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N-body potentials in simulation of point defect properties

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Abstract

This work is devoted to simulation of the diffusion features of point defects in bcc metals. The properties of point defects have been investigated with the usage of many-body interatomic potentials. This approach, based on the density-functional theory, permitted us to derive more adequate diffusion features of solids. The investigation is carried out within the framework of the Finnis-Sinclair formalism, developed for an assembly of N atoms and represents the second-moment approximation of the tight-binding theory. We used a new model, based on the molecular static method for simulating the atomic structure near the defect and vacancy migration in pure metals. This approach gives the opportunity to simulate the formation and the migration volumes of the point defects, taking into consideration the influence of pressure on structure and consequently on energy. The diffusion characteristics of bcc α-Fe and anomalous β-Zr have been simulated. The preliminary results of this research were presented and taken for publishing on the international conference "Diffusion in solids" (DiSo-2005) in May 2005.

Keywords: Diffusion, pressure, bcc metals, activation volume.

1. Introduction

There have been done a lot of experimental measurements of point defect properties. But unfortunately, in most cases it is impossible to compare the results of this researches, because the majority of practically important, especially transition metals are difficult for theoretical description. At the same time, the studying of the pressure influence on the diffusion coefficient, theoretical calculation of activation volumes in metals for different diffusion mechanisms and subsequent comparison with experimental data allows choosing the diffusion mechanism from several variants. However, microscopic calculations of volumes associated with defect migration are difficult, as emphasized by Lazarus [1]. Moreover there are no good methods for calculation of the activation volume, defining the influence of pressure on the diffusion coefficient.

Nevertheless, the determination of atomic structure and energies, associated with point defects has been the subject of a number of calculations. The primary object of the majority of them are activation energies for motion and atomic configurations in the migration zone. Therefore, metastable and saddle-point configurations must be investigated as well as stable configuration. This work is devoted to this problem with a new approach.

In a vacancy diffusion mechanism, dominant in pure metals, the main diffusion properties are the vacancy formation and migration energies E_v^f, E_v^m and the formation and migration volumes V_v^f, V_v^m. For the vacancy diffusion mechanism the diffusion coefficient is usually assumed:

$$D = D_0 \exp\left(-\frac{E_v^f + E_v^m + V_v^f p + V_v^m p}{kT} \right) \tag{1}$$

The sum of the last two characteristics is also called an activation volume and expresses the influence of pressure on the diffusion coefficient. It is defined by the expression well-known from thermodynamics:

$$V* = V^f + V^m \equiv -kT \frac{\partial \ln D(T,p)}{\partial p} \tag{2}$$

One of the main problems of the modern computer simulation is to choose a realistic way of interatomic interaction. All the first models were based on pair-potentials. However, in spite of its simplicity, the pair-potential model has some serious drawbacks [2]. Firstly, the elastic constants in a cubic crystal satisfy the Cauchy relation $C_{12} = C_{44}$, but it is well-known that it is not valid for most real metals. The second shortcoming of the pair-potential description is related to the first. If we accept $C_{12} = C_{44}$, the vacancy formation energy is always found to be equal to the cohesive energy. Experimental data show it to be about one-third of the cohesive energy [2].

Alternative empirical way to describe interatomic interactions is a set of various methods, taking into consideration the quantum character of metallic cohesion. These models are generalization on the density-functional theory and describe the energy of a system with many-body interactions. Although there are a variety of names associated with these methods, they all provide the similar description of the energetics.

In this work we used the Finnis-Sinclair formalism [2, 3] of N-body interactions, free from disadvantages of pair-potentials, for the atomic structure simulation and calculation of point defect properties. This approach declared oneself to be the most correct and accurate.

The new simulating model, used in this work is an evolution of the Johnson's approach [4]. There is a rough description and the main accents of the new model below. The detailed description is to be published [5].

