Simulation of Radiation Damage in Fe and FeCr

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Abstract

Steel is an important structural material in nuclear reactors used for example in pressure vessels and fast reactor cladding. In reactor environments it has been observed that ferritic steels are more resistant to swelling than the austenitic steels typically used. Much effort has been put into developing basic models of FeCr alloys which can serve as model alloys for describing ferritic steels. As a result, a number of interatomic potentials for Fe and FeCr alloys exist today.

For the work in this thesis, basic material properties coming from experiments or ab initio calculations were used to fit interatomic potentials for Fe, Cr and FeCr implementing both the embedded atom method and the Finnis-Sinclair formalisms. The potentials were then validated by molecular dynamic calculations of material properties such as defect formation energies, migration energies and thermal expansion. Further studies of potential performance were carried out in simulations of radiation damage cascades and thermal aging.

The influence of the interatomic potential on the primary defect state in materials under irradiation was analyzed in a study comparing results obtained using four different potentials. The objective of the study was to find correlations between potential properties and the primary damage state produced in simulations of displacement cascades. The defect evolution and clustering during different cascade stages were also investigated to try to gain a better understanding of these processes.
List of Papers

I. J. Wallenius, P. Olsson, C. Lagerstedt, N. Sandberg, R. Chakarova and V. Pontikis
   *Modeling of chromium precipitation in Fe-Cr alloys*

II. J. Wallenius, P. Olsson and C. Lagerstedt
   *Relation between thermal expansion and interstitial formation energy in Fe and Cr*
   Nuclear Instruments and Methods in Physics Research B 228 (2005) 122-125

III. D. Terentyev, C. Lagerstedt, P. Olsson, K. Nordlund, J. Wallenius, C. S. Becquart and L. Malerba
    *Effect of the interatomic potential on the features of displacement cascades in α-Fe: a molecular dynamics study*
    Submitted to Journal of Nuclear Materials, under review

IV. C. Lagerstedt, D. Terentyev, P. Olsson, J. Wallenius and L. Malerba
    *Cluster formation mechanisms during relaxation and post-relaxation cascade stages in α-Fe: a molecular dynamics study*
    To be submitted

Author’s contribution:
I performed calculations of material properties such as the thermal expansion in paper I and defect formation energies in paper II. For paper I, I also simulated and analyzed the displacement cascades presented there. For papers III and IV, I performed and analyzed a large number of the cascade simulations and wrote an appreciable part of both articles.
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Chapter 1

Introduction

About 16% of the world’s supply of electricity today comes from nuclear power [1]. As the world’s energy demand rises, this percentage is expected to increase. The production of electricity in nuclear power plants has the advantage that there is no release of greenhouse gases such as carbon dioxide. We are however left with the problem of how to handle the radioactive waste produced. The favored way of fuel disposal is to place it in deep geological repositories built to contain the radioactivity released by the waste. The geological repositories are associated with some concerns. The radioactivity of the spent fuel needs to be contained for times of the order of $10^5$ years before the radioactivity is on a level where it is deemed safe. The repositories must be constructed to contain the radioactivity for this time, a not so trivial technical problem.

One of the alternatives to direct disposal of the nuclear waste in geological repositories is transmutation, a method now under development. The concept of transmutation has existed since the 1970s [2] [3]. The idea is simple in the sense that it uses the same concept as traditional nuclear reactors; the splitting of atoms. The long lived radioactive isotopes such as Np, Pu, Am and Cm are transformed into more short lived isotopes by changing the nuclear structure. The storage times of the waste can be reduced by as much as a factor of 100 in this way, a more feasible timescale seen in the light of existing technologies.

The concept of transmutation requires some reactor features that are different from the conventional light water reactors (LWRs) that are most widely used today for electricity production. Especially of importance for this thesis is the need for neutrons of higher energy to be able to split the atoms in the fuel. More energetic neutrons means more damage to structures
surrounding the core. This can for example cause swelling and embrittlement of the steels used for structures in the reactor. Steels not designed to be radiation resistant can swell, something that seriously impairs the safety of a reactor. To ensure the safe operation of this type of future reactors and maintain the aging reactors in use today, it is important to find radiation resistant materials and to make sure that the limitations of the materials are known.

The response of a material to irradiation is not easy to predict. It depends on the dose that the material receives but also on the rate at which the material is exposed to the radiation. The damage usually does not depend linearly on the dose rate but instead shows a threshold behavior dependent on the total dose. Once the threshold dose is passed, the mechanical properties of the steel start to degrade rapidly. For steels not designed to be radiation resistant, the swelling can be as much as 1% per displacement per atom (dpa) while for ferritic steels a typical value is 0.2% per dpa. In LWRs, the dose rate is approximately 2 dpa per year and swelling in the structural materials are just starting to be seen after some 40 years of running. In fast reactors, so called because of the high energy or fast neutrons used to fission nuclei, the dose is a lot higher, ~ 40 dpa per year, and the threshold for permanent damage is reached much sooner.

Experiments focused on the study of material behavior under irradiation is both a lengthy and expensive business. It is also difficult to study the microscopic evolution of the damage to the material at the atomic level with a high degree of precision. Instead, computer simulations are employed to model materials at the atomic levels that cannot be probed experimentally.

This thesis focuses on the modelling of metals and model alloys used in reactor environment. The modelling starts with \textit{ab initio} calculations of basic material properties used for fitting interatomic potentials. The potentials are used in molecular dynamics simulations of the primary damage caused by neutron irradiation. The further evolution of the damage is studied with Monte Carlo schemes. This scheme of calculations and simulations are collectively known as multiscale modelling and covers time scales from femtoseconds to years and length scales from Ångströms to meters (see figure 1.1). Chapter 2 describes the damage caused by neutron irradiation on microscopic and macroscopic level and chapter 3 summarizes the theory behind the methods of multiscale modelling. In chapter 4, the work performed within the scope of this thesis is presented in the light of the theories discussed in the previous chapters. Finally, the thesis is summarized and an outlook for the future work is given.
Figure 1.1: The length and time scales involved in the different stages of multiscale modelling.
Chapter 2

Radiation Damage in Metals

Like human defects, those of crystals come in a seemingly endless variety, many dreary and depressing, and a few fascinating.

N. Ashcroft, N. Mermin

The materials in a nuclear reactor exist in a harsh environment where they are continually bombarded by energetic neutrons. The atoms of the metal used to construct reactor parts such as the pressure vessel or the fuel cladding are arranged in crystal structures. The structures are made up of unit cells repeated in a periodic fashion. When the metal is subjected to neutron irradiation, the atoms in the crystal structure can be displaced, knocking atoms out of their places, leaving damage in the form of vacant lattice positions and atoms in interstitial positions and inducing nuclear reactions resulting in impurities. These defects and impurities change the microscopic structure of the metal and thereby macroscopic material properties and behavior. The following sections will describe the reactions that take place in metals under neutron irradiation, the primary damage that the radiation causes and radiation effects arising due to the primary damage.

2.1 Mechanisms

Neutrons incident on a material can interact with the atoms in the lattice by elastic or inelastic collisions depending on the neutron energy. At low neutron energies of less than 1 MeV, elastic collisions dominate. In an elastic collision, the total kinetic energy of the system is conserved. It may however be redistributed between the neutron and the atom taking part in the collision and the neutron can transfer energy to the atom causing it to recoil. In this energy range, $(n, \gamma)$ reactions can also occur. Here the
neutron is absorbed by the nucleus. The nucleus de-excites by emitting a \( \gamma \)-photon causing the nucleus to recoil.

If the energy transfer to the nucleus is above a certain threshold value, the atom may be knocked out of its place and can go on to collide with other atoms in the crystal creating a collision sequence where the atom hit by the neutron is named the primary knock-on atom (PKA). The size of the threshold energy depends on the material but for bcc Fe it is in the range of tens of eV depending on the direction in which the atom is displaced.

At higher energies above 1 MeV, non-elastic processes such as \((n, n')\), \((n, \alpha)\) and \((n, p)\) reactions dominate. Both the emitted particle and the recoiling nucleus can cause displacement of other atoms in the crystal. Nuclei in the crystal can also be fissioned by neutrons. The ionized fragments can then collide with surrounding atoms again displacing atoms.

### 2.2 Primary Damage: Vacancies and Interstitials

The elastic and inelastic collisions between neutrons and atoms leads to displacements of nuclei as described in the section 2.1 where some or all of the neutron energy can be transferred to the PKA. The fate of the neutron then depends on how much energy it has left after the collision and where it is in the reactor. In the pressure vessel, it can continue to collide with atoms until its energy is dissipated or it can be absorbed either in the fuel or in the structural materials of the reactor.

If the energy transferred from the neutron to the PKA is above some threshold energy called the displacement energy, \( E_d \), the PKA atom will be knocked out of its position in the crystal structure initiating a displacement cascade as shown in figure 2.2(a). The displacement cascade results in a number of vacant lattice positions, vacancies, an equal number of atoms located in interstitial positions in the crystal, interstitials, and a number of replaced atoms. Examples of the defect configurations are shown in figure 2.1. A vacancy and an interstitial together make up what is called a Frenkel pair.

The vacancies and interstitials produced in displacement cascades constitute the primary damage state caused by neutron radiation. The amount of damage of course depends on the number of displaced atoms. Kinchin and Pease proposed a simple relationship between the damage energy and the number of displaced atoms \([4]\). According to their model, the number of displaced atoms is given by
Radiation Damage in Metals

(a) Vacancy
(b) 100 dumbbell
(c) 110 dumbbell
(d) 111 dumbbell

Figure 2.1: Different types of defects that can arise in a bcc structure due to neutron irradiation. (a) shows a vacancy which is an empty lattice space where an atom has been knocked out of its position. Here the vacancy is represented by the square. (b), (c), and (d) show examples of different kinds of interstitial configurations.
2.2. Primary Damage: Vacancies and Interstitials

\[ N_d = \begin{cases} 
0 & 0 < E < E_d \\
1 & E_d < E < 2E_d \\
\frac{E}{2E_d} & 2E_d < E < E_1 \\
\frac{E_1}{2E_d} & E_1 < E < \infty 
\end{cases} \]  

(2.1)

where \( E \) is the kinetic energy of the PKA. Below \( E_1 \), the PKA atom loses energy by hard-core elastic scattering while above this energy, energy loss comes from electron excitation only. This estimation makes a number of assumptions and several developments of the model exists. The most widely used formula in the field of radiation damage is the NRT estimate, an updated version of equation 2.1 by Norgett et al. [5]

\[ N_d = \kappa (E - \hat{Q}) \quad \frac{2E_d}{2E_d} = \frac{\kappa \hat{E}}{2E_d}; \quad \hat{E} > \frac{2E_d}{\kappa} \]  

(2.2)

where \( \kappa \) is the displacement efficiency taken to be 0.8 at all temperatures, \( \hat{Q} \) is the energy lost by electron excitation and \( \hat{E} \) is the damage energy, i.e. the energy available for atomic displacement. The size of the displacement threshold energy depends on the material studied. For bcc Fe which is the focus of this thesis, a standard threshold energy of 40 eV is assumed [5].

The cascade region where most of the interstitials and vacancies are produced represents a highly disordered state. At high cascade energy, local melting may be considered to occur. Interstitials and vacancies that are close enough to each other to interact will recombine directly during the cascade and the deposited heat will dissipate during the first picoseconds of the cascade. Recombination will be the fate of most of the point defects produced during the cascade.

The interstitials that remain after the cascade are those that end up far enough from vacancies to escape annihilation. These interstitials are created in collision sequences where atoms are substituted in a chain of replacements through the crystal transporting them away from the initially vacant lattice space. In this way vacancies are seen to be concentrated at the center of the cascade region while interstitials are located in a halo surrounding the central area of the cascade. The point defects that escape annihilation make up what is called the primary damage in the crystal, an example of which can be seen in figure 2.2(b). The evolution of the primary damage is what determines the changes of micro- and macroscopic properties of the material.

The other reactions that take place in the crystal during neutron irradiations such as \((n, \alpha)\), \((n, p)\) or \((n, 2n)\) result in a number of foreign atoms in
Figure 2.2: In this figure, different stages of a displacement cascade are exemplified. In (a) the cascade is seen at the peak stage defined as the time when the maximum number of defects are produced in the system. Most of these defects will recombine and disappear. Those that are left make up the primary damage state seen in (b).
2.3 Primary Damage Evolution

After the recombination stage of the cascade, the resulting point defects will determine the evolution of the material. At low temperatures, the defects are immobile and will not be able to migrate in the metal. At temperatures above the migration energy of the defects, interstitials and vacancies will start to move in the crystal. Should a vacancy and an interstitial encounter each other they will annihillate. If instead they encounter another defect of the same kind they will form clusters. They can also be absorbed at preexisting sinks such as grain boundaries, dislocations or surfaces. The interstitial clusters will collapse into dislocation loops as they reach a certain size. Vacancy clusters can also collapse into vacancy loops. However, they are more stable and can also form voids in the crystal [6].

The clustering of point defects can be described by standard rate theory [7]. Here, the concentration of clusters are given by the discrete master equations

\[
\frac{dC_j}{dt} = \sum_k w(k; j)C_k - \sum_k w(j; k)C_j + G_j - L_j
\]

where \( C_j \) is the concentration of clusters of type \( j \), \( w(k; j) \) is the rate per unit concentration of cluster type \( k \) of transitions to a cluster of type \( j \), \( G_j \) is the rate of direct formation of clusters of type \( j \) and \( L_j \) is the loss rate of clusters of type \( j \) by absorption at sinks, destruction in cascades, etc. These equations can in principle be solved but this is feasible in a reasonable time for only a small number of equations. Instead, simplifications and approximations are introduced giving us the Fokker-Planck equation.

\[
\frac{\partial C_j(t)}{\partial t} = -\frac{\partial}{\partial j}\left[C_j(t)[w(j; j+1) - w(j; j-1)]\right] + \frac{1}{2} \frac{\partial^2}{\partial j^2}\left[C_j(t)[w(j; j+1) + w(j; j-1)]\right]
\]

The standard rate theory used to derive the Fokker-Planck equation assumes point defect generation to be homogeneous in space and time which is not always true. Point defects are produced in cascades and defect clusters are also seen to be generated directly during cascades so the number of freely
migrating vacancies and interstitials are not equal to each other. A large fraction of interstitials end up in mobile clusters while vacancies tend to end up in immobile configurations and thus there is a production bias in favor of interstitial mobility [8].

2.3.1 Swelling

The interstitials are more mobile than the vacancies and tend to move towards dislocations, grain boundaries or surfaces where they annihilate. The vacancies on the other hand remain in the bulk and gather in growing voids causing the material to swell. The swelling shows a threshold behavior depending on both the total dose and the exposure time. Although the swelling rate actually decreases with increasing dose rate, the total dose in a fast neutron spectrum is higher than in a thermal spectrum and the threshold for swelling is reached in a much shorter time.

From the Fokker-Planck equation (equation 2.4), an expression for the growth rate of a vacancy cluster can be derived [7]

\[
\frac{dr_c}{dt} = \frac{\Omega}{r_c} (Z_{di}^d Z_v^c - Z_{d}^d Z_{v}^c) F
\]

(2.5)
where \(r_c\) is the cluster radius, \(\Omega\) the atomic volume, \(Z\) are the capture efficiencies of cavities and dislocations and \(F\) is a function of total dislocation and cavity sink strengths, of dose rate and of point defect recombination. The term \(Z_{di}^d Z_v^c - Z_{d}^d Z_{v}^c\) is called the bias and has to be greater than zero for the cluster to grow.

The presence of helium in the material increases the swelling mainly due to internal pressurization of voids. The void growth rate depends on the thermal emission of vacancies from clusters. Once the cavity has attained a critical radius it will continue to grow. A larger internal pressure in the cavity makes it easier for the cavity to attain a critical radius and continue to grow. The swelling rate can be as large as 1–2% per dpa in a fast neutron spectrum depending on the temperature and dose rate [9] as can be seen in figure 2.3.

The dose dependency of the swelling rate can be divided into three stages. At low doses the material swelling is small. After a threshold dose is attained, the swelling rate increases and then levels out again at higher doses. Temperature also influences the swelling rate of a material under irradiation [7]. At low temperatures, the thermal emission of vacancies from clusters will be high enough
2.3. Primary Damage Evolution

Figure 2.3: Swelling is shown as a function of the dose received by the material. At low doses the swelling is small while after the threshold dose is reached the swelling rate accelerates. The curves show the swelling behavior of different alloys. The 15-15Ti alloy is an austenitic steel with fcc structure with a swelling rate of 1% per dpa in the accelerated swelling phase. Bcc materials such as FeCr and the EM10 steel (Fe-9Cr-1Mo) have a lower swelling rate of 0.2% per dpa in the accelerated swelling phase. By adding Mo to the Fe-9Cr model alloy increases the threshold dose for accelerated swelling dramatically.

to compete with the influx of vacancies due to irradiation. This leaves the intermediate temperature regime where the largest swelling rates are seen. Here the thermal emission of vacancies from cavities is small and recombination is large while the flow of vacancies to voids is large. The definitions of low, high or intermediate temperature depends on the material but generally maximum swelling rates are seen at temperatures of 30 – 50% of the melting temperature, $T_{melt}$. No swelling is seen at temperatures above 60% of the melting temperature [10].

2.3.2 Hardening and Embrittlement

The mechanical properties of the material can be greatly affected by irradiation. Initially ductile materials can become hard and brittle and for
Figure 2.4: The figure shows stress-strain curves for ductile and brittle materials. The ductile material will deform plastically until it breaks while the brittle material shows almost no deformation before breaking [11].

materials with a ductile-to-brittle transition, the temperature at which this transition takes place can shift due to irradiation. These effects have complex dependencies on dose rates, material microstructure and temperature. Embrittlement is a safety issue as ductile deformation tends to occur over a longer time giving a slower fracture with a larger chance of discovery (see figure 2.4).

At temperatures below the ductile-to-brittle transition temperature, (DBTT), the yield stress of a material is larger than the fracture stress. In this region the fracture will be brittle which means that the material will break with very little plastic deformation. The yield stress is more temperature dependent than the fracture stress. As the temperature is increased, the yield stress will become smaller than the fracture stress and the fracture mode of the material will become ductile and undergo plastic deformation before fracturing.

For dislocations to move in a material, they need a certain energy to overcome barriers and obstacles. By raising the temperature in the material, the dislocations are given more energy enabling them to pass obstacles in their way. However, irradiating a material introduces more obstacles and
Figure 2.5: A general picture of the ductile to brittle transition in bcc metals such as ferritic steels. At low temperatures the material experiences brittle fracture and at high temperatures plastic fracture. In the transition region, both kinds of fracture are seen. When the material is irradiated, the transition region is shifted towards higher temperatures as shown by the arrow.

thus the dislocations need more energy to overcome the barriers. Thus the temperature at which the material turns from brittle to ductile is raised i.e. the DBTT is shifted towards higher temperatures as seen in figure 2.5.
Chapter 3

Multiscale Modelling

We all like to congregate at boundary conditions.
Douglas Adams

The most exact way of calculating material properties is to solve the Schrödinger equation directly. For complex systems such as metals however, the calculations soon become impossibly complicated and approximative methods have to be used instead. All approximative methods need some basis for comparison and development. With ab initio calculations, fundamental material properties can be provided as the basis for constructing and refining such methods.

The modelling of recoil cascades in metals requires the use of interatomic potentials which approximate the interaction between the atoms. The potentials are constructed by fitting to a combination of empirical and ab initio data. The potentials are then used in molecular dynamics and Monte Carlo simulations to study what happens in the material when it is irradiated by neutrons.

3.1 Ab Initio

To calculate basic properties of intermetallic compounds such as total energies, bulk and elastic moduli, relative stability of structures, etc ab initio methods are used. In quantum mechanics we are faced with the problem of finding a many-body wave function that solves the Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi(r) = E\Psi(r).
\]  (3.1)
The problem is addressed in methods such as the Hartree-Fock theory but for large systems the calculations are too time consuming to be practically viable. Instead we rely on density functional theory (DFT) to overcome the problem of solving the many-body system.

DFT is a quantum mechanical approach that maps the many-body electron problem onto a single-body problem by the use of the electron density \( n(\mathbf{r}) \) as a key variable from which other observables can be calculated.

DFT was first developed by Thomas and Fermi in the 1920’s. Their theory was rather inaccurate due to the fact that it neglected electron correlation. The theoretical basis of DFT was developed by Hohenberg and Kohn [12] who published a theorem proving that a one-to-one mapping exists between the ground state electron density and the ground state electron wave function of a many-body system and that the ground state density minimizes the energy of the system.

The minimization of the energy can be done using a method developed by Kohn and Sham [13]. The nuclei in a solid are seen as fixed (the Born-Oppenheimer approximation) and generate a static potential in which the electrons move. Electronic interactions are represented by an effective potential

\[
v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})
\]

where \( v(\mathbf{r}) \) is the external potential coming from the nuclei in the solid and any other external potential applied to the solid as a whole, \( v_H(\mathbf{r}) \) is the Hartree potential

\[
v_H[n](\mathbf{r}) = q^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

and the last term \( v_{\text{xc}}(\mathbf{r}) \) is the exchange correlation potential. The electronic density is written

\[
n(\mathbf{r}) = \sum_{i=1}^{N} |\Psi_i(\mathbf{r})|^2
\]

Equations 3.2 - 3.4 are known as the Kohn-Sham equations and can in principle be solved explicitly. However the function for the exchange correlation potential is not known. Several approximations of this function exist. One of the most common is the local density approximation, LDA. Here, the energy functional depends only on the electronic density at the point of evaluation. The local spin-density approximation, LSDA, is a generalization...
of the LDA that includes electronic spin. In the general gradient approximation GGA, the exchange correlation functional is expressed in terms of the density and the density gradient at each point.

