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Simulation of Vacancy and Atom Migration in B2 Type Structures

D. A. Belobraga and A. V. Nazarov

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, 115409, Russia

Abstract

The diffusion mechanism in ordered systems should ensure the conservation of long-range order in the arrangement of atoms. However, despite the large number of theoretical and experimental papers devoted to this issue, the diffusion mechanisms in such systems havenot been established to date. Earlier in our works a variant of the mechanism is suggested that ensures the fulfillment of the above-mentioned condition, and the obtained barrier values for which are of lower values than other known mechanisms. In addition, it is noted in these papers that for a wide temperature range vacancies move in a tied state jumping on the different sublattices. Therefore, the bi-vacancy diffusion mechanism with jump atoms to vacancies from the second coordination sphere is considered.

A model based on the Kinetic Monte Carlo and a set of programs for studying the migration of bivacancies and atoms in B2-type structures have been developed.

Corresponding Author:
D. A. Belobraga
danil.belobraga@gmail.com
A. V. Nazarov
avn46@mail.ru

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1. Introduction

In recent years, much attention has been paid to alloys with intermetallic hardening as functional materials or structural materials for high-temperature using [1, 2]. For example, the Ni-Al system, one of whose stoichiometric compounds has a B2 structure, is a candidate for use as a base for heat-resistant materials. The structure of B2 consists of two primitive cubic sublattices. In the fully ordered state of the stoichiometric B2 compound, the A atoms occupy one sublattice, and the B atoms are the other sublattice [1]. It is known that in metals the diffusion of atoms is realized by means of a mechanism define by the exchange of a vacancy with one of its nearest neighbors [1]. However, for the case of ordered intermetallic compounds, the realization of such a mechanism would lead to the formation of a large number of defects (the arrangement of atoms on a foreign sublattice) and, as a consequence, the disorder of long-range order. This feature of ordered systems presupposes the more complex diffusion mechanisms in such systems. Several mechanisms are being discussed that attempt

to describe diffusion in structures of type B2: the triple-defect mechanism, the six-jump-cycle mechanism, the divacancy mechanisms, the ASB mechanism [2-5,7-12]. However, despite the large number of works devoted to this problem, there is as yet no generally accepted a point of view on diffusion mechanisms in these systems.

The aim of this work is to study atom migration in B2 systems using the Kinetic Monte Carlo [13, 14] and determine the self-diffusion coefficients of the atoms and the activation energies for self-diffusion. And our model is based on the limiting case of the Dynamic Pair (DP) mechanism that is developed in [3-5].

2. Model

It is shown in [3-5] that starting from a certain temperature the vacancy migrating through different sublattices form a pair in which these vacancies are at the minimum possible distance from each other during the migration. And for this reason, diffusion of atoms of type A and B is realized. It is obvious that in this case long-range order in the arrangement of atoms is preserved. Taking this into account, in order to calculate the self-diffusion coefficients of atoms for the temperature interval in which the above condition is fulfilled, we simulate the migration of the di-vacancy at which the jumps of atoms to vacancies from the second coordination sphere are carried out. To emphasize this feature, **Figures 1a** and **1b** show the sequence of atomic jumps in vacancy under the traditional di-vacancy mechanism implemented in our model, which for brevity will be called the di-vacancy mechanism 2 (DM2).

The simulation is carried out by the Kinetic Monte Carlo, and in this model the main characteristic is only two jump rates of atoms of type A and B into the vacancy of the same sublattice, which are determined by the formula:

$$\Gamma_i = v_i e^{-\frac{Q_i}{kT}}, \quad i = A, B \tag{1}$$

where Γ_i are the jump rates of atoms A and B type, Q_i are the activation barriers of atom jumps in vacancy, v_i are frequency factors, k is Boltzmann constant and T is a temperature.

In simulation, we follow the traced atom of one of the sublattices in a system of a certain size (the size of the system determines the concentration of the divacancies), which moves due to migration of the divacancy in DM2 (in each experiment it was from $2 \cdot 10^5$ steps, since the jump of the traced atom is a infrequent event that happens only when the divacancy is near atom).