2. The model

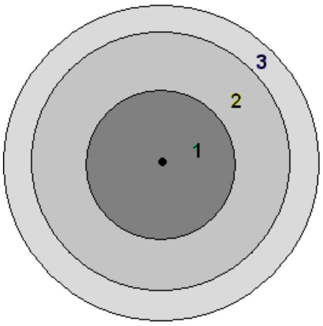

Fig. 1: Computational cell divided into three concentric zones.

We have found that the activation volume is extremely sensitive to the atomic structure in the vicinity of a defect, so it is very important to calculate the relaxed atomic positions with high accuracy. To calculate the relaxation volume we used a new scheme, based on a molecular static method [5]. A defect was created in the middle of the bulk, containing about several thousand atoms. The bulk was divided into three concentric zones. Atoms of the third external zone are embedded in an elastic continuum. Atoms of the first and the second zones relax freely in the vicinity of a defect. Simultaneously atoms of the third zone are fixed in their positions. The atomic displacements in an elastic continuum are described with the elastic equation solution. In the first-moment approximation it can be constrained with the first spherically symmetrical term

$$\vec{u} = C\frac{\vec{r}}{r^3} \tag{3}$$

C is a constant, calculated with the usage of atomic displacements in the second intermediate zone. In accordance with C, atoms of the third zone are displaced from their positions in the ideal lattice. In this way the self-consistent iterative procedure was built. We have found a stable convergence of constant *C* and atomic positions in several (about 5) steps. Then the relaxation volume has been calculated with the equilibrium magnitude of constant *C*:

$$\Delta V_{rel} = \iint u dS = 4\pi C \tag{4}$$

This algorithm also can be applied to the case of defect migration (for the vacancy migration – atomic jump from the nearest coordinative sphere into the vacancy). Now the atomic displacements aren't still isotropic, so we have decided to consider two dilatation centers. The first is in vacancy, and the second is situated in an ideal position of the migrating atom.

So we can separate the displacement field into its constituent parts in relation to two dilatation centers:

$$\vec{u} = \vec{u}_1 + \vec{u}_2; \qquad \vec{u}_1 = qC\frac{\vec{r}_{01}}{r_{01}^3}; \qquad \vec{u}_2 = (1-q)C\frac{\vec{r}_{02}}{r_{02}^3} \tag{5}$$

where q is contribution of the first dilatation center. $\vec{r}_{01}, \vec{r}_{02}$ define atomic coordinates in the first and the second dilatation center axes. Thus the *x* component of the atomic displacements

$$u_x = u_{1x} + u_{2x} = qC_x \frac{x_{01}}{r_{01}^3} + (1-q)C_x \frac{x_{02}}{r_{02}^3} \tag{6}$$

and

$$C_x = \frac{u_{1z} + u_{2x}}{q \frac{x_{01}}{r_{01}^3} + (1-q) \frac{x_{02}}{r_{02}^3}} \tag{7}$$

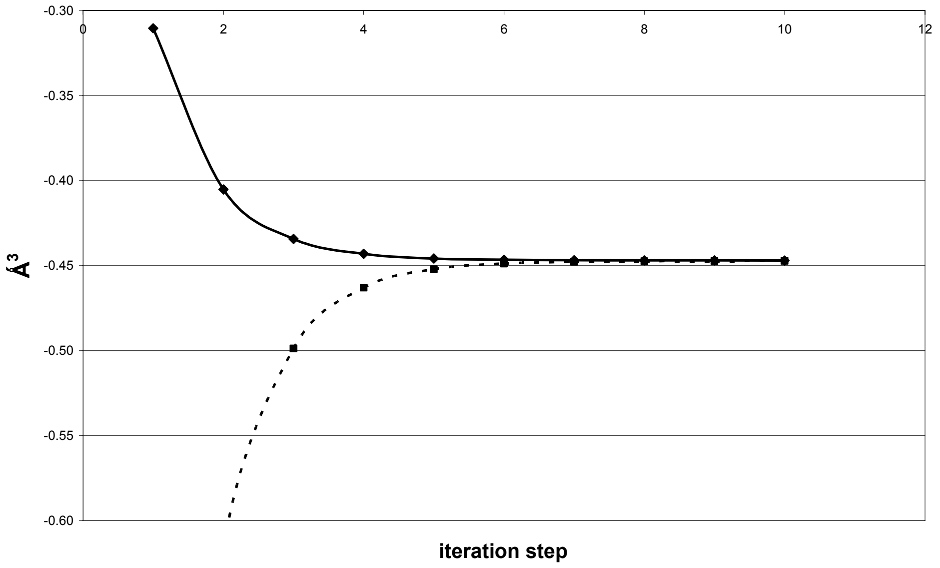

Fig. 2: The stable convergence of constant *C* in about 5 steps (Fe, N-body [3]).