3.2 Interatomic Potentials

In the previous section, methods of calculating basic properties of a material using quantum mechanical methods was discussed. This of course gives the most exact results but at the expense of long computing times. For systems with more than 500 atoms or systems with large strain field distortions, quantum mechanical calculations are not feasible with today’s computer capacity necessitating a simplified description of the system. Using approximate methods based on density functional theory, systems with a number of atoms of the order of 1000000 are possible to model.

The common factor for all atomistic methods of approximation is the description of how the particles interact in a material. This can be done by constructing interatomic potentials. Lennard-Jones introduced one of the first pair potentials in 1924 which gave a good description of the atomic interactions in noble gases. For the more complex systems of metals however, it is inadequate. In the 1980s, several methods of many-body potential construction were introduced for example by Daw and Baskes [14] [15] and Finnis and Sinclair [16]. The formalisms of relevance to this thesis are reviewed in the following sections.

3.2.1 The Embedded-Atom Method

The embedded-atom method, EAM, is a semi-empirical method used to describe metals and alloys [17]. The roots of EAM come from density functional theory (DFT) where each atom in a solid is seen as embedded into a host consisting of all the other atoms in the system and the energy of an individual atom can be expressed as a functional of the electronic density [12].

This functional, whose form is unknown, is a universal function independent of the host system. Making the approximation that the energy depends only on the local electronic density at the site of the atom, the total energy can be written

$$E_{tot} = \sum_i F_i(\rho_i)$$  \hspace{1cm} (3.5)
where $F_i$ is the embedding energy function of an atom in the solid, $\rho_i = \sum_{j \neq i} \rho(r_{ij})$ is the electronic density at atom $i$ and $r_{ij}$ is the interatomic distance. However, this approximation does not give a correct description of the solid as it neglects contributions to the energy from gradients in the electronic density and repulsion between the cores of the atoms. Instead the energy is expressed as

$$E_{\text{tot}} = \sum_i E_i = \sum_i \left[ \frac{1}{2} \sum_{j \neq i} V(r_{ij}) + F(\rho_i) \right]$$

(3.6)

$V_{ij}(r_{ij})$ is a short-range potential that gives the contribution to the energy coming from the repulsion between the cores of the atoms. The pair potential is a function of the distance and the energy coming from this term varies with the radial distance between atoms. The method can be extended to an alloy system by writing the energy as

$$E_i = \frac{1}{2} \sum_{j \neq i} V_{t_i t_j}(r_{ij}) + F(t_i)(\bar{\rho}_i)$$

(3.7)

where $t_i$ represents atom $i$ of type $t$ and

$$\bar{\rho}_i = \sum_{j \neq i} \rho_{t_j}(r_{ij})$$

(3.8)

Having found an expression for the energy of a solid, we are still left with the problem of finding $V$ and $F$. In theory, this can be done from first principles but in practice it turns out to be difficult. Instead the functions can be found empirically from known properties of the solid or alloy. The function parameters for the pair potential can be fitted from solid properties such as lattice constant, cohesive energy or bulk modulus for example. For an example see section 4.1 where the fitting is described in more detail.

Finally, we are left with the function for the embedding energy. This energy can be found using the universal expression for the energy as a function of lattice parameter (equation of state) given by the Rose equation [18]. The equation scales the cohesive energy of the solid to a universal function as follows

$$E_{\text{Rose}}(\bar{a}) = -E_{\text{coh}}(1 + \bar{a}) \exp(-\bar{a})$$

$$\bar{a} = \alpha \left( \frac{r_{1nn}}{c_{1nn}} - 1 \right)$$

$$\alpha = \sqrt{9B\Omega/E_{\text{coh}}}$$

(3.9)
where $E_{coh}$ is the cohesive energy, $B$ is the bulk modulus, $\Omega$ the atomic volume, $r_{1nn}$ is the distance to the first nearest neighbor and $r_{eq}^{1nn}$ the same distance at equilibrium. Having already chosen and fitted expressions for the pair energy, the embedding energy can be found from

$$F(r) = E_{Rose}(r) - V(r)$$  \hspace{1cm} (3.10)$$

The embedding energy is then inverted to a function of density instead of $r$ using the expression for the electronic density in the solid. An electron density function for the system is adopted depending on the solid or alloy that is to be described.

For alloys, the pure elements are fitted to their separate properties. A cross-wise pair potential is then fitted from the contributions to the energy coming from the interaction between atoms of different types. No cross-wise embedding energy needs to be calculated. The energy contribution coming from the embedding function is density dependent. The density in turn is a superposition of the separate densities of the atoms surrounding the sites and can be taken directly from the separate density functions for the pure elements.

The physical interpretation of the embedding energy term can be related to the concept of traditional chemical bonding. As more bonds are created, the total bonding energy will increase. However, the contribution from each successive bond will be smaller and smaller and the average bonding energy will decrease. Therefore, to have a physically consistent description of a material, the curvature of the embedding energy should be positive giving $\frac{d^2 F}{d\rho^2} > 0$.

The Cauchy pressure is seen to be directly proportional to the second derivative of the embedding energy. For some transition metals, the Cauchy pressure is negative and this would then imply that the bonding in the material is not correctly described arising from problems with directional bonding.

The modified embedded-atom method, MEAM, is a method developed as an extension of the EAM to include directional bonding [19] [20]. Angular terms are added to the electron density as a correction to the spherically symmetric electron density used in EAM. The embedding function is chosen as a simple function of the electron density including angular terms. The pair potential is then found using the Rose equation in the same manner as for the embedding function in EAM. The procedure for alloys will be different from EAM; this time cross-wise terms are also needed for the embedding function since the electron density now has angular terms.
3.2. Interatomic Potentials

3.2.2 The Second Moment Approximation

The second moment approximation bears a close resemblance to EAM but is based on tight binding theory, thus providing a correlation to the band structure of the electron energies in a solid [21]. The bonding energy is taken to be dependent on the density of states (DOS) of the electrons which in turn is approximated by \( \sqrt{\mu_i} \), the square root of the second moment of the DOS on atom \( i \). The expression for the energy of an atom will in this formalism be

\[
E_i = \frac{1}{2} \sum_{j \neq i} V(r_{ij}) - A(\sum_{j \neq i} h_{ij}^2(r_{ij}))^{1/2}
\]  

(3.11)

Assuming

\[
\rho(r) \equiv h_{ij}^2(r)
\]  

(3.12)

and

\[
F(\bar{\rho}) \equiv -A(\bar{\rho})^{1/2}
\]  

(3.13)

the expression is seen to be in the same form as the EAM energy expression although with a modified embedding function. This way of expressing the energy has been developed by for example Finnis and Sinclair [16].

The negative square root dependence naturally gives a positive second derivative of the embedding function and is thus consistent with the interpretation of the bonding strength as discussed for the EAM in section 3.2.1.

3.2.3 Two-Band Models

It is well known that the \( d \) electrons are responsible for the cohesive energy of transition metals. Pettifor showed however that the \( s \) electrons give a large contribution to the pressure as well as the bulk modulus [22]. The pressure is a balance of the repulsive forces of the \( s \) electrons and the attractive forces of the \( d \) electrons while the bulk modulus is dominated by contributions from the \( s \) electrons. In the original second moment approximation, the \( s \) band contribution was neglected. The cohesive energy is therefore well reproduced but for the transition metals, the contribution from the \( s \) electrons could be very important for other material properties.

The two-band models can be included into the EAM model by extending the embedding part of the energy expression [23] [24]. The total energy is then written
Multiscale Modelling

\[ E_i = \frac{1}{2} \sum_j V(r_{ij}) + F_d(\rho_d) + F_s(\rho_s) \]  

(3.14)

where the density is given by

\[ \rho_b = \sum \Phi_b(r_{ij}). \]  

(3.15)

The embedding energy is given by

\[ F_b(\rho_b) = A_1 \sqrt{\rho_b} + A_2 \rho_b^2 + A_3 \rho_b^4 \]  

(3.16)

The last two terms are added to reproduce the repulsive force of the d electrons at small distances where the electron density is high. In this way, the two-band models retain the simplicity of EAM and FS while giving a more correct physical description of the materials being modelled.

3.3 Molecular Dynamics

Molecular dynamics (MD) is based on Newton’s classical equations of motion [25]. The forces between atoms in a system of \( N \) particles are described by

\[ \mathbf{f}_i = m_i \ddot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i} V \]  

(3.17)

where \( \mathbf{f}_i \) is the force on atom \( i \) in the system, \( m_i \) is the mass of atom \( i \), \( \ddot{\mathbf{r}}_i \) is the acceleration of atom \( i \) and \( V \) is the potential defined for the atoms in the system describing their interactions. From this it can be seen that the foundation of MD rests on a potential that describes atomic interactions as correctly as possible since all dynamic properties of the solid is calculated using it.

The motivation for using classical equations of motion can be seen by looking at the de Broglie wavelength of an atom. The de Broglie wavelength is given by

\[ \lambda = \frac{h}{\sqrt{2mE_k}} \]  

(3.18)

where \( h \) is Planck’s constant, \( m \) is the mass and \( E_k \) the kinetic energy. Calculating the wavelength of an Fe atom at 100 K, this will give \( \lambda \sim 0.1 \) Ångströms. As the lattice constant of bcc Fe is of the order of Ångströms, the transition from quantum to Newtonian mechanics is valid. At lower temperatures or for atoms of smaller mass, the de Broglie wavelength will
be of the order of Ångströms, and Newtonian mechanics will no longer be applicable.

To solve the equations of motions for the system, the finite differences method developed by Alder and Wainwright [26] can be employed. At the start of the simulation at time $t_0$, each atom is assigned a position and a random velocity at the temperature $T$ specified for the system. Knowing these, the positions, velocities and accelerations of the atoms at time $t_0 + \delta t$ are obtained. From the positions and velocities of the atoms, the forces and hence the accelerations of the atoms in their new positions can be calculated. These can be compared to the predicted values and corrected to give the correct atom trajectories. This procedure is then iterated for as many time steps as wanted and any variables that are of interest can be calculated after each time step in what is called a predictor-corrector scheme. Different variants of predictor-corrector algorithm exists, such as for example those by Gear [27] and Verlet [28]. The limiting factor in these calculations are of course time. For efficient computing, the time step $\delta t$ should be as large as possible while for the precision of the calculations, $\delta t$ should be small enough to minimize errors in the atom trajectories.

When running MD simulations, normally the system is chosen to be contained within a box although other configurations such as spherical systems exist. To simulate a bulk environment, periodic boundary conditions (PBC) are normally used. The simulation box is set up with the desired number of atoms which are given initial positions and velocities. The simulations can be run with different ensembles. The microcanonical constant or NVE ensemble or the canonical or constant NVT ensemble are often used. In the microcanonical ensemble, the number of atoms $N$, the volume $V$ and the energy $E$ of the system are constant parameters while in the canonical ensemble, the temperature $T$ is kept constant instead of the energy. The ensemble chosen depends on the purpose of the simulation. When the simulation starts and the atoms close to the outer boundaries of the box begin to move, they may end up in a position outside the simulation box. With PBC, an atom that exits the box at one surface will enter the system again at the opposite surface of the box. This reduces the number of images needed to be saved during the simulation and also conserves the number density in the simulation box. The influence of PBC on thermodynamic properties and structures have been shown to be small enough to be neglected [25]. When performing cascade simulations (see section 4.3) the box has to be large enough to contain the cascade without any self-interaction at boundary crossing.

When calculating the forces on an atom, the interaction between this
atom and all other atoms should in principle be calculated. To reduce the simulation time, a potential cutoff is usually employed. The interactions with atoms further away than a certain distance are usually set to zero. As the largest contributions to the force on the atom usually comes from the closest atom this gives only a small error as long as the cutoff radius is large enough to include all atoms that are within the interaction range of the potential.

3.4 The Monte Carlo Method

The Monte Carlo (MC) method was developed at the end of the 2nd world war at Los Alamos as a way of studying diffusion in fissionable materials [29]. The name Monte Carlo originates in the fact that random numbers are so extensively used. The method is based on stochastic methods and generates a trajectory in phase space for each atom based on sampling from a chosen statistical ensemble.

A system is regarded as composed of a number of particles or objects of different kinds. A number of processes or events are defined. The particles or objects in the system are each associated with one or more of the processes meaning they can take part in this kind of activity. The rate at which a certain process occurs for an object in the system is then defined as

\[ r_i = \nu_i e^{-\Delta E_i / kT} \]  

(3.19)

where \( \nu_i \) is a prefactor associated with process i, \( \Delta E_i \) is the activation energy for process i, \( k \) is the Boltzmann constant and \( T \) is the temperature. If \( n_i \) particles or objects are associated with a certain process, then the rate at which this particular process takes place will be

\[ R_i = n_i r_i \]  

(3.20)

and the total rate of the system can be written

\[ R = \sum_i n_i r_i \]  

(3.21)

The probability of a certain process or event taking place is then given by

\[ p_i = \frac{R_i}{R} \]  

(3.22)

For each MC step, a process or event that will take place is chosen according to its probability and the particle that will take part in the process or event is
selected randomly from the number of particles associated with this process $n_i$.

In the above version of the Monte Carlo method, time is not included in the simulation. To introduce time, the kinetic Monte Carlo scheme was constructed. In the residence time algorithm by Young and Elcock [30], diffusion in the system is due to vacancy jumps, the rate of which are described by equation 3.19. The time associated with the process is then given by the inverse of the rate:

$$\Delta \tau = \frac{1}{\sum n_i R_i} \quad (3.23)$$

Different versions of the kinetic MC scheme exist such as atomistic kinetic Monte Carlo (AKMC) and object kinetic Monte Carlo (OKMC) depending on the purpose of the simulations [31]. AKMC is run on a rigid lattice and retains an atomistic level of description of the system. It always includes a calculation of the total energy of the system making it detailed but making simulations of larger systems time consuming. OKMC is so called since it treats what is termed as objects instead of atoms. Objects can be point defects, point defect clusters, solute atoms or any other system feature that the simulant wants to include in the system. This way of simulating makes longer time scales feasible. However, only interactions between objects defined and included in the system can be simulated. Any new processes cannot be found using this method. It is often used in conjunction with MD where the primary damage state of the system is found and used as input in the OKMC simulations.
Chapter 4

Applications

The work performed within the scope of this thesis has been concerned with modelling the FeCr system which serves as a model alloy for studying more complex systems such as those of steel. Ferritic steels, which are steels with a body-centred cubic (bcc) structure, are a common material used in reactor environments and knowledge of its behavior under irradiation is crucial for the upkeep of existing reactors and for the development of new reactor types. This section will describe applications of some of the theories and models previously described to the FeCr system.

4.1 Potential Construction

As has been mentioned, the success in modelling a material rests on the description of the atomic interactions in the system. In this work, potentials have been constructed within the EAM and FS formalisms. When looking at the binary alloy FeCr, the expression for the total energy (see equation 3.7) will be

\[
E_{tot} = \sum_{i_Fe} F_{Fe}(\rho_i) + \sum_{i_Cr} F_{Cr}(\rho_i) + \frac{1}{2} \sum_{i_Fe,j_Fe} \Phi_{Fe}(r_{ij}) + \frac{1}{2} \sum_{i_Fe,j_Cr} \Phi_{FeCr}(r_{ij}) + \frac{1}{2} \sum_{i_Cr,j_Cr} \Phi_{Cr}(r_{ij}) + \frac{1}{2} \sum_{i_Cr,j_Fe} \Phi_{FeCr}(r_{ij}).
\]

From this can be seen that we need to fit pair potentials for the pure elements Fe and Cr and a mixed potential for FeCr while for the embedding energy,
functions are needed for the pure elements only.

4.1.1 Pair Potentials and Embedding Functions for Fe and Cr

The potentials fitted for Fe, Cr and FeCr are presented in papers I and II and examples are shown in figure 4.3. Those in paper I use the EAM formalism while those in paper II use the FS formalism. In each case, the pair potentials were chosen as spline functions of the form

\[ V(r) = \sum_{i=1}^{n} a_i (r - r_i)^3 H(r_i - r) \]  \hspace{1cm} (4.2)

where \( H \) is the Heaviside step function and \( r_i \) are the knot points of the spline. The pair potential fitting parameters \( a_i \) and the spline knot points \( r_i \) were fitted to material properties from experiments or \textit{ab initio} calculations such as cohesive energy, lattice parameter and elastic moduli. The cohesive energy is given by the total energy of the system at equilibrium, the lattice constant can be found using the condition that the first derivative of the total energy should be zero at equilibrium and the elastic constants are given by the second derivatives of the total energy. The fitting is performed using the MERLIN code package developed for multiparametric optimization [32]. Once the pair potentials are fitted for the pure elements, the embedding functions can be found using the Rose expression (see section 3.2.1).

In the case of Cr, the applicability of the EAM method is not evident. At low temperatures, Cr is antiferromagnetic and has a negative Cauchy pressure. However, above the Néel temperature of 311 K, Cr turns paramagnetic and the Cauchy pressure becomes positive [33]. Here, the elastic constants are seen to depend linearly on the temperature as shown in figure 4.1. Extrapolating the values of the elastic constants of the paramagnetic material to 0 K, these can be used to fit the potential for the pure element. The potential will be valid for paramagnetic Cr only but in the case of materials used in reactor environments, operation temperatures are well above the Néel temperature.

To correctly reproduce atomic interactions at small distances, the potentials are stiffened at short range. For the Fe potential in paper I, this is done after fixing the embedding function which means that the pressure-volume relation given by the Rose equation is violated. For high densities resulting from anisotropic compression as in the vicinity of interstitials however, the material is not expected to be in equilibrium and this relation and
4. Applications

Figure 4.1: The figure shows the elastic constant $C_{11}$ for Cr as a function of temperature. Notice the sharp cusp at the Néel temperature where Cr changes from the antiferromagnetic to the paramagnetic phase. Above 450 K, the curve is linear. The function above this temperature is extrapolated to 0 K and the value used as a fitting parameter for paramagnetic Cr.

the stiffening, though arbitrary, is motivated by being able to fit experimental values for phase stability, correct interstitial stability and thermal expansion. The potential for pure Cr in paper I is stiffened by fitting to the thermal expansion of the material. In paper II, the FS approach was adopted to be able to fit the embedding functions in a consistent way.

4.1.2 Pair potentials for FeCr

Having found expressions for both the pair and the embedding energy of the pure elements, an expression for the energy of the interaction between two atoms of different types can be found using equation 4.1. The potential can then be further adjusted to reproduce relevant material properties.

For the FeCr system, 

\textit{ab initio} calculations show that the mixing enthalpy seen in figure 4.2 is negative at low concentrations of Cr [34]. Different methods for reproducing the change in mixing enthalpy can be envisioned. For example, concentration dependent potentials can be fitted giving different mixing enthalpies as was done in paper I. Here, two potentials were provided, one fitted to the negative mixing enthalpy of the alloy with 5% Cr and one fitted to the positive mixing enthalpy at 20% Cr. This method makes it possible to reproduce the mixing enthalpy and to model the $\alpha'$ precipitation
Figure 4.2: the mixing enthalpy of FeCr as a function of Cr content. The paramagnetic phase is shown in the graph at the top. The mixing enthalpy is seen to be positive at all Cr concentrations. For the ferromagnetic phase of the alloy shown in the graph at the bottom, it can be seen that for small Cr concentrations, the mixing enthalpy becomes negative. In this region, no formation of the $\alpha'$ phase should be seen.

occurring at higher Cr concentrations, but working with a set of potentials is of course more cumbersome than having one potential that can describe the full range of concentrations of the alloy. A different approach is to employ the two-band model under development [24] which can reproduce the mixing enthalpy for all concentrations where the mixing enthalpy can be reproduced at all concentrations by one potential.

4.2 Verification of Potentials

Having constructed pair potentials and embedding functions for the FeCr system, they are tested by using them to calculate relevant material and defect properties to see that experimental and ab initio values are reproduced.
Below, examples of the calculation of several material and defect properties of relevance are given. To perform the calculations, molecular dynamics can be used. The work presented in papers I-IV includes a number of such calculations for different potentials. All of the MD calculations were performed using the DYMOKA code [35] except in the case of thermal expansion where the XMD code [36] gave a faster convergence.

### 4.2.1 Calculations of Material and Defect Properties

#### Formation Energy

The formation energy of a defect of the kind $X$ in the crystal can be calculated as

$$
E_f^X = N E_{coh}^{relaxed}(X) - N E_{coh}^{relaxed}(ref)
$$

The first term gives the cohesive energy of the relaxed system including $X$ while the second term gives the relaxed energy of the reference system, i.e. without $X$ and $N$ is the number of atoms in the system. $X$ can be defects such as vacancies or interstitials. A box representing the crystal is set up
4.2. Verification of Potentials

with atoms at positions corresponding to the crystal structure, in our case bcc. This gives the energy of the reference structure without \( X \) included. The object \( X \) is then inserted into the simulation box, the structure is relaxed and the difference between the energies of the crystal with and without the defect can be calculated. When performing calculations for an alloy, the energies should be normalized to the number of atoms of each type.

