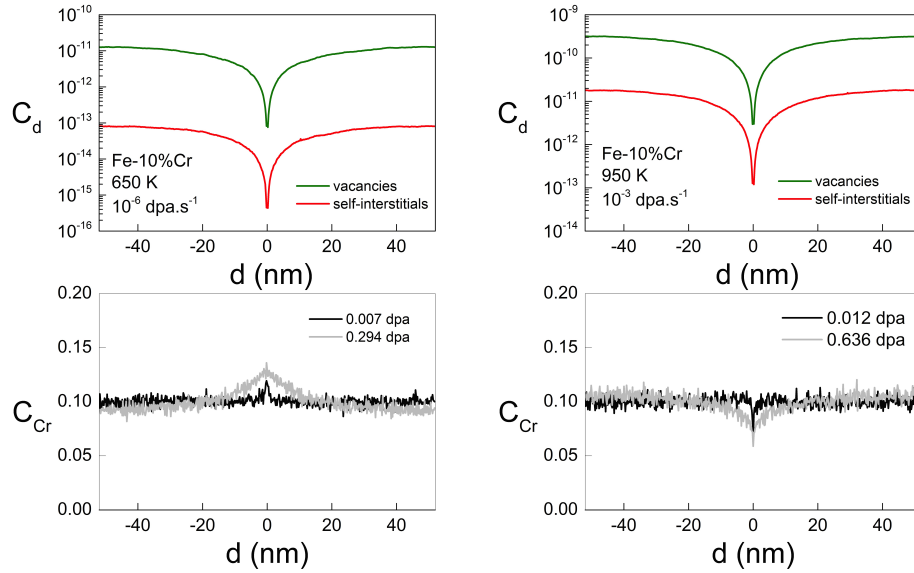


Figure 5: Steady-State point defects and Cr concentration profiles in the vicinity of a perfect planar sink for an alloy at 10%Cr left) at 650 K irradiated by a flux of  $10^{-6}$  dpa.s $^{-1}$  (at 0.007 and 0.294 dpa) right) at 950 K irradiated by a flux of  $10^{-3}$  dpa.s $^{-1}$  (at 0.012 and 0.636 dpa).

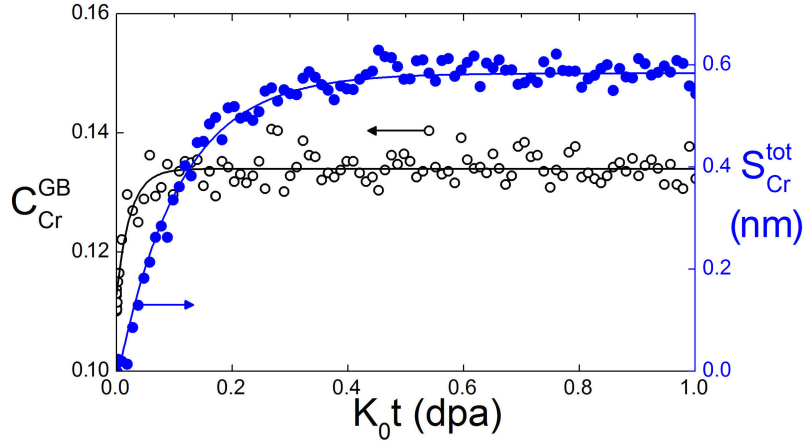


Figure 6: Concentration of Cr at sink ( $C_{Cr}^{GB}$ ) and total quantity of Cr segregated ( $S_{Cr}^{tot}$ ) as a function of dose. Simulations for an alloy at 10%Cr and 650 K using a simulation box of  $256 \times 64 \times 64$  bcc sites.

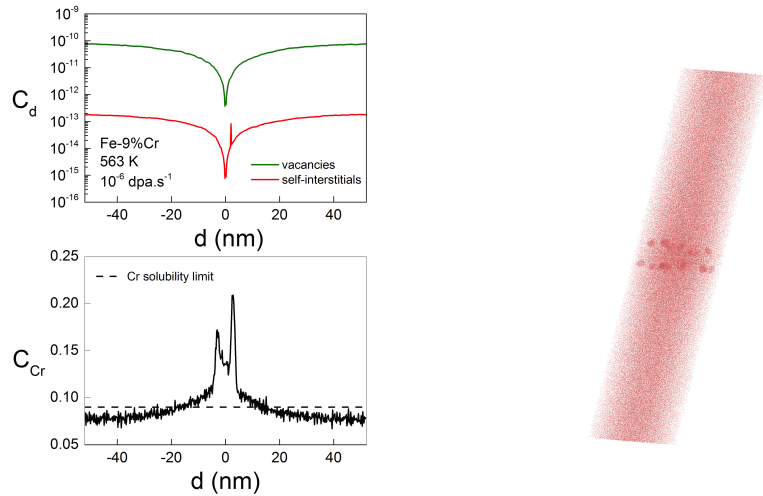


Figure 7: AKMC simulations of RIS and RIP near the grain boundary in a Fe-9%Cr alloy at 563K under a dose rate of  $10^{-6}$  dpa.s $^{-1}$  and a dose of 0.200 dpa. (left) point defects and Cr concentration profiles and (right) map of Cr atoms in the simulation box



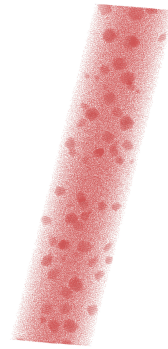
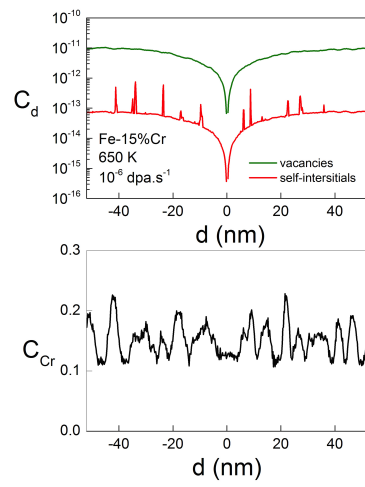


Figure 8: AKMC simulation of RIS near a grain boundary in a Fe-15%Cr alloy at 650K under a dose rate of  $10^{-6}$  dpa.s $^{-1}$ . (left) Steady-State point defects concentration profiles and (right) Atomic configuration at 0.136 dpa (only the Cr atoms are shown).