C_y and C_z are similar. The average value of C is used to define the atomic displacements in the third zone:

$$x' = x_0 + C\left[q \frac{x_{01}}{r_{01}^3} + (1-q) \frac{x_{02}}{r_{02}^3} \right] \tag{8}$$

With the usage of constant *C* equilibrium magnitude we can define the ordinary term of the migration volume as the difference between relaxation volume in the basic state and the saddle point

$$V^m = \Delta V_{rel}^w - V_{rel}^v = 4\pi(C^w - C^v) \qquad (9)$$

3. N-body interactions

It is well-known that semi empirical methods are capable of treating much larger systems (thousants and millions of atoms), than *ab-initio* or first-principles methods. And simultaneously, they are free from limitations of models, based on pair interactions.

There are several models, turning into account N-body potentials, involving many-body interactions. The main are the Finnis-Sinclair formalism [2,3], and the embedded-atom method [6], based on the second-moment approximation of the tight-binding theory and the density-functional theory.

Within the framework of the Finnis-Sinclair formalism, the energy of an assembly of N atoms is given by

$$E = \frac{1}{2}\sum_{i\neq j=1}^{N} \Phi_{ij}(R_{ij}) - A\sum_{i=1}^{N}\left(\sum_{j=1}^{N}\varphi_{ij}(R_{ij})\right)^{1/2} \qquad (10)$$

$$R_{ij} = \left|Rij\right| = \left|\vec{R} = -\vec{R}_i\right|$$

where Φ_{ij} is the pairwise repulsive part of the potential and φ_{ij} is the many-body cohesive term.

The physical interpretation of this approach based on the results of tight-binding theory. So the cohesive energy, the second term of (10) is interpreted as a local electronic density [2]

$$\rho_i = \sum_{j=1}^{N} \varphi_{ij}(R_{ij}) \qquad (11)$$

In the framework of current model the generalized force could also be performed as a sum of the consequent terms. The first attractive term of the force could be found traditionally as a sum of pair atomic interactions in a form of $\Phi'(r)\mathbf{r}/r$. The x-component of the force, acting on *i-th* atom is [2]

$$\begin{aligned}\frac{1}{A}\frac{\partial E_N}{\partial r_{ix}} &= f_i'\sum_{k\neq i}\varphi'(r_{ik})r_{ikx}/r_{ik} - \sum_{k\neq i} f_k'\,\varphi'(r_{ki})r_{kix}/r_{ki} \\ &= -\sum_{k\neq i}(f_i' + f_k')\varphi'(r_{ik})\,r_{ikx}/r_{ik}\end{aligned} \qquad (12)$$

Derivative of the cohesion function *f* is

$$f_i' = \left.\frac{\partial f}{\partial \rho}\right|_{\rho=\rho_i} \tag{13}$$

4. Pressure-dependent activation volume contribution

In this work we have used a new approach to define the influence of elastic fields on a diffusion jump in crystal [7]. This approach is based on the following idea. Equilibrium positions of atoms in crystal change in the elastic field and the potential energy of atoms changes accordingly. In [7] the new expression for the migration volume contribution was received for the case of hydrostatic pressure using the pair potential model. This approach can be extended for the case of N-body interactions:

$$\begin{aligned} \Delta V_p^{E_m}{}_{N-body} = & -\frac{1}{3K_0}\sum_i^N \left[(f_i' + f_s') R_{is}^W \left.\frac{\partial \varphi}{\partial R}\right|_{R_{is}^W} + R_{is}^W \left.\frac{\partial \Phi}{\partial R}\right|_{R_{is}^W} \right] + \\ & + \frac{1}{3K_0}\sum_i^N \left[(f_i' + f_s') R_{is}^v \left.\frac{\partial \varphi}{\partial R}\right|_{R_{is}^v} + R_{is}^v \left.\frac{\partial \Phi}{\partial R}\right|_{R_{is}^v} \right] \end{aligned} \tag{14}$$