**Binding Energy**

The binding energy between two objects \( X \) and \( Y \) is given by

\[
E_{b}^{XY} = N E_{\text{coh}}^{\text{relaxed}}(X \text{ } Y \text{ separated}) - N E_{\text{coh}}^{\text{relaxed}}(X \text{ } Y \text{ together})
\]  

(4.4)

The first term gives the energy of the system when the two objects \( X \) and \( Y \), though included in the system are positioned far enough from each other so that they cannot interact. The calculation procedure is the same as for the formation energies except that \( X \) and \( Y \) are included in the reference system.

**Substitution Energy**

When working with an alloy, the energy of the system changes as the atomic configuration changes, for example when an atom of type A is replaced or substituted by an atom of type B. The substitution energy is given by

\[
E_{\text{sub}} = N E_{\text{coh}}^{\text{relaxed}}(AB) - N E_{\text{coh}}^{\text{relaxed}}(\text{ref})
\]  

(4.5)

where \( E_{\text{coh}}^{\text{relaxed}}(AB) \) is the energy of the system where an atom of type A has been replaced by an atom of type B.

**Migration Energy**

How defects move in the solid is important since it governs the evolution of the primary damage state. It also has an impact on how defect clusters are formed. Clustering is, as we have seen, responsible for macroscopic effects such as swelling and embrittlement of the material. The migration energy between two sites in the crystal lattice can be calculated as

\[
E_{m}^{X} = E_{\text{coh}}^{\text{relaxed}}(\text{saddle point}) - E_{\text{coh}}^{\text{relaxed}}(\text{initial position})
\]  

(4.6)
where the saddle point is defined as the place along the minimum energy path between the two positions where the migrating object is in its maximum energy state. This can be compared to the experiments by calculating the activation energy measured in diffusivity studies which is given by

$$E^X_A = E^V_f + E^X_m$$  \hspace{1cm} (4.7)

**Thermal Expansion**

The thermal expansion of a material is characterized by the thermal expansion coefficient $\alpha$ which is a measure of how the lattice constant changes as a function of temperature. $\alpha$ is given by

$$\alpha = \frac{1}{a(T)} \cdot \left( \frac{da(T)}{dT} \right)$$  \hspace{1cm} (4.8)

where $T$ is the temperature $a(T)$ is the lattice constant as a function of temperature.

### 4.2.2 Potential Performance

The potentials presented in papers I and II generally reproduce fitted properties well. They are also able to reproduce the thermal expansion better than most potentials found in literature such as those of Simonelli et al. [37] and Mendelev et al. [38]. The thermal expansion given by the thermal expansion coefficient $\alpha$, is related to the third derivative of the total energy. Thus $\alpha$ can be seen as a measure of the anharmonicity of the potential. The stiffening performed at short distances for the potentials in paper I corresponds to making the potential more anharmonic giving a larger thermal expansion. From the potentials in paper II it was seen that changing the potentials at long range gives the same result but in this case motivated by the more physical approach of applying the FS formalism in fitting the potentials. As a result of the potential being stiff at short range, the activation energy for vacancy self-diffusion of the potentials in paper I is higher than those of other potentials found in the literature although they agree very well with those reported by Seeger et al. [39]. The correct interstitial configuration is predicted although the absolute value of the formation energies are higher than those of potentials found in the literature.

The mixing enthalpies of the two mixed potentials in paper I is well reproduced. Simulations of thermal aging show that precipitation of Cr clusters takes place when using the potential fitted to the positive mixing
enthalpy while no precipitation is seen for the potential fitted to the negative mixing enthalpy. The time and temperature scale of precipitation is seen to agree with what is found in experimental studies of hardening. The mixed pair potentials of paper I predicts the mixed \(\langle 110\rangle\) FeCr dumbbell to be the most stable defect followed by the \(\langle 111\rangle\) Cr-Cr dumbbell and the \(\langle 110\rangle\) Fe-Fe dumbbell. Thus, Cr should tend to end up in defect structures during displacement cascades.

4.3 Cascades Using Molecular Dynamics

For further studies of the primary damage in material under neutron irradiation, simulations of displacement cascades have been performed using MD for the potentials presented in paper I. Papers III and IV concern cascade simulations done using four different potentials found in the literature with the aim of comparing the defect evolution of the different potentials and to try to correlate it to the properties of the potential. For all simulations, the simulation box was set up with the atoms in a bcc configuration where the Cr atoms were initially randomly distributed when working with the alloy. The NVE ensemble was used and periodic boundary conditions without temperature control after equilibration were applied as discussed in section 3.3.

4.3.1 Cascades in FeCr

Analysis of the displacement cascades performed in FeCr alloys using the potentials of paper I show a general trend of a lower number of produced defects compared to displacement cascades performed in pure Fe. This is a result of the high interstitial formation energies of these potentials. It is also seen that the Cr tends to end up in defect configurations as expected since the mixed Fe-Cr dumbbell is predicted to be more stable than the pure Fe dumbbell (see section 4.2.2).

4.3.2 Cascades in Fe

By studying the behavior of defects in cascade simulations using different potentials, correlations between potential properties and the defect evolution can be studied as has been done in papers III and IV. Four different potentials found in [40], [41], [42] and [43] were chosen. With these potentials, a set of displacement cascades were produced using a standardized simulation procedure so that the results could be compared.
The analysis of the cascades include calculations of magnitudes such as the final number of defects, cascade density and volume, the number of sub-cascades and clustered fractions for both vacancies and interstitials. Contrary to expectation it was found that the number of Frenkel pairs produced in a cascade does not correlate with the threshold energy of the potential. Instead a correlation between the stiffness of the potential and the number of defects created in cascades is seen. A high interstitial formation energy usually means that the potential is stiff giving diluted cascades with small average cluster sizes for both vacancies and interstitials. The number of final defects produced by the different potentials were found to be approximately the same independent of the potential properties. Thus the final number of defects is largely independent of how the cascade behaves at peak time. The clustering of the defects were seen to be quite different between the potentials, but a straightforward correlation between defect properties and clustering features is difficult to find.
Chapter 5

Summary and Outlook

Before I came here I was confused about this subject. Having listened to your lecture I am still confused. But on a higher level.

*Enrico Fermi*

This thesis concerns the field of multiscale modelling, starting from the level of *ab initio*, via MD and to Monte Carlo. A modelling scheme is discussed for the FeCr system, which is a basis point for the modelling of commercial steels. The FeCr system is described by constructing many-body interatomic potentials based on *ab initio* and experimental data governing the interaction between atoms in the material. The performance of the potential is then studied using molecular dynamics simulations.

We see that it is possible to construct potentials that reproduce many important material properties. However, we also find that it is not always straightforward to find the correlation between the potential description of microscopic features and the resulting macroscopic details of the material under irradiation. The development of new two-band potentials that include the separate contributions of the s and d valence electrons in Fe for example, are expected to give better physical validity of the potential and thus a better control over the relationship between the potential and its performance in simulations.

We are still far from describing a material that resembles the commercial steels in use today. One step in the direction of real life is to include C into the matrix as it is a basic constituent of steel influencing many material properties. Further efforts will go into producing potentials for the ternary system FeCrC which is close enough to reality to be able to give predictions of use in constructing the nuclear reactors of the future.
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Modeling of chromium precipitation in Fe-Cr alloys

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We have implemented a set of Embedded Atom Method (EAM) potentials for simulation of Fe-Cr alloys. The functions for the pure elements were fitted to the respective elastic constants, vacancy formation energy, and thermal expansion coefficients. For Cr, properties of the paramagnetic state were applied, providing a positive Cauchy pressure and hence applicability of the EAM. By relaxing the requirement of reproducing the pressure–volume relation at short interaction distances, stability of the (110) self-interstitial could be obtained. Our Fe-potential gives \( E_{\text{FM}}^{(110)} - E_{\text{PM}}^{(111)} = -0.23 \) eV. Mixed Fe-Cr pair potentials were fitted to the calculated mixing enthalpy of ferromagnetic Fe-Cr, which is negative for Cr concentrations below 6%. Simulation of thermal aging in Fe-Cr alloys using a potential fitted to the mixing enthalpy of Fe-20Cr exhibited pronounced Cr-precipitation for temperatures below 900 K, in agreement with the phase diagram. No such ordering was observed at any temperature using a potential fitted to the mixing enthalpy of Fe-5Cr. Applied to recoil cascade simulations the new potentials predict a smaller number of surviving defects than potentials found in the literature. We obtain a cascade efficiency of 0.135 NRT for damage energies inbetween 10 and 20 keV. An enhanced probability for Cr atoms to end up in defect structures is observed.

I. INTRODUCTION

An improved understanding of the radiation effects in ferritic steels is of importance for development of new reactors and maintenance of already operating systems. Neutron and proton irradiation cause hardening, embrittlement, and dimensional instability of the construction components. The material response is complicated with a strong dependence on the particular composition. Experiments on irradiation of Fe-Cr alloys at doses below 15 DPA, where impact of He generation is possible to neglect, show that adding 2%–6% of Cr leads to a decrease in swelling as compared to pure Fe.1–2 There is a general trend towards a minimum in ductile life dimension of the construction components. The experimental values of the lattice parameter of the alloy. The experimental values of the 0.23 eV. Mixed Fe-Cr pair potentials were fitted to the calculated mixing enthalpy of ferromagnetic Fe-Cr, which is negative for Cr concentrations below 6%. Simulation of thermal aging in Fe-Cr alloys using a potential fitted to the mixing enthalpy of Fe-20Cr exhibited pronounced Cr-precipitation for temperatures below 900 K, in agreement with the phase diagram. No such ordering was observed at any temperature using a potential fitted to the mixing enthalpy of Fe-5Cr. Applied to recoil cascade simulations the new potentials predict a smaller number of surviving defects than potentials found in the literature. We obtain a cascade efficiency of 0.135 NRT for damage energies inbetween 10 and 20 keV. An enhanced probability for Cr atoms to end up in defect structures is observed.

The Molecular Dynamics (MD) method is widely used as a basic theoretical tool, providing physical insight into kinetic processes and interactions leading to the formation of defect clusters, dislocation loops, etc. The validity of the conclusions is directly related to the validity of the interaction potential adopted. A binary alloy potential is usually constructed on the basis of the potentials of the elements constituting the alloy.3–9 Thus the quality of the potential is determined by the extent to which the pure element, and the alloy properties, are reproduced.

Two different types of many-body potentials have been used in MD studies of bcc-iron reported in the literature, namely Finnis-Sinclair potentials, relying on a second moment approximation to the tight binding theory,10–12 and Embedded Atom Method (EAM) potentials,13–18 having their roots in Density Functional Theory.

Fe-Cr alloy potentials have also been constructed using the Finnis-Sinclair approach19 as well as the EAM.20 These are fitted to measurements of mixing enthalpy and to the lattice parameter of the alloy. The experimental values of the heat of mixing used in those works are however valid only for the paramagnetic state of the material (above the Curie temperature). Further, properties of antiferromagnetic (AFM) Cr were used in fitting of the Cr potential used by these authors, in spite of the negative Cauchy pressure of the AFM state.

The objective of the present work is to construct a set of Fe-Cr potentials that can reproduce essential properties of the alloy, such as the mixing enthalpy of the ferromagnetic (FM) state. The potentials should be applicable to simulations of the primary defect formation induced by high energy recoils, as well as to modeling of the subsequent defect evolution. It has to be noted that experimental data describing basic Fe-Cr alloy characteristics of use to the potential fitting, are not always available. In our case, there are experimental data for the bulk modulus of Fe-Cr alloys with different Cr contents. However, no measurements are reported for the mixing enthalpy of ferromagnetic Fe-Cr. Therefore, our modeling approach integrates ab initio calculations of Fe-Cr alloy properties, design of an EAM potential fitted to these data, and usage of the potential in MD cascade simulations.

In what follows, we will describe our approach to obtain physically consistent EAM-potentials for ferromagnetic iron, paramagnetic (PM) chromium, and ferromagnetic alloys of these elements. The applicability of our potentials is corroborated by kinetic Monte Carlo simulation of thermal ageing of alloys with varying concentrations of chromium. We then account for results from recoil cascade calculations, pointing out significant differences in defect production in the alloy, as compared to pure iron. Finally we discuss the impact of our results on the general understanding of Fe-Cr properties in- and out of pile.
II. CONSTRUCTION OF THE EAM POTENTIAL

Within the EAM formalism, the total energy of the system of \( n \) atoms is written as a sum over atomic energies,

\[
E_{\text{tot}} = \sum_{i=1}^{n} E_i = \sum_{i=1}^{n} \left[ \frac{1}{2} \sum_{j=1}^{n} \Phi(r_{ij}) + F(\rho_i) \right],
\]

where \( \Phi(r_{ij}) \) is the pairwise (electrostatic) interaction between atoms \( i \) and \( j \); the function \( \rho_i = \sum_{j \neq i} \rho(r_{ij}) \) represents the electron density of the host system with atom \( i \) removed and \( r_{ij} \) is the scalar distance between atoms \( i \) and \( j \). \( F(\rho_i) \) is the many body term, i.e., the quantum mechanical energy required to embed atom \( i \) into a homogeneous electron gas of density \( \rho_i \). Because the electron density depends only on scalar distances to neighboring atoms, the many body term here has no angular dependence. The curvature of \( F \) may be interpreted in terms of the traditional chemical bonding concept, where a new bond increases the total bonding energy but decreases the average energy per bond. In this context, \( \rho_i \) becomes a measure of the total bond order and \( \rho(r) \) is a bond sensor. The weakening of successive bonds corresponds to a positive curvature of \( F \),

\[
\frac{\partial^2 F}{\partial \rho^2} > 0.
\]

The complete EAM energy expression in the case of binary Fe-Cr alloys involves definitions for the pair potentials \( \Phi_{\text{Fe}}(r), \Phi_{\text{Cr}}(r) \) of pure Fe and Cr, the mixed pair potential \( \Phi_{\text{FeCr}}(r) \), the electronic density functions \( \rho_{\text{Fe}}(r), \rho_{\text{Cr}}(r) \) and the embedding functions \( F_{\text{Fe}}(\rho) \) and \( F_{\text{Cr}}(\rho) \),

\[
E_{\text{tot}} = \sum_{i=\text{Fe}} \Phi_{\text{Fe}}(\rho_i) + \sum_{i=\text{Cr}} \Phi_{\text{Cr}}(\rho_i) + \frac{1}{2} \sum_{i=\text{Fe},j=\text{Cr}} \Phi_{\text{FeCr}}(r_{ij})
\]

\[
+ \frac{1}{2} \sum_{i=\text{Fe},j=\text{Fe}} \Phi_{\text{Fe}}(r_{ij}) + \frac{1}{2} \sum_{i=\text{Cr},j=\text{Cr}} \Phi_{\text{Cr}}(r_{ij})
\]

\[
+ \frac{1}{2} \sum_{i=\text{Cr},j=\text{Fe}} \Phi_{\text{FeCr}}(r_{ij}).
\]

It is seen from Eq. (3) that the potentials of the pure elements potentials are part of the alloy potential.

The following parametric form of the pair interaction terms is assumed:

\[
\Phi(r) = \sum_{i=1}^{5} a_i (r - r_i)^3 H(r_i - r).
\]

Here, \( r_i \) are knot points of the cubic splines used to represent the potential, \( H \) is the Heaviside step function, and \( a_i \) are spline coefficients. The atom electron density is approximated by the Thomas-Fermi screening function suggested in Ref. 15.

The Fe and Cr embedding functions are calculated by fitting the cohesive energy to the Rose expression, which gives the equation of state of a perfect crystal as a function of the reduced lattice parameter \( \alpha \),

\[
E_{\text{Rose}}(\alpha) = -E_{\text{coh}}(1 + \alpha) e^{-\alpha}
\]

with

\[
\alpha = \sqrt{\frac{9 \Omega \bar{E}}{E_{\text{coh}}(R_1 - 1)}},
\]

where \( R_1 \) is the equilibrium value of the distance to the nearest neighbor, \( \Omega \) is the atomic volume and \( B \) denotes the bulk modulus. Note that the alloy bulk modulus is not involved in expression (6), but only the bulk modulus of the pure elements. Since the range of the interactions needs to be finite, a cut-off is introduced in the electron density, with a corresponding modification of the Rose expression for large lattice parameters.

A. Potentials for Fe and Cr

The fitting procedure has been performed in several steps. Three of the spline coefficients for ferromagnetic iron, corresponding to knot points larger than \( R_1 \), were obtained by fitting to the lattice parameter, cohesive energy, vacancy formation energy, and elastic constants as measured at 0 K. A modified version of the MERLIN code package was written for this step of the procedure. The package is based on elastic theory of deformation, including multiparametric optimization with options for different algorithms. The conditions of equilibrium are expressed as a requirement of no stresses in a perfect crystal. Stresses are evaluated by expanding the energy to the first order with respect to an infinitesimal homogeneous strain applied to the system. The second order elastic constants are evaluated by expanding the energy of the system to the second order with respect to an infinitesimal homogeneous strain. For example,

\[
C_{44} = \frac{\partial^2 E_{\text{tot}}}{\partial \gamma^2}
\]

with \( \gamma \) being the angle of distortion by shear deformation imposed on the crystal when keeping the volume constant. In the case of compression in one direction and expansion in the other, the amplitude of deformation for a constant volume is denoted by \( \epsilon \), and the corresponding elastic constant is

\[
C' = \frac{1}{2} (C_{11} - C_{12}) + \frac{1}{4} \frac{\partial^2 E_{\text{tot}}}{\partial \epsilon^2}.
\]

The bulk modulus is obtained by simulating isotropic compression,

\[
B = \frac{1}{9} \frac{\partial^2 E_{\text{tot}}}{\partial \epsilon^2}.
\]
dence of the thermal expansion coefficient in the temperature range 0–600 K. The molecular dynamics code XMD was used for this purpose, in which the condition of constant pressure is imposed by the pressure clamp command. The final spline coefficient was set to ensure a smooth transition of the pair potential into the universal screened Coulomb function of Biersack et al. \cite{11,12,26}.

A similar procedure was implemented to obtain the potential for pure chromium. Previous attempts to fit a central many-body potential to the elastic constants of antiferromagnetic chromium have failed, as may be expected from the negative value of the Cauchy pressure at 0 K,

\[ \frac{1}{2} (C_{12} - C_{44}) \approx -13 \text{ GPa.} \]  

(10)

We note however, that at temperatures relevant for reactor operation (T > 450 K), chromium is paramagnetic, featuring a positive Cauchy pressure. \cite{27} Further, it is sufficient to add a few percent of iron or vanadium to obtain an alloy that is paramagnetic at room temperature. \cite{28,29} We therefore fit our Cr potential to the elastic constants of paramagnetic chromium, linearly extrapolated down to 0 K. Stiffening of the pair potential is made by fitting to thermal expansion coefficients measured for paramagnetic Cr–5V, being equal to the expansion coefficient of pure Cr when T > 600 K. \cite{29} Considering that the Cr precipitates observed in real Fe-Cr alloys contain about 15% iron, we believe that our potential for paramagnetic Cr should be valid for describing Cr–Cr interactions in the present context.

In Table I we list the resulting spline coefficients and knot points for Fe and Cr. In Fig. 1 the pair-potentials are plotted as function of r. Note the slightly larger depth of the potential for paramagnetic Cr, reflecting the larger vacancy formation energy predicted for Cr.

We note that by stiffening the pair potentials inside the equilibrium nearest neighbor distance, after having fixed the embedding function, we violate the pressure–volume relation given by the Rose expression (5). The reason for doing so, is that we otherwise were unable to simultaneously fit experimental values for \( E_{\text{hcp}} - E_{\text{fcc}} \), \( E^{(110)}_{\text{hcp}} - E^{(111)}_{\text{hcp}} \) and the thermal expansion coefficient. Our potentials are hence not applicable to simulation of isotropic compression under high pressure. However, the presence of high electron densities in recoil cascades as well as in defect configurations are of local character, which may be difficult to characterize through an equation of state like the Rose expression.

B. Mixed Fe-Cr pair potentials

The potentials obtained for the pure elements have been further used in Eq. (3) to calculate the parameters \( a_i \) for the mixed Fe-Cr pair potential, fitting them to the mixing enthalpy of the ferromagnetic alloy. Table II displays the formation energy of ferromagnetic Fe-Cr calculated with the EMTO method. \cite{31}

Previous attempts to construct mixed pair potentials for Fe-Cr (Refs. 18,20) relied on fitting to the formation energy of the paramagnetic state of the alloy, which is strictly positive. A single pair-potential for the Fe-Cr interaction would however not be able to reproduce the change in sign of the formation energy of the relevant magnetic state. Therefore, a set of potentials have to be created, providing the correct total energy of the random ferromagnetic alloy. In the present paper, we have performed the fitting for Cr-concentrations of 5% and 20%. The lower concentration should yield a potential with small but negative mixing enthalpy, thus ensuring phase stability at all temperatures. The larger concentration was selected to study a region where the predicted mixing enthalpy is positive, and Cr precipitation (formation of the \( \alpha' \) phase) is observed in real materials. \cite{3,5}

<table>
<thead>
<tr>
<th>Cr-fraction</th>
<th>( \Delta H_f ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>-1.8</td>
</tr>
<tr>
<td>0.04</td>
<td>-1.3</td>
</tr>
<tr>
<td>0.06</td>
<td>+0.6</td>
</tr>
<tr>
<td>0.08</td>
<td>+5.1</td>
</tr>
<tr>
<td>0.10</td>
<td>+10.4</td>
</tr>
<tr>
<td>0.15</td>
<td>+27.9</td>
</tr>
<tr>
<td>0.20</td>
<td>+45.3</td>
</tr>
</tbody>
</table>
TABLE III. Knot points and spline coefficients for the mixed Fe-Cr pair potentials obtained in the present work. The knot points are given in units of nearest neighbor distance.