Here K_0 is a bulk modulus, ρ – local electronic charge density, φ and Φ are N-body potentials, R_{is}^v, R_{is}^w are interatomic distances in the base position and the saddle point respectively, and f is a cohesive function.

In the same way we can define the formation volume contribution.

$$\begin{aligned} \Delta V_p^{E_f}{}_{N-body} = & -\frac{1}{6K_0}\sum_i^N\sum_j^N \left[\left(f_i' + f_j'\right) R_{ij}^v \left.\frac{\partial \varphi}{\partial R}\right|_{R_{ij}^v} + R_{ij}^v \left.\frac{\partial \Phi}{\partial R}\right|_{R_{ij}^v} \right] + \\ & + \frac{1}{6K_0}\sum_i^N\sum_j^N \left[\left(f_i' + f_j'\right) R_{ij}^0 \left.\frac{\partial \varphi}{\partial R}\right|_{R_{ij}^0} + R_{is}^0 \left.\frac{\partial \Phi}{\partial R}\right|_{R_{ij}^0} \right] \end{aligned} \tag{15}$$

Here R_{is}^0, R_{is}^v are interatomic distances in ideal and defective crystal respectively.

5. Results and discussions

Approaches, described above, were realized in algorithms, compiled with Fortran 90. According to them, we considered the activation volumes to be a sum of the relaxation term and the pressure-dependent term. So we used the following final expressions to define the activation volume:

$$V^f = \Omega + \Delta V_{rel} + \Delta V_p^{E_f}; \qquad V^m = \Delta V'_{rel} - V_{rel}^0 + \Delta V_p^{E_m} \tag{16}$$

Ω is the volume per atom.

In recent researches we used the original Finnis-Sinclair potential, but it turned to be not the best to describe interatomic interactions, especially within short distances. Ackland *et al.* [3] has developed a new iron potential using the same fitting method, with fits to the lattice parameter, elastic constants, and cohesive energy and estimated unrelaxed vacancy formation energy. To carry out these parameterizations, fitting to (computationally-convenient) cubic splines was used

$$\begin{aligned} \Phi(x) &= \sum_{k=1}^{m} a_k H(r_k - R)(r_k - R)^3 \\ \varphi(x) &= \sum_{k=1}^{2} A_k H(R_k - R)(R_k - R)^3 \end{aligned} \tag{17}$$

In this notation H is the Heaviside function.

This potential gives more adequate results in comparison with the experimental data and it has been chosen for current simulation.

The β–Zr simulation was performed with the usage of exponential N-body potential, developed by Willaime and Massobrio, so called WM1 [8]:

$$\Phi(r) = A\exp\left(-p\left(\frac{R}{r_0}-1\right)\right) \qquad \varphi(r) = \xi^2 \exp\left(-2q\left(\frac{R}{r_0}-1\right)\right) \tag{18}$$

The relaxation of atoms of the first three coordinative spheres is shown. (Fig. 1). It is worth emphasizing the unexpectedly large values of the atomic displacements for β-Zr.

We have received the following potential barriers for the vacancy migration in α-Fe (upper chart Fig.2) and β-Zr (lower chart Fig.2). It is necessary to emphasize that the energetic peaks for α-Fe are situated on the 1/3 and 2/3 of vacancy way accordingly with the good accuracy. And the results, obtained with pair and N-body potentials differ only in a value of the migration energy (the barrier height). The value, obtained with N-body potential has a better agreement with experimental data.