<table>
<thead>
<tr>
<th>i</th>
<th>$r_i$</th>
<th>$a_i$</th>
<th>$r_i$</th>
<th>$a_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.945</td>
<td>2239</td>
<td>0.945</td>
<td>2624</td>
</tr>
<tr>
<td>2</td>
<td>0.967</td>
<td>−2199</td>
<td>0.967</td>
<td>−2476</td>
</tr>
<tr>
<td>3</td>
<td>1.030</td>
<td>0.000</td>
<td>1.030</td>
<td>10.000</td>
</tr>
<tr>
<td>4</td>
<td>1.400</td>
<td>−12.737</td>
<td>1.320</td>
<td>−24.500</td>
</tr>
<tr>
<td>5</td>
<td>1.650</td>
<td>4.210</td>
<td>1.53</td>
<td>7.620</td>
</tr>
</tbody>
</table>

The parameters obtained for the Fe-Cr mixed pair potentials are given in Table III. The sharp dip in the measured bulk modulus at Cr concentrations about 5% (Ref. 30) lead us to assume a longer range for the corresponding pair potential. Due to the lack of thermal expansion data for the alloy, stiffening of the potentials at short distances was made in a rather arbitrary fashion, simply requiring a smooth transition to the universal Coulomb screening function at $r = 1.7$ Å.

### III. VERIFICATION OF THE POTENTIALS

The quality of the potential has been inspected by calculations of elastic constants, structural stability, and formation energies of various defect configurations. The results are shown in Tables IV, V and VII. Comparing with experimental data and values obtained by other authors, one may note the following: The potential here presented reproduces more closely the experimental elastic characteristics and structural stability of pure iron than the EAM-potentials published by Simonelli et al.. Our relaxed vacancy formation energy (2.04 eV) was fitted to the resistivity measurements by De Schepper et al., indicating a significantly higher value for $E_{\text{vac}}^f$ than earlier measurements in less pure materials. The potential predicts an activation energy for self-diffusion equal to 2.91 eV, in very good agreement with data obtained at high temperatures (Ref. 29).

Our fit to thermal expansion data was made using a single spline coefficient, and can thus not be expected to reproduce measured data over the whole temperature range. One may note however that potentials not fitted to thermal expansion underestimates the expansion by a factor of 2 or more.

In comparison with the Finnis-Sinclair potential developed by Ackland and co-workers, our potential yields a stability of the $\{110\}$ interstitial with respect to the $\{111\}$ configuration that is in better agreement with measured data. The predicted absolute formation energy of the Fe self-interstitial is higher than what results from using any other potential found in literature. We note that the experimental values are derived from measurements of stored energy release per resistivity recovery ($dQ/d\rho$) in samples irradiated at low temperature. The enthalpy for formation of a Frenkel pair is obtained by multiplying $dQ/d\rho$ with an assumed resistivity $\rho_F$ for a single Frenkel pair. Estimates of $\rho_F$ vary from 0.20 to 0.30 mO\·cm$^{-1}$. Selecting the higher value,

### TABLE IV. Properties of pure iron obtained with the potential for ferromagnetic Fe here presented. Elastic constants are given in units of GPa, energies in eV, and thermal expansion coefficients in units of $10^{-6}$. Comparison is made with experimental data and values calculated using the potentials of Simonelli (Ref. 15) and Ackland (Ref. 12).

<table>
<thead>
<tr>
<th>Fe property</th>
<th>This work</th>
<th>Expt.</th>
<th>Sim A</th>
<th>Sim B</th>
<th>Ackland</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>172</td>
<td>173 $^a$</td>
<td>146</td>
<td>146</td>
<td>178</td>
</tr>
<tr>
<td>$C'$</td>
<td>56.7</td>
<td>52.5 $^a$</td>
<td>48.0</td>
<td>48.0</td>
<td>49.0</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>135</td>
<td>122 $^a$</td>
<td>115</td>
<td>115</td>
<td>116</td>
</tr>
<tr>
<td>$E_{\text{coh}}$</td>
<td>4.28</td>
<td>4.28</td>
<td>4.28</td>
<td>4.28</td>
<td>4.316</td>
</tr>
<tr>
<td>$E_{\text{vac}}-E_{\text{foc}}$</td>
<td>−0.047</td>
<td>−0.050 $^b$</td>
<td>−0.03</td>
<td>−0.007</td>
<td>−0.054</td>
</tr>
<tr>
<td>$E_{\text{vac}}^f$</td>
<td>2.04</td>
<td>2.0±0.2 $^c$</td>
<td>1.63</td>
<td>1.56</td>
<td>1.70</td>
</tr>
<tr>
<td>$E_{\text{vac}}^{\text{SD}}$</td>
<td>2.91</td>
<td>2.91±0.04 $^d$</td>
<td>2.32</td>
<td>2.29</td>
<td>2.48</td>
</tr>
<tr>
<td>$E_{{110}}$</td>
<td>7.72</td>
<td>3.12 $^e$</td>
<td>3.66</td>
<td>4.11</td>
<td>4.87</td>
</tr>
<tr>
<td>$E_{{110}}-E_{{111}}^f$</td>
<td>−0.23</td>
<td>−0.30 $^f$</td>
<td>+0.12</td>
<td>−0.19</td>
<td>−0.13</td>
</tr>
</tbody>
</table>

$^a$Reference 32.
$^b$Reference 33.
$^c$Reference 34.
$^d$References 35, 36.
$^e$References 37, 38.
$^f$Reference 38.

### TABLE V. Properties of paramagnetic Cr calculated with the potential here presented. Comparison is made with experimental data for Cr in AFM and PM states, as well as values calculated using the potential of Farkas (Ref. 20). PM elastic constants were obtained by extrapolation to 0 K of high temperature data (Ref. 27). The paramagnetic thermal expansion coefficient at $T=300$ K refers to measurements on Cr–$\delta$V (Ref. 29).

<table>
<thead>
<tr>
<th>Cr property</th>
<th>This work</th>
<th>Expt. (AFM)</th>
<th>Expt. (PM)</th>
<th>Farkas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>207</td>
<td>195 $^a$</td>
<td>207 $^a$</td>
<td>148</td>
</tr>
<tr>
<td>$C'$</td>
<td>153</td>
<td>153 $^a$</td>
<td>155 $^a$</td>
<td>42.5</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>105</td>
<td>104 $^a$</td>
<td>105 $^a$</td>
<td>...</td>
</tr>
<tr>
<td>$E_{\text{coh}}$</td>
<td>4.10</td>
<td>4.10</td>
<td>4.10</td>
<td>4.10</td>
</tr>
<tr>
<td>$E_{\text{vac}}-E_{\text{foc}}$</td>
<td>−0.025</td>
<td>...</td>
<td>−0.053</td>
<td>...</td>
</tr>
<tr>
<td>$E_{\text{vac}}^f$</td>
<td>2.14</td>
<td>...</td>
<td>2.0±0.2 $^b$</td>
<td>1.12</td>
</tr>
<tr>
<td>$E_{\text{vac}}^{\text{SD}}$</td>
<td>2.93</td>
<td>...</td>
<td>2.95 $^c$</td>
<td>2.30</td>
</tr>
<tr>
<td>$E_{{110}}$</td>
<td>5.16</td>
<td>...</td>
<td>3.03</td>
<td>...</td>
</tr>
<tr>
<td>$E_{{110}}-E_{{111}}^f$</td>
<td>−0.62</td>
<td>...</td>
<td>0.19</td>
<td>...</td>
</tr>
<tr>
<td>$\alpha$ ($T=300$ K)</td>
<td>7.5</td>
<td>4.4 $^d$</td>
<td>7.9 $^d$</td>
<td>5.2</td>
</tr>
<tr>
<td>$\alpha$ ($T=600$ K)</td>
<td>9.8</td>
<td>...</td>
<td>9.6 $^d$</td>
<td>9.5</td>
</tr>
</tbody>
</table>

$^a$Reference 27.
$^b$Reference 44.
$^c$Reference 45.
$^d$Reference 29.
Wollenberger arrives at a formation energy $E_f^p = 6.6$ eV for a Frenkel pair in electron irradiated $\alpha$-Fe, and $E_f^p = 13.6$ eV for a neutron irradiated sample. Subtracting a vacancy formation energy of $2.0$ eV would then give $E_f^{110} = 4.6$ eV in the former case, and $11.6$ eV in the latter. The uncertainty of these values is obviously large, since just by assuming $\rho_F = 0.20 \, \text{m}\Omega \times \text{cm}$, one could obtain $E_f^{110} = 7.7$ eV for the neutron irradiated sample. Note that results from the electron irradiation not necessarily are more accurate, since experimental boundary conditions are more difficult to control in stages $I_A$ to $I_C$ (absent in neutron irradiation) than in stage $I_D$.

The SIA formation energy in iron have recently been calculated with the $ab$ initio package VASP as $E_f^{110} = 3.4$ eV. This result is compatible with data from electron irradiations. However, since the calculation did not take into account possible effects of noncollinear magnetism, the discrepancy with data from neutron irradiated samples remains an open question. As will be seen later, the magnitude of the interstitial formation energy has a significant impact on defect recombination in recoil cascades, and we will argue that a high value is consistent with defect distributions actually observed.

Concerning the properties of chromium predicted by the potential here presented, we emphasize that the fit was made to elastic constants of paramagnetic chromium, extrapolated to 0 K. Hence we are able to retain a positive Cauchy pressure at all temperatures. The relaxed vacancy formation energy is compatible with experimental data, in contrast to the prediction of the potential by Farkas $et$ $al.$, for which an apparently incorrectly quoted value of $E_f^{vac}$ has been used in the fit. We further note that the activation energy for vacancy diffusion predicted by the potential is in excellent agreement with measured data.

As seen in Table VI, the alloy potentials well reproduce the mixing enthalpies of Fe-5Cr and Fe-20Cr calculated with the EMTO method. The heat of mixing obtained with Farkas’ potential should be considered to represent the paramagnetic state of the alloy, and is hence not applicable for MD or KMC simulations below the Curie temperature.

Table VII displays formation and binding energies of a single mixed (110) Fe-Cr dumbbell in an iron matrix with lattice parameter $a_0 = 2.860$ Å. Predictions of the alloy potentials are compared to VASP $ab$ initio data (Ref. 47) and values calculated with Farkas’ potential (Ref. 20). $-E_f^{110} = E_f^{Fe} - E_f^{Cr} - E_f^{s}$ is calculated relative to the energy of an Fe-Fe dumbbell, subtracting the substitution energy $E_f^{s}$ of a single Cr atom.

<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
<th>Fe-5Cr</th>
<th>Fe-20Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_f^{FeCr}$ (meV)</td>
<td>This work</td>
<td>$-0.04$</td>
<td>$+45$</td>
</tr>
<tr>
<td></td>
<td>EMTO</td>
<td>$-0.05$</td>
<td>$+45$</td>
</tr>
<tr>
<td></td>
<td>Farkas</td>
<td>$+24$</td>
<td>$+86$</td>
</tr>
</tbody>
</table>

IV. APPLICATION OF THE Fe-Cr POTENTIAL IN SIMULATION OF THERMAL AGEING

It is well known that precipitation of Cr occurs under thermal aging at $T<900$ K in FeCr alloys with Cr content ranging from 10% to 90%. The formation of the so-called $\alpha'$ phase is responsible for hardening of the binary alloy. The magnitude of the miscibility gap for low Cr concentrations could be theoretically explained only recently, when $ab$ initio calculations showed that the mixing enthalpy of Fe-Cr is negative for the ferromagnetic state of the random alloy, if the Cr concentration is below 6%. Above this limit, the formation energy is positive, providing a driving force for phase separation. In order to obtain the temperature dependence of the solubility, one needs to perform molecular dynamics, or rather kinetic Monte Carlo (KMC) simulations. We have performed such simulations of thermal aging at a range of temperatures, using several different techniques implemented in the DYMOKA code, developed by Electricité de France (EDF) and University of Lille.

The out-of-pile process of segregation is assumed to be driven purely by vacancy assisted migration. According to classical diffusion theory, the frequency for a lattice atom to exchange lattice position with a neighboring vacancy is

TABLE VII. Formation and binding energies of a single mixed (110) Fe-Cr dumbbell in an iron matrix with lattice parameter $a_0 = 2.860$ Å. Predictions of the alloy potentials are compared to VASP $ab$ initio data (Ref. 47) and values calculated with Farkas’ potential (Ref. 20). $-E_f^{110} = E_f^{Cr} - E_f^{Fe} - E_f^{s}$ is calculated relative to the energy of an Fe-Fe dumbbell, subtracting the substitution energy $E_f^{s}$ of a single Cr atom.

<table>
<thead>
<tr>
<th>Property</th>
<th>$E_f^{110}$</th>
<th>$E_f^{s}$</th>
<th>$E_f^{p}$</th>
<th>$E_f^{110} - E_f^{p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-5Cr</td>
<td>$7.63$</td>
<td>$+0.18$</td>
<td>$+0.27$</td>
<td>$-0.03$</td>
</tr>
<tr>
<td>Fe-20Cr</td>
<td>$8.19$</td>
<td>$+0.46$</td>
<td>$-0.01$</td>
<td>$-0.20$</td>
</tr>
<tr>
<td>VASP</td>
<td>$3.06$</td>
<td>$-0.35$</td>
<td>$-0.00$</td>
<td>$+0.36$</td>
</tr>
<tr>
<td>Farkas</td>
<td>$4.31$</td>
<td>$+0.70$</td>
<td>$+0.05$</td>
<td>$+0.07$</td>
</tr>
</tbody>
</table>
where \( n \) is the attempt frequency of the jump and \( C_{\text{vac}} \) is the equilibrium concentration of vacancies. The vacancy concentration as function of temperature is given by

\[
C_{\text{vac}}(T) = e^{-(G_f/k_B T)},
\]

where \( G_f = E_{\text{vac}}^f - TS_{\text{vac}}^f \) is the Gibbs energy of vacancy formation. The entropy of formation may be calculated from the following formula: \( S_{\text{vac}}^f = k_B (3(N-1) \ln \omega_{\text{vac}} - (N-1) \sum_n \ln \omega_n^{\text{bulk}}) \),

where \( \omega_n \) are eigenfrequencies of the force-constant matrices with and without a vacancy in the system, respectively. MD simulations using our potential for ferromagnetic iron gives \( S_{\text{vac}}^f = 1.78 \ k_B \) for a relaxed system of \( N=432 \) atoms.

Similarly, the attempt frequency \( \nu \) may be calculated from:

\[
\nu = \frac{k_B}{2\pi} \frac{1}{\prod_{n=1}^{3N} \omega_{\text{TST}}^n},
\]

where \( \omega_{\text{TST}} \) are the eigenfrequencies evaluated at the transition state of the vacancy jump. For the present potential we obtain \( \nu = 9.15 \times 10^{13} \ \text{s}^{-1} \) which gives us a prefactor for self-diffusion in ferromagnetic iron: \( D_0 = 2.13 \times 10^{-5} \ \text{m}^2/\text{s} \). This value, valid in the harmonic approximation, is very close to the one observed in experiments. \( ^{36} \)

In general, the probability of all possible vacancy jumps in an alloy (8 first nearest neighbors in a bcc structure) should be computed for every Monte Carlo step, selecting one of them to be performed, weighted with that probability. Time is then introduced as the inverse of the system averaged jump frequencies. In our case, the vacancy assisted migration energy for Fe and Cr atoms are close to each other; 0.87 eV and 0.84 eV, respectively. We hence make a concentration weighted average for our system and calculate an average time step as

\[
\Delta \tau = \frac{1}{8\Gamma(T)}.
\]

We performed simulations of vacancy migration assuming a single vacancy in a box with 16000 atoms. It was checked that the rate of energy loss in the Fe-20Cr alloy did not change significantly when increasing the box size.

In order to arrive at a fully segregated final state, we used a Metropolis Monte Carlo algorithm, together with the vacancy KMC. The metropolis algorithm exchanges all atoms of differing type if it is energetically favorable. If an exchange increases the energy it is accepted with a weight exp\((-E/2k_B)\), where \( E \) is the potential energy of the system. The Metropolis MC method is much faster, but provides no explicit time scale. However, it was found that a time step could be assigned to each Metropolis MC step by fitting energy losses to the explicit vacancy KMC simulation.

In Fig. 2, the total energy of an initially random Fe-20Cr alloy is plotted as function of time and temperature. Since the mixing enthalpy of the random alloy is positive, a loss in energy is a sign of segregation. For infinite segregation, the energy loss would equal the formation energy \( \Delta H_{\text{Fe-20Cr}} = 45 \ \text{meV} \). In a finite box, however, there will always remain a surface to bulk factor. The surface atoms of a Cr cluster will all have Fe neighbors and thus a higher energy. In our most segregated case (\( T = 500 \ \text{K} \)) we arrive at 84\% of the mixing enthalpy. This may be understood from the fact that a single Cr cluster of spherical shape in our simulation box has a surface to bulk ratio of Cr atoms equal to about 30\%. On the cluster surface, half of the neighbors to Cr atoms are Fe atoms, and hence the surface energy of final Cr cluster provides the missing 16\%.

We note that for 700 K, the time needed to obtain a significant energy loss is of the order of months, which is consistent with the experimental time threshold for observation of hardening in Fe-45Cr alloys aged at 673 K. \( ^{50} \) For 800 K segregation occurs in a matter of days, while for 900 K, the energy loss saturates within a few hours, before complete phase separation has taken place. At 1000 K, less than half the energy loss is achieved, which corresponds to a limited ordering of the system, without actual phase separation.

The process of segregation is illustrated in Fig. 3, where the distribution of Cr atoms is shown before and after ageing during 30 years at 700 K. This simulation was done with an initial Cr content equal to 12\%, using the Fe-20Cr potential.

The final Cr-precipitate appearing during the simulation is free of Fe atoms, due to the fact that our potential incorrectly predicts a positive mixing enthalpy even for Cr concentrations in the vicinity of 90\%.

In order to quantify the temperature dependence of the phase separation, we define the degree of segregation \( \xi \) as

\[
\xi = \frac{1}{\xi_{\text{max}}} \frac{N_{\text{Emg}}}{N_{\text{Cr}}^0},
\]

where \( N_{\text{Emg}} \) is the number density of embedded Cr atoms and \( N_{\text{Cr}}^0 \) is the initial number density of Cr atoms.

\[
\xi_{\text{max}} = \frac{N_{\text{Emg}}}{N_{\text{Cr}}^0}.
\]
Here, $N_{Cr}^{Tot}$ is the number of Cr atoms in the system, $N_{Cr}^{Emb}$ is the number of Cr atoms that only have Cr first nearest neighbors, and $\xi_{max}$ is the theoretical maximum number of Cr atoms that may have Cr first nearest neighbors, accounting for the surface layer of a spherical cluster.

The degree of segregation produced by the Fe-20Cr potential after the energy loss has reached its asymptotic value is shown in Fig. 4. If an arbitrary limit of $\xi > 0.5$ is set to distinguish the $\alpha'$ phase from $\alpha$, we find that this corresponds to $T < 900$ K. Considering that the range of temperature where the phase transition takes place is uncertain, quoted as $750 \pm 125$ K in Ref. 7, our results may be considered to be in reasonable agreement with the phase diagram.

Performing the same type of simulations using the potential fitted to the mixing enthalpy of Fe-5Cr, no significant energy loss is found at any temperature, which means that the alloy remains random. We may thus conclude that our potentials reproduce the out-of-pile state of ferromagnetic Fe-Cr as function of temperature and time at Cr concentrations of 0%, 5%, and 20%.

It is important to note that in reality, the driving force for the decomposition would be lost when the local concentration of Cr becomes too high or too low. Hence, in order to obtain the physically observed final states with an iron content in the $\alpha'$ precipitates ranging from 10% to 20%, we would have to switch potentials during the simulation according to the local density of Cr, a feature not yet implemented in the codes we have used. Therefore the size of the clusters we observe at infinite times cannot be expected to agree with the measured size distribution, being of the order of 2–4 nm.

### Table VIII. Average number of surviving Frenkel pairs as function of recoil damage energy. The quoted uncertainty corresponds to one standard deviation.

<table>
<thead>
<tr>
<th>$E_{dam}$</th>
<th>5 keV</th>
<th>10 keV</th>
<th>20 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>7.4 ± 0.7</td>
<td>13.4 ± 0.9</td>
<td>27.0 ± 1.0</td>
</tr>
<tr>
<td>Fe-5Cr</td>
<td>8.9 ± 0.7</td>
<td>14.0 ± 0.8</td>
<td>28.7 ± 1.6</td>
</tr>
<tr>
<td>Fe-20Cr</td>
<td>8.5 ± 0.6</td>
<td>13.6 ± 0.7</td>
<td>27.0 ± 1.3</td>
</tr>
</tbody>
</table>

### V. Application of the Fe-Cr Potential in Cascade Simulations

The potentials here presented were applied in molecular dynamics simulations of collision cascades initiated by recoils having energies up to 20 keV. Periodic boundary conditions were used, and the sizes of the MD boxes were adjusted to make sure that the cascade did not interact with its periodic image. For 10 keV cascades, it was found that 128 000 atoms (40×40×40 lattice units) was sufficient for recoils in the $\langle 135 \rangle$ direction, while 250 000 atoms had to be used when launching in the $\langle 111 \rangle$ direction. The initial atom velocities were sampled from a Maxwellian distribution for a particular temperature, set to $T = 100$ K in the present study. The block is equilibrated for about a picosecond before launching an energetic recoil in the central region. The time step was varied from 0.02 fs (when the recoil is generated) up to 0.5 fs at the end of the simulation period (10 ps). The first thing to be noted is that the new potentials predict a much smaller number of surviving defects than potentials found in the literature. This is a direct result of the higher interstitial formation energy, leading to larger probability for recombination of Frenkel pairs during cooling down of the cascade. Table VIII shows the average number of surviving defects in Fe and Fe-20Cr, for a set of representative recoil energies in the $\langle 135 \rangle$ direction.

As seen the difference between the alloy and pure iron is statistically insignificant. For recoil energies between 10 and 20 keV, we arrive at a cascade efficiency of 0.135 ± 0.005 NRT, which may be compared to a value of 0.3 NRT in pure Fe obtained at $T = 100$ K with a Finnis-Sinclair potential yielding an SIA formation energy of 4.9 eV.

The main impact of introducing chromium is found in the relative population of the elements in the defects produced by the cascade. In Fe-5Cr, where the Fe-Cr dumbbell is more stable than the pure Fe-Fe dumbbell, the fraction of chromium atoms in the surviving interstitial defects is as large as 19%, fairly independent of recoil energy. The mixed dumbbells are less mobile than pure Fe interstitials, and will thus act as obstacles for migration of Fe interstitial clusters. In Fe-20Cr, where the mixed Fe-Cr and pure Fe-Fe dumbbells have about the same energy, chromium atoms constitute roughly 30% of the interstitial atoms.
VI. CONCLUSIONS

The set of EAM potentials for Fe-Cr alloys implemented in the present work yield activation energies for vacancy migration in the pure elements that are in very good agreement with experimental data. The predicted SIA formation energies arising from fitting to thermal expansion coefficients are higher than values obtained by other authors using both EAM and ab initio methods. While electron irradiation data seems to support lower numbers, the stored energy release measured in neutron irradiated samples is compatible with our results. Our potentials further correctly predict the (110) interstitial to be the stable form in both the pure elements as well as in the alloy.

Applied to simulation of thermal aging, there is no sign of precipitation taking place when using the potential fitted to the negative formation energy previously calculated for ferromagnetic Fe-5Cr. KMC simulations using the potential fitted to the mixing enthalpy of Fe-20Cr yield formation of Cr clusters on a time and temperature scale that is in good agreement with measurements of hardening in high Cr binary alloys.

We predict that the (110) Fe-Cr and Cr-Cr dumbbells are more stable than the corresponding defect in pure iron. Consequently, Cr will tend to end up in defect structures forming during cooling down of recoil cascades, and we register that 19% of the interstitial atoms in Fe-5Cr are chromium atoms.

The total number of defects surviving after recoil cascades is smaller than predicted by Fe potentials from the literature. This fact is directly related to the higher SIA formation energy. For damage energies between 10 and 20 keV, we obtain a cascade efficiency of 0.135 ± 0.005 NRT at T = 100 K, which in part may explain the long standing mystery of the small number of freely migrating defects observed in experiments.55

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Relation between thermal expansion and interstitial formation energy in pure Fe and Cr

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Abstract

By fitting a potential of modified Finnis–Sinclair type to the thermal expansion of ferromagnetic Fe and paramagnetic Cr, stability of the $\langle 110 \rangle$ self-interstitial atom is obtained. The resulting potentials are relatively hard, yielding high SIA formation energies. Less hard potentials give lower interstitial formation energy, but predict too small thermal expansion. We also show that the formation energy of the $\langle 111 \rangle$ SIA depends on distances in-between the 2nd and 3rd neighbour. By raising the value of the pair potential in this region, the energy difference with respect to the $\langle 110 \rangle$ configuration calculated with VASP in the PAW approximation can be reproduced.

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Keywords: Finnis–Sinclair potential; Iron; Chromium; Thermal expansion

1. Introduction

Conventional wisdom has it that the properties of Cr cannot be fitted by a many-body potential including only central interactions [1]. The present authors have however shown that paramagnetic Cr, having a positive Cauchy pressure, may be described by a classical EAM potential [2]. In our previous work, the many-body term was fixed in an arbitrary fashion. Here, we introduce a modified Finnis–Sinclair term to obtain the many body interaction for Fe and Cr in a consistent manner. We further refit our potentials to exactly reproduce elastic constants measured at 0K and recent ab initio data for vacancy formation energies. As these properties only determine the value and shape of the potential in the vicinity of perfect lattice distances, we use thermal expansion data to fit our potentials inside the first nearest neighbour distance. In what follows, we will account for details of the fitting procedure, comparing the performance of the resulting iron potential with those of other authors. We clarify the difference
between EAM and FS type of potentials and discuss the impact of the shape of the potential in-between 2nd and 3rd neighbours on the relative stability of self-interstitial configurations.

2. Modified Finnis–Sinclair potentials for Fe and Cr

In previous work [2], we found that by fitting an EAM potential to thermal expansion data of iron, we could obtain stability of the \( h_{110}^i \) SIA if the shape of the many-body function given by the Rose expression was fixed before stiffening the pair interaction inside the nearest neighbour distance. This approach obviously is somewhat arbitrary. In order to arrive at a physically consistent procedure, we instead choose to cast our potentials in the effective pair form [1], using a modified Finnis–Sinclair expression for the many-body term [3]. In the effective pair approach, it is assumed that the derivative of the many-body term is set to zero for the free electron density of the perfect crystal. As a result, \( C_0 , C_{44} , a_0 \) and the unrelaxed vacancy formation energy are given exclusively by the pair potential, while the bulk modulus and the cohesive energy are fitted by the many-body term, i.e. the contribution to the total energy from the valence electron density. Consequently we need only the sum of two splines to fit the pair potential exactly to the selected properties, if we adopt the spline cut-offs as fitting parameters.

The following parametric form of the pair interaction terms is assumed:

\[
\phi(r) = \sum_{i=1}^{n} a_i (r - r_i)^3 H(r_i - r).
\]

Here, \( r_i \) are cut-offs of the cubic splines used to represent the potential, \( H \) is the Heaviside step function and \( a_i \) are spline coefficients. Three parameters are required to fit the bulk modulus and cohesive energy with the many-body term, as the condition of zero derivative at equilibrium is imposed. We hence write the modified Finnis–Sinclair expression as

\[
F(\rho) = A_0 \sqrt{\rho} + A_1 \rho + A_2 \rho^2,
\]

where the term proportional to the square of the free electron density \( \rho \) corresponds to the electron kinetic energy neglected in the original derivation of the second moment tight binding approximation [4]. The term linear in electron density may be transferred to the pair interaction, if desired.

We emphasize that the valence electron density in the Finnis–Sinclair formalism includes electrons generated by the atom at the position where the density is calculated. In the EAM model these electrons are neglected, which lead to inconsistencies in the case of alloys. Hence we should adopt electron density functions that are finite at the origin, here we assume a Fermi–Dirac function

\[
\phi(r) = \frac{N}{1 + \exp[(r - R)/a]},
\]

where the norm \( N \) is set for the equilibrium electron density to reproduce the number of \( d \)-band electrons calculated with the ab initio method described in [5], being 6.56 for Fe and 4.61 for Cr.

Having fitted six properties of ferromagnetic iron at 0 K exactly, it was found that adding a single spline was sufficient to reproduce measured thermal expansion coefficients up to \( T = 500 \) K, where effects of magnetic transitions start to play a role. A similar procedure was undertaken for Cr, with elastic constants of paramagnetic Cr at 0 K obtained by extrapolation from high temperature data [6], adopting thermal expansion coefficients of Cr–5V [7]. In the case of Cr, it was found that four splines in the representation of the pair interaction were required to achieve a good fit. Table 1 shows the resulting potential parameters for ferromagnetic Fe and paramagnetic Cr.

In Table 2 properties calculated with the above parametrised iron potential are compared with experiment, VASP calculations and the Fe-potential of Mendelev [3]. Note that the PAW approximation used by us when running VASP gives higher SIA formation energies than ultra-soft pseudo potentials [8] or the procedure used in SIESTA [9]. Our potential reproduces better the measured activation energy for vacancy self-diffusion than any other potential in the literature. It over-estimates the SIA formation energy measured in electron irradiation [10], but provides correct
configuration stability, using just three splines. Mendelev's FS-potential, using 15 splines for the pair interaction, reproduces better $E_{\text{f}}^{\text{h}110}/C_{0} - E_{\text{f}}^{\text{h}111}/C_{0}$ but yields too low vacancy activation energy.

Thermal expansion coefficients as function of temperature are displayed in Fig. 1. The potential of Mendelev et al. yields too small expansion coefficients. This is typical for potentials predicting "low" SIA formation energies, being relatively soft inside the nearest neighbour distance.

In order to further analyse the dependence of the interstitial formation energy on the shape of the potential, the relaxed distances to neighbouring atoms were calculated. It was found that the $\langle 111 \rangle$ configuration had a larger number of neighbours in-between 3.2 and 3.5 Å, a region where the fitted properties provide very little information. Hence, by increasing the value of the pair potential in this region, the formation energy of the $\langle 111 \rangle$ SIA as well as the $fcc$ crystal energy is raised, while

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_3$</th>
<th>$r_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>+4.276043</td>
<td>−17.642833</td>
<td>−1280</td>
<td>−</td>
<td>1.610</td>
<td>1.328</td>
<td>0.969</td>
<td>−</td>
</tr>
<tr>
<td>Cr</td>
<td>+4.023728</td>
<td>−71.420562</td>
<td>+71.364433</td>
<td>−450</td>
<td>1.610</td>
<td>1.223</td>
<td>1.151</td>
<td>0.967</td>
</tr>
</tbody>
</table>

The cut-offs are given in units of 1st neighbour distance.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Experiment</th>
<th>VASP-PAW</th>
<th>Mendelev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>2.860</td>
<td>2.860</td>
<td>2.83</td>
<td>2.855</td>
</tr>
<tr>
<td>$C^*$ (GPa)</td>
<td>52.5</td>
<td>52.5 [11]</td>
<td>–</td>
<td>49.2</td>
</tr>
<tr>
<td>$E_{\text{coh}}$ (eV)</td>
<td>4.28</td>
<td>4.28</td>
<td>–</td>
<td>4.01</td>
</tr>
<tr>
<td>$E_{\text{f}}^{\text{vac}}$ (eV)</td>
<td>2.15</td>
<td>2.0 ± 0.2 [12]</td>
<td>2.12</td>
<td>1.73</td>
</tr>
<tr>
<td>$E_{\text{f}}^{\text{SD vac}}$ (eV)</td>
<td>2.95</td>
<td>3.0 ± 0.1 [13]</td>
<td>–</td>
<td>2.38</td>
</tr>
<tr>
<td>$E_{\text{f}}^{\text{f}} - E_{\text{n}}$ (eV)</td>
<td>0.07 (0.09)</td>
<td>0.05 [14]</td>
<td>0.09</td>
<td>0.12</td>
</tr>
<tr>
<td>$E_{(110)}^{\text{f}}$ (eV)</td>
<td>6.53</td>
<td>3.0–5.4 [10]</td>
<td>4.01</td>
<td>3.45</td>
</tr>
<tr>
<td>$E_{(110)}^{\text{f}} - E_{(111)}^{\text{f}}$ (eV)</td>
<td>−0.04 (−0.67)</td>
<td>–</td>
<td>−0.67</td>
<td>−0.50</td>
</tr>
</tbody>
</table>

Comparison is made with experiment, VASP ab initio calculations made by us in the PAW approximation, and Mendelev’s FS-potential. Values given in parentheses are obtained after modifying the potential in-between 2nd and 3rd neighbour distances, as described in the text.

![Fig. 1. Thermal expansion coefficient for α-iron as function of temperature. Filled circles denote experimental data [15], lower solid line values obtained with the potential of Mendelev and co-workers.](image)
leaving other properties untouched. Multiplying the effective pair interaction with $1 - 0.79 \times \text{Exp}[-(r - 3.52)^4/0.006]$, the difference in energy between the $\langle 111 \rangle$ and $\langle 110 \rangle$ configurations is raised to 0.67 eV, identical to the value calculated with VASP. The modification changes the potential by a factor less than $10^{-5}$ at distances below 3.0 Å. The $f_{cc}$ energy is raised by 0.02 eV to a value in agreement with VASP calculations. A similar effect on the relative stability of the SIA:s is obtained by imposing a short range cut-off [16,17], though in the present case the magnitude of the SIA energy difference is considerably larger, thanks to stiffening at distances inside the nearest neighbour.

3. Conclusions

A systematical procedure for fitting a potential of modified Finnis–Sinclair type to elastic constants and thermal expansion of ferromagnetic Fe and para-magnetic Cr has been presented. The potentials obtained yield values for vacancy activation energy in good agreement with experiment, but overestimate absolute magnitude of interstitial formation energies. Stability of the $\langle 110 \rangle$ SIA in Fe is obtained without any additional effort. By further modifying the pair interaction at distances in-between 2nd and 3rd neighbour, the energy difference between $\langle 111 \rangle$ and $\langle 110 \rangle$ configurations calculated with VASP in the PAW approximation (0.67 eV) is reproduced.

Acknowledgements

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References

Effect of the interatomic potential on the features of displacement cascades in $\alpha$-Fe: a molecular dynamics study

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Abstract

The primary state of damage obtained in molecular dynamics (MD) simulations of displacement cascades in $\alpha$-Fe, particularly the fraction of point-defects in clusters, depends on the interatomic potential used to describe the atomic interactions. The differences may influence the microstructural evolution predicted in damage accumulation models which use results from MD cascade simulations as input. In this work, a number of displacement cascades of energy ranging from 5 to 40 keV have been simulated using the same procedure with four different interatomic potentials for $\alpha$-Fe, each of them providing, among other things, varying descriptions of self-interstitial atoms (SIA) in this metal. The behaviour of the cascades at their different phases and the final surviving defect population have been studied and compared applying the same cascade analysis criteria for all potentials. The outcome is discussed trying to identify the characteristics of the potential that have the largest influence on the predicted primary state of damage.

Keywords: Molecular Dynamics, Displacement Cascades, Interatomic Potentials, $\alpha$-Iron

PACS codes: 31.15.Qg; 61.72Cc; 34.20Cf; 61.82.Bg

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1. Introduction

Displacement cascades are the fundamental process of radiation damage production under neutron and ion irradiation. Their study by means of numerical simulation based on the use of an interatomic potential dates back to the 1960s [1-3]. In these pioneering works, the choice of the potential and the dependence of the results on it were priority issues [1]. On the contrary, over the last fifteen years, in spite of a real boom of displacement cascade simulations using many-body potentials [4-17], relatively little attention has been paid to this problem [15,16]. Nonetheless, different potentials do appear to produce cascades with different features, as demonstrated in a review of existing results for α-Fe, proposed in these proceedings as companion paper to the present work [17]. Therefore, the question of determining which characteristics of the interatomic potential are mostly responsible for the result of the simulation arises as an important one. This paper strives to address this question, by comparing the characteristics of cascades simulated by molecular dynamics (MD) using four recent potentials for α-Fe, each providing different descriptions of point-defects and featuring different threshold displacement energies (TDE) and stiffness. The comparison is significant because a sufficient number of cascades per case was simulated with the different potentials following exactly the same procedure and analysed using the same criteria. Therefore, differences in the results can only be ascribed to the inherent features of the potential used.

2. Simulation technique

2.1 Interatomic potentials

Four potentials for α-Fe were used for the MD simulations here reported, namely: (i) the short-range (cutoff between 2nd and 3rd nearest neighbour distance) Finnis-Sinclair-type potential proposed by Ackland et al. [18], henceforth denoted as ABC; (ii) the long-range (cutoff between 3rd and 4th nearest neighbour distance) embedded-atom method (EAM) potential fitted by Chakarova et al. [19], henceforth denoted as CWP; (iii) the long-range EAM potential recently developed by Ackland et al. [20], denoted as AMS; and (iv) a
version of the long-range EAM potential recently developed by Wallenius et al. [21],
denoted as WOL. These potentials were selected for being relatively recent and for
providing significantly different descriptions of, in particular, self-interstitial atoms (SIA).
While CWP incorrectly predicts the ⟨111⟩ crowdion to be the most stable configuration,
ABC, AMS and WOL feature the correct stability of the ⟨110⟩ dumbbell. However, the
energy difference between these two configurations is very small according to ABC and
increasingly larger according to WOL and AMS (see Table 1, where the main properties of
the four potentials are summarised). AMS belongs to a family of potentials for α-Fe which
has been shown to reproduce fairly closely the behaviour of the SIA as described by ab initio
calculations [41]. WOL, on the other hand, predicts formation energies that are too
large for all SIA configurations. These different descriptions of the SIA are expected to
influence the mobility of SIA and SIA clusters predicted by each of these potentials [42,43].
In particular, the mobility of the SIA will be lower according to AMS, because rotation to
and glide along the ⟨111⟩ direction are not favoured compared to other potentials [43].
The selected potentials also exhibit partially different TDE and different range (R) and stiffness
(S). The latter parameters are defined, respectively, as the interatomic distance where the
interaction energy equals 30 eV and the gradient of the potential at the same distance. These
magnitudes have been introduced in ref. [44] to describe the behaviour of the potential in
the intermediate interval of interatomic distances, where the transition between near-
equilibrium atomic oscillations and high energy regime occurs. In this interval, the many-
body potentials used for MD simulations of cascades are typically joined to a high energy
pair potential, more appropriate to describe collisions at close distances (stiffening of the
potential, see e.g. [5,8,15]). The most frequently used high energy pair potential is the so-
called ZBL universal potential [45]. The function used to smoothly join the equilibrium
potential to the ZBL is arbitrarily chosen and the only criterion generally used to test it is
that the TDE should be reasonable [5,8,15]. As an illustration of this point, in Fig. 1 the
curves for the Fe-Fe pair interaction corresponding to the four potentials used in this work
are presented. It can be seen that, although eventually, for high enough energies, all curves
join the ZBL, the way the connection is made can greatly differ in the intermediate energy
and distance region, thereby leading to possible differences in the cascade outcome. In
particular, the parameters R and S have been shown, in a binary collision approximation
(BCA) study [44], to correlate with the number of replacement collision sequences (RCS) of the cascade. In addition, the stiffness at higher energies (~200 eV), here denoted as $U$, has been seen to influence the cascade density [44]. This BCA study suggests therefore that the features of the function chosen to stiffen the potential may have an important role on the outcome of the cascade. This suggestion is considered and tested here in the case of MD cascade simulations.

2.2 Cascade simulation

All simulations were performed using the MD code Dymoka [15] and following standard practice [4-16]. A block of atoms was initially equilibrated for 1 ps at 100 K. After equilibration, temperature was not controlled any more (microcanonical statistical ensemble with periodic boundary conditions) as this parameter has been shown to have negligible effect on the cascade simulation results [12,46]. However, the average temperature of the box at the end of the simulation was recorded and was seen never to rise by more than 100-200 K, compared to the initial temperature. The cascade was initiated by imparting the desired kinetic energy to a primary knock-on atom (PKA, or recoil), here referred to as cascade energy. Note that this energy will entirely go into defect creation and atomic oscillations, since electronic excitation is not an effect included in the simulation. Therefore, the energy of the corresponding real PKA is higher (see e.g. ref. [12]). The PKA was chosen to be at the centre of the cubic box and to move along $\langle 135 \rangle$ directions in order to avoid channelling [11,12]. The cascade energies ranged between 5 and 40 keV and at least 10 cascades per potential and energy were produced. This is on the order of the number of cascade simulations per case typically produced in past, high-energy MD cascade investigations in $\alpha$-Fe [4-15,46] and is therefore considered to be enough to have statistics comparable with previously published studies. The cascade evolution was visually monitored in each case during the collisional and post-collisional stages, to make sure that there was no self-interaction when boundary crossing occurred [12]. The size of the box was increased for increasing cascade energies, as summarized in Table 2, and the box-size/cascade-energy/ ratio was kept comparable with, or larger than, the same ratio in ref. [12]. It was decided that the same box-size was to be used for simulations of the same
cascade energy for all four potentials, independently of the cascade volume provided by the potential. This decision made it impossible to simulate 40 keV cascades with WOL, because of the particularly large volume of cascades according to this potential (see below) and the subsequently unavoidable self-interaction.

In order to ensure that the finite difference method used in the MD code to integrate the equations of motion does not produce uncontrolled errors, the time-step, $\Delta t$, was adapted to the cascade phase as summarised in Table 3. During the ballistic phase, when some atoms possess very high kinetic energy and undergo long displacements in very short times, $\Delta t$ was set to $\sim 10^{-17}$ s (within this time, even the displacement of an Fe atom with 40 keV of kinetic energy is still on the order of $10^{-3}$ nm, which is sufficiently short to guarantee the stability of the algorithm). During the post-collisional phase, in order to speed up the simulation without affecting the precision, $\Delta t$ was extended to $\sim 10^{-16}$ s. After the recombination phase of the cascade, the near-equilibrium evolution was followed for $\sim 23$ ps using, for the last 10 ps, the typical time step of MD simulations ($\Delta t \sim 10^{-15}$ s), until the block of atoms was fully thermalised. The temperature reached in the box at this point was recorded and used to determine the temperature increase induced by the introduction of the PKA.