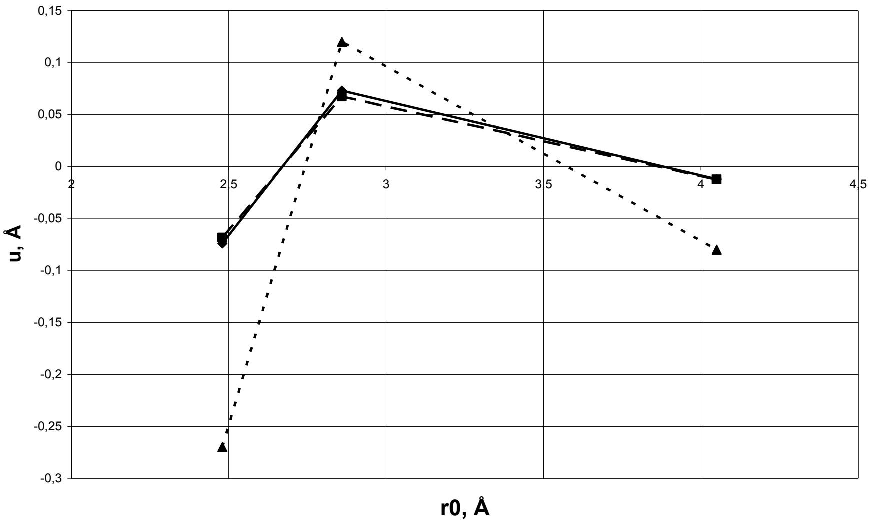

Fig. 3: The average atomic displacement of the first three coordinative spheres near vacancy (α-Fe – solid, dashed, β-Zr -dotted).

It is emphasizing result that the consequent peaks for β-Zr are displaced closer to the centre of the vacancy way. And the distance between them is less then 1/3. This result seems to be unusual and there could be a variety of reasons for it. The most probable reason of it is the specific of exponential Zr N-body potential.

The characteristics, obtained for two metals are performed in Table 1. The special interest was to study both normal, and anomalous metals, and to compare the results for these cases. Also we perform the comparison of the results, obtained for N-body and pair-potentials.

The activation energies, obtained for Fe are in good agreement with the results of Ackland [3], since the various methods, but the same potentials were used. This approach also gives the proper value of E_v^f .

Some of the results are especially worth emphasizing. Since the atomic displacements in the basic state are small, the pressure-dependent term of the formation volume is quite small. But for the case of the migration volume pressure-dependent term gives the main contribution. And it is easy explicable, because in the saddle point the surrounding atomic displacements have the largest values.

Some diffusion characteristics of α-Fe, obtained in simulation and experiment by different authors in different times are adduced in Table 2.

The authors know of no reliable results of activation volume calculations in β-Zr. The energetic characteristics, obtained with the WM1 N-body potential are in good agreement with [8] and known experimental data.