2.3 Cascade analysis

Point-defects were identified and counted in two ways: (1) using the Wigner-Seitz (WS) cell method, and (2) using "displacement" (also called "equivalent spheres") analysis. The former method requires WS cells to be defined around each perfect lattice position: an empty cell means a vacancy, while two (or more) atoms in the same cell mean an interstitial configuration. The second method corresponds to using spheres instead of WS cells: the distance between the perfect lattice position and the displaced atom is measured and appropriate cut-off radii are used to decide whether a displacement has occurred and to identify the defect type [5,8]. This method was mainly used for comparison purposes, to make sure that the criterion used to identify point-defects did not significantly influence the result of the analyses. Either way, the evolution in time of the number of defects can be monitored so as to identify (i) the peak stage, in terms of time since cascade initiation, in
correspondence with the maximum number of defects, (ii) the recombination, or relaxation, phase and (iii) the number of surviving Frenkel pairs (FP). The defect analysis also allowed the defect positions to be recorded, thereby enabling the cascade evolution to be visualised with the aid of appropriate tools. Through visualisation, a rough estimate of the number of subcascades produced at high enough energy could be given as well.

As an indication of the duration of the recombination phase, which is roughly coincident with the thermal spike, the characteristic relaxation time, $\tau_r$, was also determined. Following Calder and Bacon [5], this parameter was estimated using an exponential decay approximation from peak time ($t_{\text{peak}}$) for the number of FP ($\nu_{\text{FP}}$) as a function of time:

$$\{\nu_{\text{FP}} - \nu_{\text{FP}}^{\text{end}}\}(t - t_{\text{peak}}) = A \exp\left[-(t - t_{\text{peak}})/\tau_r\right],$$

where $\nu_{\text{FP}}^{\text{end}}$ is the number of FP that survived recombination at the final, steady state of the cascade.

The cascade volume and density at peak stage were evaluated using so-called component analysis, described in detail elsewhere [47,48]. According to this procedure, the volume of the cascade is associated with an ellipsoid, whose axes (components) are defined based on the variance of the spatial point-defect distribution. The major axis has the direction maximising the variance, the second one maximises the variance of the distribution projected onto a plane perpendicular to the first one, and the third one has the direction minimising this variance. These directions are parallel to the directions of the eigenvectors of the covariance matrix of the point-defect distributions and the associated eigenvalues are the variances of the distribution projected onto the directions of the eigenvectors. Thus, the problem is reduced to the diagonalisation of a $3 \times 3$ symmetrical, real and positive matrix, which is a straightforward operation. This method is of course not completely justified when subcascade formation becomes important. Still, it provides a reference for comparison purposes, if used systematically for all cascades.

The number of defects in clusters (and the number of clusters) produced during the evolution of the cascade were determined using an automated procedure: point-defects located at a mutual distance below a certain cutoff were searched for and associated with the same cluster. However, the situation at the end of the cascade was further analysed by visual inspection. Different criteria (i.e. different cutoff distances) for the automated procedure were used: vacancy clusters were defined using both 2\textsuperscript{nd} and 4\textsuperscript{th} nearest neighbour (nn) criteria [12] and SIA clusters using both 1\textsuperscript{st} [8,15] and 3\textsuperscript{rd} nn [49] criteria. The visual
inspection was used in addition because it has been observed that automated procedures tend to provide somewhat smaller fractions of SIA in clusters [50].

3. Results

3.1 Peak stage and recombination phase

The main features characterising the cascade peak stage are the maximum number of defects, the time elapsed from the initiation of the cascade when this number is reached (peak time), the cascade volume (according to the component analysis) and the cascade density (i.e. the number of defects per unit volume, given by the ratio between the maximum number of defects and the cascade volume, as provided by the component analysis), all of them as functions of cascade energy. Another feature that can be roughly estimated by visually inspecting the shape of the cascade at peak time is the number of subcascades.

The number of defects and the cascade density at peak time are shown in Fig. 2 for all four potentials used in this work. Clearly, WOL provides significantly less defects at peak time than any other potential and the cascade density is the smallest as a consequence of a large average cascade volume (figure not shown). At the other extreme, AMS produces the largest number of defects at peak time (a factor 2 to 5 compared to WOL) and exhibits the highest cascade density. The other two potentials lie in-between, with the ABC density closer to AMS and the CWP density closer to WOL. Fig. 3 shows the relaxation time as a function of cascade energy for the four potentials and it appears that the potential ranking according to this parameter is roughly the same as for the peak number of defects and cascade density. This fact will be discussed below.

Fig. 4 shows the average number of subcascades produced versus cascade energy, obtained by visual inspection. With WOL, the cascades appeared too dilute for subcascades to be identified, so no curve is given. These curves must be taken as indicative only, due to the arbitrariness of the criterion used to define a subcascade (visual appearance) and to the fact that the number of simulated cascades is too small to consider the sample statistically representative and to be fully quantitative in this particular case. The impression is,
however, that only above 20 keV can the average number of subcascades be larger than one, i.e. cascade splitting actually occurs only above this threshold, in agreement with what was reported by Stoller [12]. Finally, CWP seems to exhibit a stronger tendency to result in cascade splitting than the other potentials.

3.2 Primary state of damage

3.2.1 Defect production efficiency

Fig. 5 presents the defect production efficiency, $\eta = \nu_{FP}^{end} / \nu_{NRT}$, versus cascade energy, for all four potentials considered in this work. Here, $\nu_{NRT} = 0.8E_D/2E_d$ is the standard number of NRT displacements [51], where $E_D$ is the damage energy, coincident with the cascade energy in the MD simulation (i.e. the kinetic energy imparted to the recoil in the simulation), and $E_d$ is an average TDE which, following common practice [7,12,15,39,40,52], has been taken to equal 40 eV. Potentials providing different TDE (Table 1), as well as different numbers of defects and densities at peak time (Fig. 2), produce roughly the same number of defects at the end of the simulation. The only partial exception is WOL, which stands out for a slightly higher $\eta$ (note that at peak time this potential produced the fewest defects). However, all potentials agree in providing efficiencies in the 0.3±0.1 range, in line with results obtained with other potentials available from the literature and in agreement with existing experimental assessments (see ref. [17] for a discussion on this point). AMS seems to exhibit a minimum efficiency at 10 and 20 keV, the latter minimum being in agreement with the behaviour observed by Stoller and attributed to onset of cascade splitting [12]. However, CWP displays a minimum at 5 keV which is not ascribable to sub-cascade formation above this energy (Fig. 4) and ABC presents an $\eta$ steadily decreasing with increasing cascade energy, so most likely these minima and maxima should be attributed to statistic oscillations. The main observation is that no significant difference is found in the amount of surviving FP going from one potential to another at the same cascade energy.
3.2.2 Defect clustered fractions

The fraction of point-defects found in clusters and the cluster size distribution are fundamental information provided by displacement cascade studies to be used as input in damage accumulation models [53]. In Fig. 6, the point-defect clustered fraction, \( f_{\text{cl}}^t \) \((t = V \text{ or SIA})\), is given as a function of cascade energy for the four potentials: \( f_{\text{SIA}}^\text{cl} \) was determined by visual inspection, while \( f_{V}^\text{cl} \) is the result of an automated analysis using a 2\(^{\text{nd}}\) nn criterion. These magnitudes are known to be affected by large oscillations and a completely smooth, monotonous behaviour versus cascade energy is hardly ever obtained [12,15]. However, trends can be identified.

In broad agreement with observations made in previous works [7,9,12-14], the SIA clustered fraction tends to increase with increasing cascade energy until saturation well into the subcascade regime. This increase is particularly steep according to CWP and much less according to the other potentials. This fact may have some relationship with the tendency of CWP to form more subcascades (Fig. 4) since subcascade overlap seems to favour the formation of larger clusters [50]. AMS tends to produce smaller fractions of SIA in clusters than the others.

The vacancy clustered fraction, with the exception of a few outlying points, remains fairly constant for all potentials at all cascade energies. Its value is around 0.2-0.3 for three of the four potentials, but AMS stands out for a particularly high value \( (f_{V}^\text{cl} \sim 0.4-0.5) \). This value broadly equals the fraction of SIA in clusters produced by the same potential, which therefore predicts the same amount of vacancies and SIA in cluster.

4. Discussion

4.1 Number of surviving defects

It is perhaps surprising that potentials which: (i) give different descriptions of point-defects, (ii) predict different TDE and (iii) provide largely different numbers of defects and cascade densities at peak time, end up producing essentially the same number of surviving FP. There must be features of the potentials that induce opposite effects, which compensate each other.
As explained in what follows, Figs. 2 and 3 suggest that the mutually offsetting results may be higher cascade density (and number of defects) at peak time, followed by longer relaxation (recombination) times.

As anticipated in the introduction, work on comparison of potentials performed in the BCA has shown that the cascade density may correlate with the stiffness $U$ of the repulsive potential at energies around 200 eV: stiffer potentials in that region produce denser cascades [44]. At the same time, the stiffness $S$ and the range $R$ at 30 eV correlate with the production of RCS: stiffer and shorter-ranged potentials (i.e. characterised by a high $S/R$ ratio) favour the process of energy transfer during the binary collision, thereby favouring the production of more, and longer, RCS [44]. In our study, WOL exhibits the largest $S/R$ ratio (~183) and one of the lowest $U$ and the cascades produced with this potential have the lowest density and a slightly higher number of surviving defects. In addition, at peak time WOL cascades appear very dilute, suggesting that indeed a significant part of the FP were the consequence of RCS (Figure 7). This is in contrast with the "cascade regime", observed and described by Calder and Bacon for cascades above 1 keV [5], characterised by shock-induced collective effects whereby whole regions of the crystal are displaced along close-packed directions. This regime seems to be easily reached with the other three potentials and in the case of AMS, which presents the smallest $S/R$ ratio (~50) and the highest $U$, very dense and compact cascades are produced (Figure 7). In line with these observations, it has been observed in Ref. [17] that the potential there denoted as HA-VD [8] has $S/R$~267, i.e. the highest of all, and that indeed this potential produces very dilute cascades, with an abnormally high number of surviving FP, as reported also in ref. [15]. Thus, it appears that the correlations observed in the BCA study of ref. [44] between potential stiffness and cascade density or number of RCS hold also in MD simulations. Too high a stiffness and too short a range in the ~30 eV energy region, accompanied by a low stiffness at ~200 eV, hinders the attainment of a full cascade regime. On the contrary, the attainment of the cascade regime is favoured when the potential is soft and long-ranged in the ~30 eV energy region and stiff in the ~200 eV energy region.

A full cascade regime involves a high energy density at peak time and the production of a state close to a melt [5]: how close will depend on the actual defect density at peak time and also on the melting point predicted by the potential. The cascade density is therefore an
index of the attainment of the cascade regime. In addition, in a dense and partially melted cascade region, the thermal spike will last longer and lead to more recombinations than in a dilute and still solid cascade region, where defects have been produced mostly by RCS. Consistently, Figs. 2 and 3 show that a higher density correlates not only with a higher number of peak time defects but also, roughly, with a longer relaxation time, i.e. with longer thermal spikes and more defect recombination. In the four potentials considered in this work, a lower $S/R$ ratio roughly correlates with a higher $U$ (see Table 1) Thus, a simplified picture based on the $S/R$ ratio only can be adopted and both the density of the cascade and the relaxation time can be said to scale with the reverse of this ratio. The level of the curves in Figs. 2 and 3 can be hence roughly anticipated from the $S/R$ value (CWP: $S/R$~101; ABC: $S/R$~73). Low-$S/R$ potentials, such as AMS, induce a full cascade regime and produce at peak time a much higher number of atomic displacements through collective motion (without RCS). However, in this case recombination will also be more important. The two phenomena (a large number of defects at peak time and a long relaxation time), although having the same origin (low $S/R$), will therefore offset each other, eventually leading to a similar number of surviving FP as for potentials with higher $S/R$. The latter will in turn exhibit a smaller peak defect number, but also a shorter recombination time and therefore a number of surviving defects similar to that of low-$S/R$ potentials.

Nonetheless, high-$S/R$ potentials, such as WOL, can still produce a higher number of surviving defects, because relaxation is not, or only marginally, assisted by thermal effects and the larger dilution of damage reduces the probability of spontaneous recombination between SIA and vacancies. This effect is only mildly visible in WOL but reaches an extreme manifestation in the case of the HA-VD potential [8,15] discussed in ref. [17].

Thus, potential range and stiffness ($R$, $S$ and also $U$) appear to offer a means to rationalise some of the cascade features that vary from one potential to another. On the contrary, however surprising it may seem, no explicit correlation is found between the number of defects, both at peak time and in the final defect state, and the TDE values. The potential with the largest average TDE (CWP) does not produce the smallest number of defects, during any of the phases of the cascade.
4.2 Clustered fraction

While the stiffness of the potential is of use to explain the differences concerning defect production, it is not as useful when it comes to rationalise differences in defect clustered fractions. In this case, the potential exhibiting the most peculiar behaviour is AMS, for which it is easy to see (Fig. 6) that the difference $f_{SIA}^{cl} - f_{V}^{cl}$ is very close to zero in most cases. The other potentials display more uniform behaviour, although the steep increase of $f_{SIA}^{cl}$ with CWP stands out as a peculiarity, too. In order to try to understand the reasons for the differences between AMS and the other potentials, the evolution of the clustered fraction for 23 ps after peak time has been monitored using automated procedures for both vacancies (2nd nn criterion) and SIA (3rd nn criterion). An example is given in Fig. 8 for cascades at 15 keV (the results for CWP are not presented because they are almost coincident with those of ABC). The reader should be warned that, strictly speaking, clusters cannot be defined at peak time based on a lattice site occupation criterion. In this case, the "clustered fraction" as we define it is in fact simply an index of how many of the displaced atoms appear to be at a mutual distance comparable to the distance between defects in a cluster. The physical interpretation of the "clustered fraction" versus time will therefore keep changing, as will be clear in the discussion below.

According to Bacon et al [9], two mechanisms of SIA cluster in-cascade formation can be devised. Partly they form at the end of the thermal spike, as a consequence of collective atomic motion in conditions of highly enhanced defect diffusion, due to high local temperature; partly by later local defect re-organization, driven by strain-field interaction among neighbouring and mobile SIA and SIA clusters. The upper graph in Fig. 8 reveals that both mechanisms may occur, but their respective weight is different depending on the potential. According to both AMS and ABC, the "clustered fraction" at peak time is close to unity. Since, as mentioned, speaking of clusters is inappropriate at peak time, this is a way of saying that collective atomic displacements are taking place, whereby the displaced atoms remain all very close to each other (high density) and are therefore recognised "as if" they were forming clusters. However, during relaxation this "clustered fraction" drops by about 50%. WOL, on the other hand, produces only a relatively small SIA "clustered fraction" at peak time, a sign that little or no collective displacement of atoms occurs, in
agreement with the above discussion on the dilution of damage, and the subsequent drop is limited to about 10%. That is, with WOL even at peak time the computed "clustered fraction" is mostly due to actual clusters. After relaxation, when the plotted clustered fraction becomes indeed the result of defect clustering, WOL and ABC exhibit similar behaviour: SIAs rearrange themselves into an increasing fraction of defects in cluster, via (perhaps thermally enhanced) diffusion. On the contrary, the fraction of SIA in clusters remains unchanged according to AMS. This is probably the effect of the different SIA mobility predicted by the two classes of potentials. According to AMS, glide of the SIA along the $\langle 111 \rangle$ close-packed direction is unlikely, because of the large difference between the stable $\langle 110 \rangle$ configuration and the $\langle 111 \rangle$ crowdion configuration (see Table 1), which prevents rotation from one to the other. Migration is therefore fully three-dimensional and relatively slow, with an effective energy of $\sim 0.3$ eV [41,43]. On the contrary, according to the other two potentials glide is possible and the effective SIA migration energy is much lower (a few tens of meV) with a consequently higher mobility [42,43]. Thus, SIA reorganisation via diffusion is possible on the scale of ps with all potentials, except with AMS.

Concerning vacancies, because of their much slower diffusivity compared to SIA, very similarly described by all potentials (Table 1), clustering is a priori only expected to occur during the ballistic phase and the thermal spike (unless collapse, so unusual in $\alpha$-Fe, occurs [49]). The lower graph of Fig. 8 shows, however, that this is not always the case. The peak and relaxation time behaviour is, with the three potentials, similar to the SIA case. But later, three different evolutions are possible. According to WOL, the vacancy clustered fraction experiences a mild decrease, most likely because of further, diffusion-driven recombination with rapidly migrating SIA. According to ABC the clustered fraction remains essentially unchanged. But according to AMS a clear increase is seen to occur. This is difficult to explain, because vacancy diffusion should be negligible on a ps scale. Different factors may combine to produce this post-relaxation vacancy clustering. The density of the cascade may be so high that a very small number of vacancy jumps may be sufficient to drive further clustering. Alternatively (or in addition), the temperature in the cascade region during this phase may for AMS be closer to the melting point predicted by the potential, thereby allowing enhanced vacancy diffusion and clustering compared to the other potentials. In fcc
metals, for example, it has been shown that the melting point affects the ion beam mixing and how vacancies are pushed towards the centre of the cascade to cluster [54]. In particular, the fact that following relaxation AMS exhibits a larger $f_{v,cl}$ compared to the other potentials may be related to partial cascade collapse during the thermal spike and may correlate with either a lower melting point predicted by the potential or a higher cascade core temperature, due to the high density, or both. However, the effect of the melting point becomes negligible when the density of defects is not especially high. Indeed, the melting point of CWP has been calculated to be between 1800 and 1850 K [55], while the melting point of ABC is around 2200 K [56], but no difference in vacancy clustering has been observed. Further studies are therefore in course to clarify the origin of this behaviour of AMS [57]. Still, it is clear that the clustered fractions predicted by a certain potential are determined by a complicated combination of interacting factors, related partly to the point-defect mobility according to the potential, partly to the description that the potential gives of the cascade regime (i.e. to the influence of its stiffness in the repulsive region) and partly to other properties, such as the melting point.

5. Conclusions

The main goal of the present paper, driven by the review done in ref. [17], was to produce a set of cascade results for different potentials, adopting standard simulation procedures and rigorously identical analysis techniques, in order to find out whether different potentials provide different results and which, among the potential features, are primarily responsible for the differences. It can be concluded that:

- The number of Frenkel pairs produced in a cascade during the whole displacement process does not correlate with the threshold displacement energies predicted by the potential (provided that these are reasonable).
- A correlation is found instead with the stiffness and range of the potential in the region of tens and hundreds of eV interaction, as suggested by BCA studies [44], i.e. in the region of transition between equilibrium and repulsive potential, which is largely arbitrary [5,8,15]. With potentials too stiff and short-ranged in the 30 eV energy region, but with a lower stiffness around 200 eV, replacement collision sequences become the
main mechanism of damage production and a full cascade regime is never reached, even at high cascade energies. The dilute damage produced at peak time in these cases exhibits fewer defects and on average a larger distance between SIA and their vacancies (low density), partially preventing SIA-vacancy recombination during relaxation. On the other hand, a full cascade regime, characterised by collective atomic displacements, massive defect production at peak time, higher damage density and a pronounced thermal spike, is typical of potentials which are soft and long-ranged at low energy (~30 eV) and stiff at higher energy (~200 eV). The length of the thermal spike in this case may however also be influenced by the melting point predicted by the potential.

- In spite of largely different cascade processes, all potentials predict roughly the same final amount of surviving Frenkel pairs (with the only exception of specially pathological cases, as discussed in ref. [17]). This is likely to be the result of mutually offsetting effects of the stiffness. A larger stiffness ($U$) causes a higher defect density at peak time, but also induces, as a consequence, a longer relaxation time with more recombinations, so that the final number of surviving defects is largely independent of the cascade features at peak time.

- Vacancy and SIA in-cascade clustering are potential dependent. Differences are the result of a complicated interplay between different features of the potential, from the description of the mobility of point-defects, to the density of the cascade at peak time (related to the stiffness) and the extent of the thermal spike, as well as the possibility of cascade collapse, which may also depend on the melting point predicted by the potential.

The most worrying conclusion is that the result of cascade simulations using a given potential may be greatly influenced by the partially arbitrary choices made when stiffening the potential in the region of tens to hundreds of eV [5,8,15], i.e. in the region of the transition between the equilibrium part of the potential and the high-energy ZBL pair potential typically used for very short interatomic distances [45]. The fit to the TDE in that region appears to be of little use as a guide for the stiffening [17]. For example, would cascades simulated with the AMS potential, probably the best one available right now for radiation damage in α-Fe, still predict the same large amount of vacancies in clusters, if the connection in the transition region was significantly stiffer at tens of eV and softer at hundreds of eV? For the moment, there is no answer to this question.
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Agreement (EFDA), task TTMS-007.

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73.
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Tables

Table 1 – Summary of the main properties of the four interatomic potentials used in this work for cascade simulations. Legend: $a_0$ (lattice parameter); $E_{coh}$ (cohesive energy); $\Delta E_{fcc-bcc}$ (energy difference between the two phases); $E^f_\langle 110 \rangle$ and $E^m_\langle 110 \rangle$ (vacancy formation and migration energy); $Q^{SD}$ (self-diffusion activation energy); $E^f_\langle 111 \rangle$ and $E^m_\langle 111 \rangle$ (SIA configuration formation energy); $\Delta E_\langle 111 \rangle-\langle 110 \rangle$ (relative stability of SIA configurations); $db$ (dumbbell); TDE along the three main directions and in average, including median value, see ref. [22]; $S$ and $U$ (stiffness) and $R$ (range), see text.

<table>
<thead>
<tr>
<th>Equilibrium properties</th>
<th>ABC</th>
<th>CWP</th>
<th>AMS</th>
<th>WOL</th>
<th>Exp.</th>
<th>Ab initio</th>
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<td>2.867</td>
<td>2.866</td>
<td>2.855</td>
<td>2.860</td>
<td>2.86$^a$</td>
<td>2.85-2.86$^b$</td>
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<td>-4.013</td>
<td>-4.28</td>
<td>-4.28$^c$</td>
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<td>$\Delta E_{fcc-bcc}$ [meV]</td>
<td>54</td>
<td>50</td>
<td>121</td>
<td>47</td>
<td>50$^d$</td>
<td>35$^e$</td>
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<th>Point-defect energies [eV]</th>
<th>ABC</th>
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<th>AMS</th>
<th>WOL</th>
<th>Exp.</th>
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<tr>
<td>$E^f_\langle 110 \rangle$</td>
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<td>1.54</td>
<td>1.71</td>
<td>2.08</td>
<td>2.0±0.2$^i$,1.5$^e$,</td>
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<td>$E^m_\langle 110 \rangle$</td>
<td>0.78</td>
<td>0.73</td>
<td>0.63</td>
<td>0.81</td>
<td>0.55$^f$,</td>
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<tr>
<td>$Q^{SD} = E^f_\langle 110 \rangle + E^m_\langle 110 \rangle$</td>
<td>2.48</td>
<td>2.27</td>
<td>2.34</td>
<td>2.89</td>
<td>2.48$^m$-3.13$^n$*</td>
<td>2.52-2.76</td>
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<tr>
<td>$E^f_\langle 111 \rangle$</td>
<td>4.87</td>
<td>4.15</td>
<td>3.59</td>
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<td>Stable config is</td>
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<td>$E^m_\langle 111 \rangle$</td>
<td>5.00</td>
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<td>(110) db; $E^f$=4.7-5$^o$</td>
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<td>0.42</td>
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<th>TDE [eV]</th>
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<td>$\langle 100 \rangle$</td>
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<td>18</td>
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<td>34</td>
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<td>$\langle 111 \rangle$</td>
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<th>Exp.</th>
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<td></td>
<td>45.8±0.4 (42)</td>
<td>54.5±0.5 (54)</td>
<td>40±0.3 (36)</td>
<td>41.8±0.3 (38)</td>
<td>(40)$^q$</td>
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<th>AMS</th>
<th>WOL</th>
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<td>R [Å]</td>
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<td>1.23</td>
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<td>S [eV/Å]</td>
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<td>-124</td>
<td>-65</td>
<td>-203</td>
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<td>U [eV/Å]</td>
<td>-3448</td>
<td>-2511</td>
<td>-5123</td>
<td>-2886</td>
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</tbody>
</table>


$^*$ The value 1.3 seems to be the result of not high enough purity of Fe [33]

* About 15 experimental measurements reported, giving values within this range, see e.g. website: [http://diffusion.nims.go.jp/index_eng.html](http://diffusion.nims.go.jp/index_eng.html)
Table 2 – Summary of recoil energies, simulation box size and number of simulated cascades in this work.

<table>
<thead>
<tr>
<th>PKA energy [keV]</th>
<th>Box size [number of atoms]</th>
<th>Number of cascades (per potential)</th>
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<tr>
<td>5</td>
<td>250000 (50a₀)</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>250000 (50a₀)</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>432000 (60a₀)</td>
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<td>20</td>
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<td>30</td>
<td>778034 (73a₀)</td>
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<tr>
<td>40</td>
<td>778034 (73a₀)</td>
<td>10*</td>
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* In the case of WOL no 40 keV cascades could be simulated (see text)
Table 3 – Time-step scheme used for cascade simulations in this work.

<table>
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<th>Duration</th>
<th>Adopted time-step</th>
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<td>Ballistic</td>
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<td>0.01 fs</td>
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<tr>
<td>Post-collisional</td>
<td>0.5 – 3.0 ps</td>
<td>0.05 fs</td>
</tr>
<tr>
<td>Recombination</td>
<td>3.0 – 13.0 ps</td>
<td>0.1 fs</td>
</tr>
<tr>
<td>Short-term defect evolution</td>
<td>13.0 – 23.0 ps</td>
<td>0.5 fs</td>
</tr>
</tbody>
</table>
Figure captions

**Figure 1** – Fe-Fe pair interaction curves in the energy and distance intermediate region for the four potentials used in this work.

**Figure 2** – Number of defects (above) and cascade density (below) at peak time versus cascade energy according to the four potentials used in this work. Lines are guides for the eyes. Note that the error bars in the number of defects are "smaller than the symbol".

**Figure 3** – Relaxation time versus cascade energy according to the four potentials used in this work. Lines are linear interpolations used as guides for the eyes.

**Figure 4** – Estimated average number of subcascades (in addition to the single cascade always produced) versus cascade energy according to the four potentials used in this work, after visual inspection. Lines are guides for the eyes. The estimation is necessarily only a very rough one.

**Figure 5** – Defect production efficiency compared to NRT displacements (see text) according to the four potentials used in this work.

**Figure 6** – Fraction of SIA (above) and vacancies (below) in cluster according to the four potentials used in this work. The SIA clustered fraction was determined by visual inspection, while for the vacancies an automated procedure with 2\textsuperscript{nd} nn distance criterion was applied.

**Figure 7** – Appearance at peak time of a typical 20 keV cascade simulated with WOL (above) and with AMS (below). The two potentials predict opposite cascade behaviour and the former is the softest, while the latter is the stiffest (at ~200 eV).

**Figure 8** – Evolution in time of the fraction of SIA (above) and vacancies (below) in cluster in 15 keV cascades, according to potentials AMS, ABC and WOL. (CWP provides results extremely similar to ABC and the relevant curves are therefore not shown). SIA and V clusters are defined, respectively, using a 3\textsuperscript{rd} nn and a 2\textsuperscript{nd} nn criterion.
Figure 1

Fe-Fe pair interaction

V (eV)

r (Å)

ABC
WOL
CWP
AMS
ZBL Universal
Figure 3

 그래프는 이론과 실험 데이터 간의 관계를 보여줍니다. x축은 에너지 (keV)이며, y축은 방忪 시간 (ps)입니다. 그래프에는 AMS, ABC, CWP, WOL의 4개의 데이터 세트가 포함되어 있으며, 각 세트는 다른 색상의 도형으로 구분됩니다. 에너지의 증가와 방忪 시간의 증가가 선형関係를 보입니다.
Figure 4

The figure shows the relationship between energy (in keV) and the number of sub-cascades for three different datasets: AMS, ABC, and CWP. The energy ranges from 15 to 40 keV, and the number of sub-cascades ranges from 0 to 4.

- **AMS**: Represented by black squares.
- **ABC**: Represented by red circles.
- **CWP**: Represented by green triangles.

As the energy increases, the number of sub-cascades also increases for all three datasets, with CWP consistently showing the highest number of sub-cascades across the energy range.
Figure 5

Defect production efficiency vs. Energy, keV

- AMS
- ABC
- CWP
- WOL
Figure 6

- AMS
- CWP
- ABC
- WOL

Visual inspection

Vacancy clustered fraction

2nn criterion
Figure 7
Figure 8

**SIA clustered fraction**

- AMS
- ABC
- WOL

**3nn distance criterion**

**Vacancy clustered fraction**

- AMS
- ABC
- WOL

**2nn distance criterion**
Cluster formation mechanisms during relaxation and post-relaxation cascade stages in $\alpha$-Fe: a molecular dynamics study

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Abstract

This work presents an analysis of cascade configurations aimed at gaining a better understanding of the processes taking place in the primary damage region. Previously, a comparative study of molecular dynamic simulations of displacement cascades up to 40 keV in bcc Fe using four different interatomic potentials was performed. Here the work is continued with the main purpose of finding mechanisms responsible for self interstitial atom (SIA) and vacancy clustering. Studying the clustered fraction and the mechanisms whereby clusters form during the different stages of the cascade is indeed vital to correctly assess the impact of cascade phenomena on radiation damage production and evolution. In the present work the following processes have been considered: formation of clusters during the relaxation stage and further clustering caused by high-temperature enhanced defect diffusion and spontaneous gathering of self interstitial atoms (SIA) driven by strain-field interactions. It is found that the mechanisms of defect diffusion and clustering are potential-dependent and that the stiffness of the potential in the intermediate energy and distance region, also related to the formation energy of the SIA, determines the processes taking place during the various stages of the cascade, as well as the final defect configuration. The defect clustered fractions and the recombination efficiencies are also influenced by which stable SIA configuration the potential reproduces.

Keywords and PACS codes: Molecular dynamics (M0200 31.15.Qg), Displacement cascades (R0100 61.72.Cc), Point-defect clusters (61.72.Ji), Mechanism of cluster formation.
1. Introduction

The production of self interstitial atom (SIA) clusters in cascades is nowadays an accepted fact [refs to MD cascade simulations in Fe and Cu where clusters are seen + R. Rauch, J. Peisl, A. Schmalzbauer and G. Wallner, J. Nucl. Mater. 168 (1989) 101 for exp observation by Huang diffusion scattering of SIA cluster formation in cascades in Cu]. However, the detailed mechanisms of formation of such defects directly within the cascade are not well known and even less is known concerning the influence of the potential used in the simulation on the role of these mechanisms. Nonetheless, detailed information about defect clustering is an important input parameter for the prediction of the long term evolution of radiation damage [S.J. Zinkle and B.N. Singh, J. Nucl. Mater. 199 (1993) 173]. This information can at the present moment be obtained only by applying MD tools. This is why much work devoted to the study of primary damage in α-iron has been presented and published in recent years using a wide spectrum of potentials [8,9,10,11+12(i.e. my review)].

In a previous work we have compared cascades simulated with four different interatomic potentials and found that the number of surviving Frenkel pairs is approximately the same irrespective of the potential used. However, the potentials give a wide spread in the final fraction of SIAs and vacancies in clusters, as well as in the cluster size distribution [14, that should become 13]. A correlation between sub-cascade formation and final clustering was also found [13, that should become 14], for which possible reasons have been discussed but no detailed analysis has yet been done. In addition, the considered potentials give different descriptions of the near-equilibrium state such as defect diffusion properties, predicting in particular various mechanisms and energy barriers for self interstitial atom (SIA) migration. For instance, the difference in the SIA migration energy is as large as a factor of six between the recently published Ackland-Mendelev potential (E<sub>m</sub> = 0.3 eV) [15+ref Ackland] and the Ackland-Bacon potential (E<sub>m</sub> = 0.058 eV) [16]. The dimensionality of SIA motion depends on the potential as well and can vary from full 3D motion to rather pronounced 1D motion [17]. Such discrepancies will influence the motion of
SIAs and small SIA clusters during the post-collisional stage which lasts a few tens of picoseconds and thus the cascade recombination stage and relevant clustering mechanisms will be affected as well. However, the relative importance of these and other potential features needs to be quantitatively assessed. [12].

A correlation between the stiffness and the range of a potential and the predicted cascade morphology and relaxation behavior was found in our previous work [14], in agreement with BCA studies [C.S. Becquart, A. Souidi and M. Hou, Phys. Rev. B 66 (2002) 134104.]. The range and stiffness describes the potential behavior at interatomic distances where the transition between the near-equilibrium and the high energy regimes occurs. The potential is stiffened by joining the many-body potential with a high energy potential such as the ZBL universal potential [Ref. ZBL]. The function joining the two parts is often chosen arbitrarily as long as the threshold displacement energy of the potential is seen to be reasonable. More specifically, potentials exhibiting long range R (distance where the interaction energy is ~30 eV), low stiffness S in correspondence with R and high stiffness U at somewhat higher energy (~200 eV) form relatively dense cascade cores and provide a subsequent long relaxation stage. In contrast, potentials with a high stiffness S and a short range R at ~30 eV, and low stiffness at ~200 eV, produce a smaller number of defects at peak time, primarily via replacement collision sequences (RCS) and undergo a shorter relaxation stage. Since generally a low S/R ratio correlates with high U and vice versa, only the former parameter can be looked at and, for simplicity and compactness, potentials with low S/R ratio and large U, producing high cascade densities and long recombination stages, will be called "soft", while potentials characterized by large S/R ratio and low U, producing low cascade densities, will be said to be "hard".

When the cascade energy is high enough for sub-cascades to form, the influence of the stiffness of the potential appears again, although in a less clear. A "soft" potential will generally tend to produce a number of cascade cores, with a certain probability of overlapping. Moving from a "softer" to a "harder" potential, the sub-cascade cores start to become spread out allowing less overlapping between the cores.

In the present paper we try to give a more detailed and quantitative description of the contribution to defect clustering from the different features of the cascades at peak
time and the different mechanisms of defect diffusion and to discuss physical aspects associated with them.

2. Simulation method

2.1 Potentials

Four different potentials for α-Fe were used for the MD simulations in this work:

(i) the Finnis-Sinclair-type (FS) potential proposed by Ackland et al. [16], which will henceforth be denoted as ABC;

(ii) the embedded-atom method (EAM) potential fitted by Chakarova et al. [18], which we shall call CWP;

(iii) the EAM potential recently developed by Ackland et al. [19], which we will denote as AMS;

(iv) a version of the EAM potential recently developed as part of an Fe-Cr potential by Wallenius et al. [20], that we will label WOL.

Table 1 summarises the defect properties of the four potentials used in. Some of these properties will be shown to have an influence on the SIA and vacancy clustering processes.

Table 1. Summary of the main properties of the four potentials used in this work.

<table>
<thead>
<tr>
<th>Point-defect energies [eV]</th>
<th>ABC</th>
<th>CWP</th>
<th>AMS</th>
<th>WOL</th>
<th>Exp.</th>
<th>Ab initioa</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\Gamma}^f )</td>
<td>1.70</td>
<td>1.54</td>
<td>1.71</td>
<td>2.08</td>
<td>2.0±0.2, 1.5；</td>
<td>1.6±0.10d, 1.6-1.75e；</td>
</tr>
<tr>
<td>( E_{\Gamma}^m )</td>
<td>0.78</td>
<td>0.73</td>
<td>0.63</td>
<td>0.81</td>
<td>0.55f；</td>
<td>0.57±0.14g(1.3)h,±0.59-0.67</td>
</tr>
<tr>
<td>( Q^{SD} = E_{\Gamma}^f + E_{\Gamma}^m )</td>
<td>2.48</td>
<td>2.27</td>
<td>2.34</td>
<td>2.89</td>
<td>2.48±3.13j,*；</td>
<td>2.52-2.76</td>
</tr>
<tr>
<td>( E_{(110)}^f )</td>
<td>4.87</td>
<td>4.15</td>
<td>3.59</td>
<td>6.45</td>
<td>Stable config is</td>
<td>3.64</td>
</tr>
<tr>
<td>( E_{(111)}^f )</td>
<td>5.00</td>
<td>4.02</td>
<td>4.03</td>
<td>6.87</td>
<td>( \langle 110 \rangle ) db; ( E^f=4.7-5k )</td>
<td>4.34</td>
</tr>
<tr>
<td>( \Delta E_{(111)-(110)} )</td>
<td>0.13</td>
<td>-0.13</td>
<td>0.44</td>
<td>0.42</td>
<td></td>
<td>0.70</td>
</tr>
<tr>
<td>( E_{\text{SIA}}^m )</td>
<td>0.058</td>
<td>0.056</td>
<td>0.31</td>
<td>0.061</td>
<td>0.25-0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>( E_{\text{DL,VAC}}^\text{bind} (1^{st} \text{nn}) )</td>
<td>0.14</td>
<td>0.19</td>
<td>0.14</td>
<td>0.20</td>
<td>N.A.</td>
<td>0.14</td>
</tr>
<tr>
<td>( E_{\text{DL,VAC}}^\text{bind} (2^{nd} \text{nn}) )</td>
<td>0.20</td>
<td>0.21</td>
<td>0.24</td>
<td>0.27</td>
<td>N.A.</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Stiffness
R [Å]  | 1.30  | 1.23  | 1.29  | 1.11  \\
S [eV/Å] | -95   | -124  | -65   | -203  \\
U [eV/Å]  | -3448 | -2511 | -5123 | -2886 |

\(^a\)Ref [21]  \(^b\)Ref [25]  \(^c\)Ref [29]  \\
\(^d\)Ref [22]  \(^e\)Ref [26]  \(^f\)Ref [30]  \\
\(^g\)Ref [23]  \(^h\)Ref [27]  \(^i\)Ref [31]  \\
\(^j\)Ref [24]  \(^k\)Ref [28]  \(^l\)Ref [32]  

\(^k\) The value 1.3 seems to be the result of not high enough purity of Fe [27]

\(^*\) About 15 experimental measurements reported, giving values within this range, see e.g. website:
http://diffusion.nims.go.jp/index_eng.html

2.2 Calculation details

The details of the MD aspects of the simulations are described in our previous article [14] and only a brief description will be given here. The classical MD code DYMOKA [32] was used in the NVE ensemble at a temperature of 100 K with periodic boundary conditions. The number of successfully simulated cascades for each potential was at least 10 per cascade energy and the total simulation time was 23 ps. After equilibrating of the system for 1 ps, the cascade was initiated by giving kinetic energy or cascade energy to a primary knock-on atom (PKA) chosen to be situated at the center of the cubic simulation box. To avoid channeling, the PKA was chosen to move in the \(\langle 135 \rangle\) direction. Overall, the simulation technique was standard and the results can therefore be safely compared with results available from the literature.

The defect space distributions were estimated using the Wigner Seitz cell criterion: an empty cell means a vacancy while two (or more) atoms in the same cell mean an interstitial configuration. The number and size of clusters were determined using a 2\(^{nd}\) nearest neighbor (nn) distance criterion for vacancies and visual inspection for SIAs. In the case of vacancies, a distance criterion is enough since vacancy mobility is very limited within the simulation time frame at the simulation temperature. The high mobility of SIAs, especially in the case of the CWP potential, which incorrectly predicts the fast-gliding \(\langle 111 \rangle\) crowdion to be the most stable interstitial configuration instead of the \(\langle 110 \rangle\) dumbbell, requires more care. SIA clusters move in the \(\langle 111 \rangle\) direction by gliding, but the collective motion of a cluster is realized through independent jumps of the crowdions forming the cluster [33,34]. From time to time, a single SIA can jump as far apart from the others as 4\(^{th}\) or even 5\(^{th}\) nn distance, the binding energy of the SIA cluster being strong enough to prevent it from breaking up
[35]. The use of a large distance criterion like 5\textsuperscript{th} nn for example would not solve the problem since it could lead to the inclusion of SIAs not actually belonging to it in the same cluster. Visual inspection over successive snapshots is hence the only way of correctly assigning all SIAs to the right cluster, provided that the clusters are not too large. Nonetheless, distance criteria have been widely used in previous work concerning Fe [8,9,10,11], so an analysis of the SIA clustered fraction as a function of time using a 3\textsuperscript{rd} nn numeric distance criterion was done to be able to compare with the published results of others.

As an indication of the duration of the different phases, or stages, of the cascade, characteristic times were introduced. Three cascade stages were defined. The ballistic, or collisional, stage starts when the PKA is introduced and ends at peak time, $\tau_{p}$, which is defined as the time when the maximum number of defects (atomic displacements) is observed. The duration of the relaxation, or recombination, stage, roughly coincident with the so-called thermal spike, is measured by the relaxation time, $\tau_{r}$, which is defined following Calder and Bacon [Calder93+our previous paper]. The thermal spike is characterized by a rapid, local increase of temperature, during which a state close to a melt can be produced, followed by fast quench, thereby inducing atom mixing, enhanced defect diffusion and recombination. The relaxation stage is over when the number of defects is seen to be stable. Finally, the post-relaxation, or post-cascade, stage starts at $\tau_{p}+\tau_{r}$ and lasts for the rest of the simulation time. During this phase the system reaches full thermalization and the defect population should reach a steady state known as the primary state of damage, although it will be shown that some diffusion processes are already active, so that the definition of the end of the post-cascade stage, which can also be denoted as "diffusional" stage remains arbitrary. In our case, we monitored the third cascade stage for approximately 15 ps. At the temperature at which the cascades were performed, this corresponds to about tens of SIA jumps at the most, depending on the potential used.

In order to understand how clusters evolve during the different stages of a cascade, the clustered fractions and the average cluster sizes were monitored as functions of time for the four considered potentials at all simulated cascade energies starting from $\tau_{peak}$ to end of the simulation at 100 fs intervals using distance criteria for both
vacancies (2\textsuperscript{nd} nn) and interstitials (3\textsuperscript{rd} nn). Of course, at peak time and during most of the relaxation phase it is not appropriate to speak of clusters. Still, the "clustered fraction" will give an idea of the level of aggregation and depletion of displaced atoms during the cascade process, thereby giving an insight into the mechanisms playing a role in the final formation of clusters. Once the post-cascade stage is reached, additional magnitudes have been estimated such as the separate contribution to SIA and vacancy clustering occurring during the relaxation and post-cascade stages and the number of recombined defects within the post-cascade stage as a functions of cascade energy.

3. Results and discussion

In this section, results concerning SIA and vacancy clustering for the relaxation and post-cascade stages will be presented and discussed. We assume that clustering is the effect of defect accumulation during both of those stages. The final clustered fractions produced during the post-relaxation stage studied using different clustering criteria are presented in the section 3.1. In section 3.2, clustering as a function of time is analyzed and the influence of the thermal motion of defects (primarily SIAs and SIA clusters) and its contribution to the final clustered fractions is discussed.