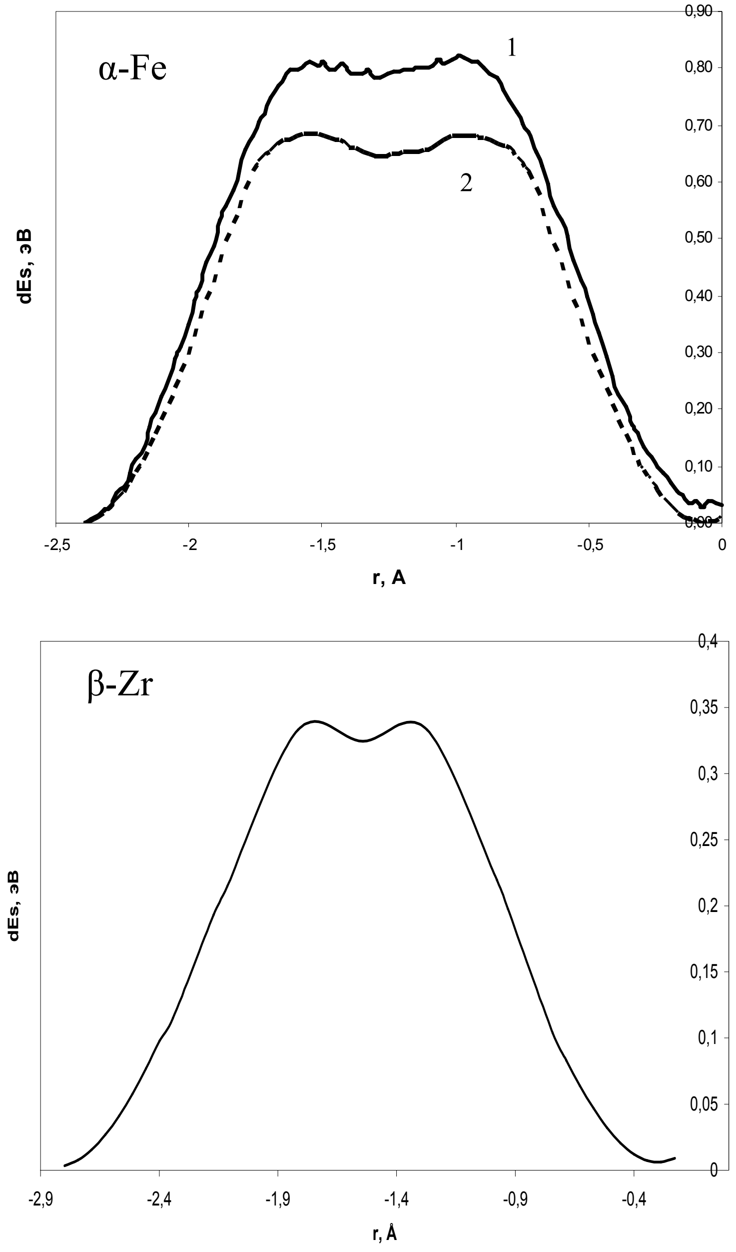

Fig. 4: Potential barriers of the vacancy migration in α-Fe and β-Zr.
(1 – N-body [3], 2 – pair potential [4]).

Table 1: The diffusion characteristics of α-Fe and β-Zr for the vacancy diffusion mechanism.

	α-Fe		β-Zr
	N-body [3]	Pair-potential [7]	N-body WM1 [8]
$E_v^f \quad [eV]$	1,70	2,91	1,55
$E_v^m \quad [eV]$	0,79	0,69	0,32
$E_v^{SD} \quad [eV]$	2,49	3,78	1,87
$\Delta V_{rel}/\Omega$	-0,159	-0,132	-0,472
$\Delta V_p^{E_f}/\Omega$	0,021	0,015	0,014
V_v^f/Ω	0,862	0,854	0,542
$(\Delta V'_{rel} - \Delta V^0_{rel})/\Omega$	0,009	0,011	10^{-4}
$\Delta V_p^{E_m}/\Omega$	0,041	-0,032	0,089
V_v^m/Ω	0,050	-0,022	0,089
V_v^{SD}/Ω	0,912	0,832	0,631

Table 2: The diffusion characteristics of α-Fe, obtained in simulation and experiment by different authors in different times.

	E_v^f, эВ	E_v^m, эВ	V^f/Ω	Simulation
Ackland *et al.* (1997)	1,70	0,82	0,78	
Osetsky *et al.* (1995)	2,05	0,71	0,53	
Simonelly *et al.* (1994)	1,57/1,67	0,86/0,89		
Calder and Bacon (1993)	1,83	0,79		
Schaefer *et al.* (1977); **Furderer *et al.* (1987)**	1,6 – 1,7	0,9 – 1,3		Experiment
Ehrhart *et al.* (1979) ; **De Schepper *et al.* (1987)**	~2,0	~0,6		

3. Conclusion

A computer model allowing defining the diffusion characteristics of bcc metals has developed and realized. The new approach allowed us to achieve the finest structure in the vicinity of a defect, and consequently to perform more accurate calculations. Except of the energetic characteristics, the activation volumes have been calculated with the usage of new approach. Also it is necessary to emphasize that N-body potentials give more adequate results, especially in cases of formation energy and pressure-dependent term of the migration volume for Fe.

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