3.1 Final clustered distributions

3.1.1 Interstitials

In figure [Y] the final SIA clustered fraction determined by visual inspection is shown as a function of cascade energy for all four potentials considered in this work. The general tendency is that the fraction increases with cascade energy except in the case of the WOL potential which exhibits a decrease. The absolute values clearly differ between individual potentials, but the correlation between potential properties and clustering is not straightforward. The ABC potential is soft and predicts correctly the \textless 110\textgreater dumbbell to be the lowest energy interstitial configuration and exhibits a high clustered fraction. However the AMS potential is also soft and predicts the correct SIA configurations, but predicts a low clustered fraction. The average size of SIA clusters also increases with rising cascade energy as can be seen in figure [Z]. Again, the WOL potential has the most aberrant behavior showing a much smaller rise than the other potentials.
SIA clusters have been counted both using distance criteria implemented in automated procedures and by visual inspection [ref to my review]. It is hence useful to study the difference in the results obtained using these two techniques. Figure [X] shows a comparison between the clustered fractions calculated using visual inspection and 3rd nn distance criterion for all studied potentials. In all cases, the fraction determined using the distance criterion is smaller than the fraction attained using visual inspection. The largest discrepancy is found for the CWP potential. This result should be taken into account when comparing the results of other authors who have used different approaches. Of course, using visual inspection introduces human error into the analysis. However, we find that visual inspection will not give larger errors than an automated analysis using distance criteria, unless the clusters are very large, so that it becomes easy to miscount the number of defects that they contain.

3.1.2 Vacancies

The vacancy clustered fractions determined using a 2nd nn distance criterion, are given in figure [YY] and show the same tendencies as the SIA clustered fractions of increasing with cascade energy, although the increase is less pronounced than in the previous case. The exception is once again WOL which exhibits a sharp decrease. The CWP and ABC potentials produce similar results while the clustered fraction of the AMS potential is higher. The average vacancy cluster size shown in figure [ZZ] rises with energy as expected. Here the ABC and the WOL potentials show similar behavior while the cluster size for the AMS potential is much larger.

The vacancy clustered fraction may be expected to correlate with the binding energies between vacancies (see table 1). However we see that this is not the case. The WOL potential has the highest vacancy binding energies at both 1st and 2nd nn distances but does not feature the largest vacancy clustered fraction, the most likely reason being the low density of the cascade core. With this potential, vacancies were formed mostly via RCS ending up quite far away from each other. Also, it is not possible to find a correlation between vacancy clustering and vacancy migration energy, since the values predicted by the different potentials are similar and, at any rate, with those values, vacancy migration is not expected to occur at the simulated temperature within the time frame of MD. Nonetheless, the discussion on the vacancy clustered fraction with AMS shows that vacancy migration may be playing a role there.
The conventional reason to use a 2nd nn distance criterion for vacancy cluster detection is that the di-vacancies are seen to be bound up to this order of distance, the 2nd nn distance binding energy being higher than the binding energy at 1st nn distance. In a work by Stoller [11], it was shown that the vacancy pair distributions have peaks at 2nd and 4th nn distances and for this reason he proposed a 4th nn distance criterion to detect clusters. Stoller argues that the 4th nn vacancies will eventually merge into compact clusters on longer time scales. The evolution of vacancy clustering can then be predicted by studying vacancies at this distance. All of the potentials used in this work give a good prediction of the vacancy binding energies when compared with ab initio calculations. The WOL potential has the highest 2nd nn binding energy and the ABC potential has the lowest. In order to characterize the vacancy distribution after the relaxation stage, the same calculations as those by Stoller were performed. Figure XX displays the spatial correlation of all vacancies at 15 keV for all four applied potentials. Peaks at 2nd and 4th nn distance can be seen in all cases, with the highest peak corresponding to the WOL potential which gives the largest binding energy between vacancies at 2nd nn distance.

3.1.3 Production bias

Due to the higher mobility of SIAs, their clustered fraction is expected to be larger than that of vacancies. The production bias, defined as the difference between the SIA clustered fraction and the vacancy clustered fraction, is shown in figure [YYY]. Again there is a clear difference between the potentials. The AMS potential shows a very small and for some energies negative production bias.

3.2 Clustered fractions as a function of time

3.2.1 Vacancy clustered fraction

The formation of small vacancy clusters in cascades with cascade energies of no more than 10 keV was found to be a stochastic process and no vacancy motion was observed during simulation. The formation of large vacancy clusters with more than six vacancies, takes place in high energy cascades with cascade energies of at least 20 keV. The clusters are due to the presence of an initial collision spike where they are formed. In the case of cascades where no splitting occurs, a locally heated area surrounding a large vacancy cluster forms. The heated area is enriched in vacancies
and depleted in SIAs. Isolated vacancies located inside the heated area can move towards each other or towards large vacancy clusters if they exist.

The evolution of the vacancy clustered fractions as functions of time were found to be qualitatively similar for all of the potentials, although a peculiar behavior was observed with the AMS potential during the post-relaxation phase [14], as will be discussed in more detail later. The vacancy clustered fraction as a function of time for the full range of cascade energies with this potential is presented in figure 1. Three typical features of the clustered fraction evolution should be emphasized. First, we note the presence of a minimum for each curve. Minima are indicated by circles in the figure for the lowest and highest energies. Second, there is a saturation plateau, shown by thick lines for the lowest and highest energies that can be clearly seen for all cascade energies. Third, there is a hump-like peak, shown by a rectangle, which can be observed for cascades of relatively high energies. As the cascade energy increases, the energy minima are shifted towards later times, the absolute value of the saturation level increases and as does the height of the hump increases although its position in time does not change. These features are broadly observed for the other potentials as well, but the minima are much less pronounced than for AMS. In addition, no hump-like peak is ever observed with WOL. The reason for these differences will be further discussed later. The positions of the minima were found to coincide roughly with the end of the relaxation stage. This means that there is no additional accumulation of vacancies during the relaxation stage, but only a decrease in the clustered fraction as the cavities formed during the ballistic stage shrink through recombinations.

The values of the observed minima are correlated with the stiffness of the potential and the cascade energy: the "softer" the potential and the higher the cascade energy, the shallower the minima. This can be interpreted to mean that non-dense or split cascades do not result in as high a clustering fraction as dense ones. It would also be consistent with the previously reported fact that vacancy clusters form at the center of cascade cores during the ballistic stage [3,Bacon93]. Another fact that indirectly supports the idea of larger vacancy clustered fractions in the case of soft potentials, which provide denser cascades, is the observed formation of a big planar vacancy cluster oriented along the $<100>$ direction in one of the cascades produced using the AMS potential at 40 keV. Note that in that cascade, a pronounced collision spike with no sub-cascade splitting was detected [36]. The situation is quite similar to the one
reported by Soneda in [37]. Dense cascades and cascades with no splitting would thus correspond to larger vacancy cores with some probability to collapse, while the possibility of this scenario is suppressed by cascade splitting.

The clustered fraction curves undergo oscillations in the saturation region. This can be explained by further recombination processes driven by mobile SIAs, which can lead to an increase (if single vacancies recombine) or a decrease (if clustered vacancies recombine) of the clustered fraction and only in very rare cases to no change at all. The amount of recombinations will depend on the spatial distribution of the defects, which is mainly defined during the ballistic stage. On the other hand, the description of defect mobility (i.e. the diffusion properties) defined by the potential will also play a role in the recombination process.

Figure 1 shows that with AMS, there is also a significant contribution to vacancy clustering during the post-relaxation stage, since the clustered fraction increases. This contribution can be evidenced by taking the difference between the final value of the clustered fraction and the value at the minimum (end of the relaxation stage). This contribution of the post-cascade stage to the clustered fraction is shown in figure 2 for all potentials. The contribution of 0.15 corresponds to 30% of the final vacancy clustering fraction at a cascade energy of 40 keV for the AMS potential. It can be seen that only the AMS potential predicts a substantial increase in the vacancy clustering during the post-cascade stage. Through visualization we observed that, except with the AMS potential, single vacancies were almost always immobile which is reasonable with an initial simulation temperature of 100 K. For the AMS potential, single vacancies were seen to migrate close to large vacancy clusters. This is surprising and can only be explained by considering that the cascade causes local heating in the area at the center of the cascade core which enhances vacancy diffusion. AMS is the softest potential among the considered ones [14] and thus the cascade core is particularly dense. The temperature reached in the core is expected to be higher and the thermal spike to linger longer than for the other potentials. As discussed already, the conditions are thus favorable for large vacancy clusters to form and, apparently, also for single vacancies around them to diffuse rapidly towards them due to the higher temperature, possibly combined with the attraction exerted on single vacancies by cavities.
Figure 3 shows the number of recombined atoms during the post-relaxation stage versus cascade energy. For two of the potentials (WOL and CWP), the tendency can be defined as linear as expected, since the probability of recombination can be considered proportional to the amount of defects. The smallest number of recombined atoms was found for the CWP potential and this can be ascribed to the character of SIA motion with this potential. As reported in previous studies [17 but also others: Osetsky et al.], if the potential predicts the <111> crowdion to be the most stable configuration, the motion of SIAs occurs exclusively by one-dimensional by glide in the close packed direction with only occasional changes of direction which are very rare at low temperature. It is also known that the probability that one-dimensionally moving defects will encounter uniformly distributed spherical sinks (vacancies in this case) is orders of magnitudes lower than for three-dimensionally migrating defects [ref to Trinkaus, e.g. H. Trinkaus, BN Singh and S.I. Golubov, J. Nucl. Mater. 283-287 (2000) 89]. Thus, it is no surprise that CWP provides the lowest recombination rate during the post-cascade stage of the cascade.

The presence of a hump was observed only for high cascade energies where the formation of sub-cascades was also seen. Thus we assume that the presence of a hump can be correlated with sub-cascade formation processes. In the case of the WOL potential, no splitting of the cascades was ever seen, and no humps in the clustered fractions were observed at any energy which is another confirmation of our assumptions. The hump appears during the relaxation stage, which means that it is not due to the overlapping of sub-cascade cores. Probably the formation of sub-cascades somehow affects the motion of SIAs after the peak stage hindering recombination processes. The appearance of the humps could also be connected with the fact that above a certain energy when cascade splitting occurs, the SIAs in the clouds surrounding the cascade cores will interfere with each other and their motion will be hindered. The second maximum would be the result this interference of the clouds as less SIAs are available for recombinations with vacancies which then have a larger clustering probability. This could be checked by seeing if the humps grow at even larger cascade energies.

The estimation of the number of single vacancies which have recombined shows that for the AMS potential, about 80% of the annihilation events were reactions between single vacancies and SIA clusters. The other potentials give a 50/50 ratio in average,
meaning that the probability for single vacancy to recombine with a single SIA or with an SIA cluster was roughly the same. Since SIA clusters are more mobile than single SIAs, this behavior could explain the deviating trend of the vacancy clustering for the AMS potential during the post-cascade stage.

### 3.2.2 SIA clustered fraction

The SIA clustered fractions for the four studied potentials at 15 keV cascade energy are shown in figure 4. Minima and saturation levels are seen for SIAs as well as for vacancies. However, evidence of a hump was not seen at any cascade energy with any of the potentials. The dependence of the minima and the saturation levels on the cascade energy is the same as for the vacancy as for the SIA clustered fractions, i.e. as the energy rises, the minima shift towards later times and become shallower and the level of the saturation plateaus increase. The difference between the minimum and the saturation level is very small for the AMS potential, but it does exist. Analysis shows that the positions in time of the minima for the SIA clustered fractions are very close to the value of the relaxation time, $\tau_r$, just as they were for the vacancy clustered fractions.

The evolution of the clustered fraction differs significantly between the potentials. Looking at the absolute value of the "clustered fraction" during the relaxation stage, one can draw conclusions about the density of the produced cascades. As already reported in our previous paper [14], the very low clustered fraction for the WOL potential during the relaxation stage reflects the fact that the cascades were less dense compared with the cascades produced with the other potentials. The AMS potential on the other hand provides the densest cascades with the longest relaxation time.

Figure 5 gives a quantitative description of the contribution to the final SIA clustering as a function of cascade energy for all used potentials. The general tendency of a rising clustered fraction during the post-cascade stage is clear, although there are differences between potentials and variations even with the same potential. An increase in the SIA clustered fraction during the post-cascade, diffusional phase is indeed to be expected since SIAs, particularly in the $\langle111\rangle$ crowdion configuration, are highly mobile and can perform up to tens of jumps within ~10 ps. Only the WOL potential provides a contribution that is stable and increases linearly with cascade energy contributing approximately 40% to the final value. The ABC and the CWP
potentials predict between 30% and 50% contribution to the final clustered fraction during the post-cascade stage. The slightly smaller contribution with the CWP potential can be explained by the different dynamics of SIA motion, as already mentioned. With the CWP potential SIAs can aggregate only if they moving along parallel and neighboring \(<111>\) lines, since change of \(<111>\) direction is extremely unlikely at 100 K [38]. During the post-cascade stage, the clustered fraction of the CWP potential exhibits large oscillations. This possibly comes from problem with correct SIA description with the CWP potential and a discussion has already been given in section 2.2.

The values for the AMS potential look rather complicated and no definitive conclusion can be drawn. A significant contribution is present only for the lowest and highest energies and otherwise the contribution is negligible. Visual inspection and specific studies [ref to paper to be published] show that the mobility of SIAs with the AMS potential is much lower than with the other potentials, especially for isolated SIAs. Thus, a low contribution to SIA clustering during the post-cascade stage should be expected. However, the overlapping of cascades could give rise to a spontaneous accumulation of SIAs at the periphery of the cascade core, and hence, overlapping should lead not only to an increase in the SIA clustered fraction but also to an increase in the vacancy clustered fraction. With the formation of sub-cascades, the motion of SIAs at the periphery of the cascade core should be suppressed due to the spontaneous gathering of SIAs, which means that small mobile SIA clusters are located between the sub-cascade cores. Such distributions of defects would make recombinations between SIAs and vacancy clusters difficult.

Although the formation of sub-cascades for the AMS potential starts at 20 keV, a clear separation of sub-cascade cores starts only at 40 keV. This could therefore confirm the relationship between cascade overlapping and the increased contribution of the post-cascade stage to the SIA clustered fraction observed in figure 5, since the increase of such a contribution appears at cascade energies of about 30-40 keV. However, the number of cases where overlapping is seen, is too small to draw definitive conclusions from and the reason for the larger contribution at 5 keV remains unclear. One possible explanation could be that since the volume of the cascade is the smallest for the AMS potential [14] and since at 5 keV it has a relatively small density compared to the density at higher energies, the formation of a
"classical" sphere-like periphery was not always reached during the ballistic stage. It would then be possible to have further aggregation into clusters during the post-cascade phase.

3.2.3 Remarks on the mechanisms of cluster formation

For the AMS or CWP?, ABC and WOL potentials, SIA clustering at low cascade energy is largely due to the spontaneous gathering of SIAs during the post-cascade stage. A visualization of SIAs after the relaxation stage shows that for the ABC and WOL potentials some SIAs can move very short distances, so that clustering is more probable at short ranges (about 1 or 2 Burgers vector distance). Rotation of SIAs from <110> dumbbells to <111> crowdions was observed. Further, the crowdions did a few fast jumps towards other SIAs during post-cascade stage. For the AMS potential, all SIAs were frozen after the end of relaxation stage [so what has just been said does not hold for AMS?].

For higher cascade energies, sub-cascade formation begins. The probability of SIA clustering increases when sub-cascade splitting and overlapping occurs. This should give a tendency of increasing SIA clustering with higher cascade energy. For the WOL potential, the fact that no sub-cascade splitting was observed and that the formation of non-dense cascades was seen should reflect on the final SIA and vacancy clustered fractions.

With the CWP potential, only crowdions and not dumbbells are formed after the PKA introduction. In principle, the clustered fraction should depend on two processes correlated with the 1D fast motion of crowdions. First of all, such motion could lead to additional recombination between crowdions and vacancy clusters. The probability for a crowdion to recombine with a single vacancy is very low. The process would lead to an increasing SIA clustered fraction and a decreasing vacancy clustered fraction. On the other hand, while a crowdion is moving it can also couple with other collinear crowdions and form a cluster. The mobility of small <111> clusters is still rather high, but the probability for non-collinear SIAs to join the cluster is very small due to the very high rotation energy of crowdion. Hence the small cluster could also effectively interact with isolated vacancies and vacancy clusters located inside the cluster glide prism. This should result in decreasing SIA and vacancy clustered fractions.
To summarize, we expect to see the formation of large SIA and vacancy clusters with the AMS and ABC potentials and small clusters with the WOL and CWP potentials. The SIA clustered fraction should be smallest for the AMS potential while the vacancy clustered fraction should be smallest for the CWP potential.

4. Conclusion and final remarks

The objective of the present work was to perform a set of identical calculations using different potentials in order to investigate the mechanisms of in-cascade cluster formation and to try to correlate the efficiency of those mechanisms with certain features of the potential. Based on the results presented, a set of conclusions about defect clustering in cascades can be drawn:

- The ballistic phase of the cascade has the most important role in the formation of clusters and the evolution of the cascade during this phase is largely determined by the stiffness and range of the potential in the region of intermediate energies and, where the transition from equilibrium to ZBL potential occurs.

- The relaxation phase does not lead either to the formation of new clusters, or to the growth of existing ones; rather, the clustered fraction can only decrease during this phase.

- The clustered fraction can either continue to grow or remain constant during the post-cascade, post-relaxation stage of the cascade.

- The details of the process of vacancy and SIA clustering seem to be strongly dependent on the potential used and the diffusion properties of defects predicted by the potential certainly play a large role. In some cases, such as with the AMS potential, the increase of vacancy clustering due to migration can be significant.

As a result of both the work presented here and in previous papers [refs], a number of correlations between defect descriptions given by the potential and cascade results can be proposed. For example:

1. A high SIA formation energy is likely to be the result of a stiff potential, which leads to a larger distortion field around the defect and, simultaneously, favors the production of defects via RCS. In these conditions, cascades tend to be diluted, i.e. characterized by larger volumes and fewer defects at peak time. Hence, the average
size of the clusters of both vacancies and SIAs will be small and the fraction of defects in clusters will decrease with cascade energy, because defects will have increasingly less probability of meeting each other. This in turn leads to softer interactions and thus less energy losses and a longer recombination stage. It also results in larger cascade sizes which alters the recombination time and the final defect stage.

2. If the \(<111>\) crowdion is predicted as the stable SIA configuration, diffusion can take place only via crowdion glide mechanism. Since the crowdion has a very low probability to change its orientation at low temperature in order to form a cluster, it becomes less likely that SIA clusters grow during the diffusional, post-cascade stage, giving a smaller SIA clustered fraction, unless other mechanisms, such as subcascade overlapping, contribute to the clustering. The stability of the crowdion rather than the dumbbell will also reduce the recombination efficiency during the post-relaxation stage and, if the cascade happens to be particularly diluted, this could lead to a larger final number of surviving defects.

3. Even when a reasonable SIA formation energy and stability is predicted by the potential, differences may still arise in the defect clustered fraction both from different stiffening and from different defect diffusion properties predicted by the potential. A "soft" potential, in the sense specified in the introduction, will produce dense cascades and this will generally impact on larger vacancy clusters and therefore give larger vacancy clustered fractions. In addition, with a potential that favors the dumbbell migration mechanism, rather than crowdion glide, the growth of clusters during the diffusional, post-cascade stage will be largely suppressed (unless other mechanisms, such as subcascade overlapping, intervene).

The third case corresponds to that of the most recently published iron potential [19], which is at the present moment accepted to give the best description of defect properties in \(\alpha\)-Fe [ref Fu&Willaime] when compared to ab initio indications such as melting point, phonon density spectra, etc.. The results concerning defect clustered fractions in cascades are with this potential quite different from the results obtained with most previous potentials. Not only final numbers differ but also the clustering mechanisms are not the same. We believe that the two parameters primarily responsible for those differences are the stiffness and the description of SIA
properties. But while in the latter case it is possible to state that this potential represents an improvement with respect to previous ones, the stiffening applied for the transition between equilibrium and ZBL remains arbitrary. Further investigation would therefore be required to establish up to what extent this particular aspect can change the results obtained in MD cascade simulations.

In the case of the WOL potential, the "hardest" one, no sub-cascade formation is observed up to 30 keV cascade energy and a single spread core is invariably produced.

Acknowledgements

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Table 1. – References??


[COSIRES]
[33] [Barashev] Independent crowdion model, I will for it
[Bacon93]
[36] [NTDSC'05] D. Terentyev, L. Malerba and M. Hou, article accepted to be published in proceedings of SPIE, all
[38] [single SIA diffusion work] article in preparation
[COSIRES]
Figures:

Figure 1. Vacancy clustered fraction as a function of time for the AMS potential.

Figure 2. The contribution to vacancy clustered fraction due to post-cascade stage.

Figure 3. The number of recombined atoms during post-cascade stage.

Figure 4. The SIA clustered fraction as a function of time.
Figure 5. The contribution to the SIA clustered fraction during the post-cascade stage.

Figure X. The ratio between the clustered fractions of SIAs obtained using visual inspection and a 3rd nn distance criterion.

Figure XX. The number of vacancy pairs at a distance of i-th nn distance.
Figure Y. SIA clustered fraction of the final defect configurations as a function of energy. Parameters for the fitted curves can be found in table Y.

Figure YY. Vacancy clustered fraction of the final defect configuration as a function of energy. Parameters for the fitted curves can be found in table YY.

Figure YYY. Production bias between SIAs and vacancies.
Fig. Z Average SIA cluster size.

Fig. ZZ Average vacancy cluster size.

Table Y. Gives fitting parameters for SIA clustered fractions. The fit uses a power law form according to \( y = A \cdot E^B \)

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Table YY. Gives fitting parameters for vacancy clustered fractions. The fit uses a power law form \( y = A \cdot E^B \)

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