A trajectory and a displacement vector R (a vector connecting the initial and final points of the trajectory, see **Figure 2**) are built in each of the 10^3 experiments.
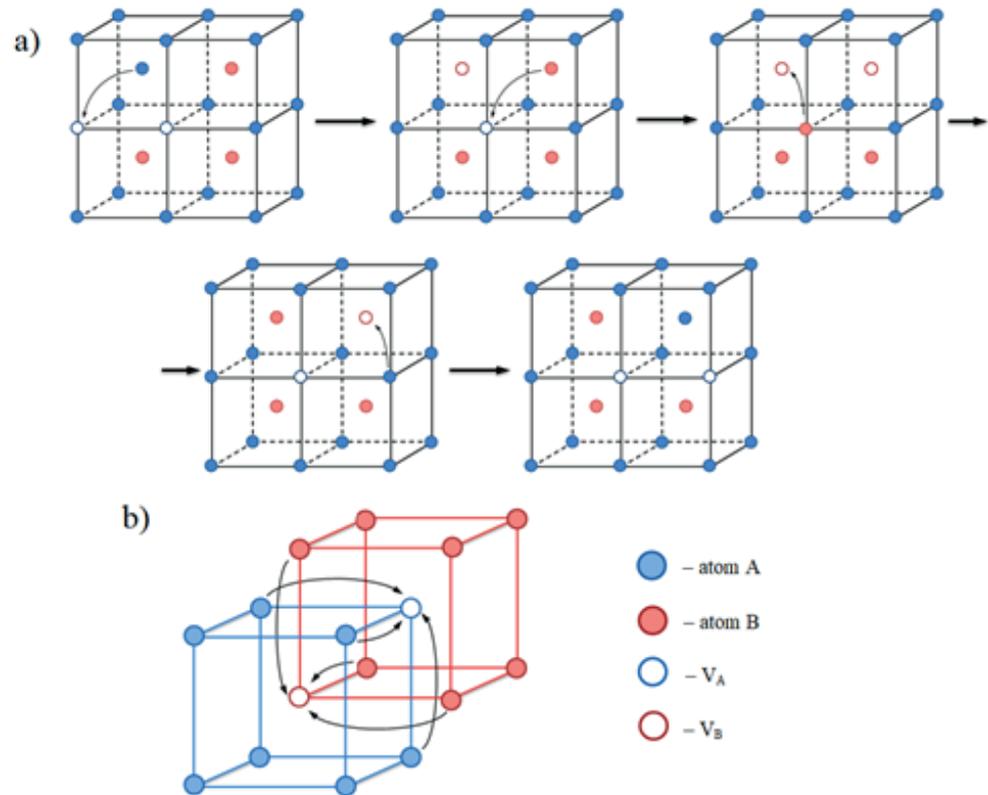
Figure 1: Sequence of atomic jumps for di-vacancy mechanisms: a - a traditional di-vacancy mechanism, b - DM2.
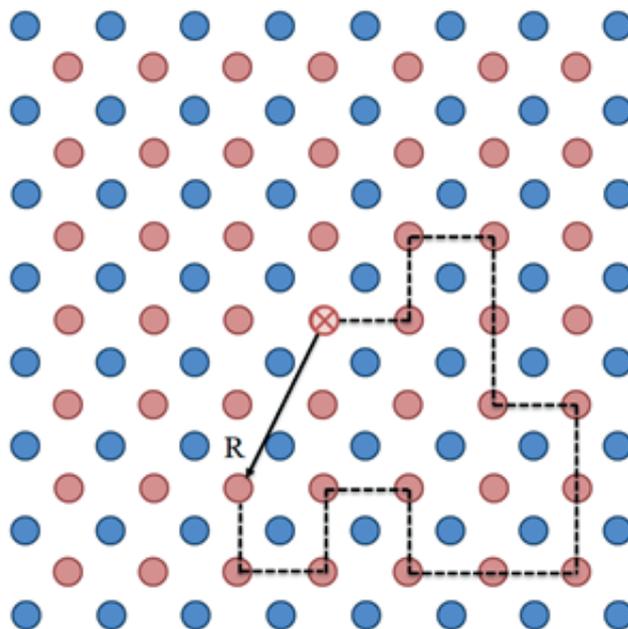

Figure 2: An example of a trajectory of a wandering of a traced atom and determination of a displacement vector.

The simulation of the walking of atoms of kind A and B is carried out separately, i.e. in some experiments, trajectories of the migration of atoms of type A are constructed,

and in others - kind B. The coefficient of self-diffusion for each of the types of atoms is determined from:

$$D_i = \frac{\langle R^2 \rangle}{2 \cdot n \cdot t} \tag{2}$$

where D is a self-diffusion coefficient, R is the displacement vector, n is a dimensionality of space, t is the time of the experiment.

The following boundary conditions for the labeled atom and di-vacancy were applied in the model. When the divacancy reaches boundary the cube of tracking (the definition is given further) along one of the directions, another divacancy appears in the random position of the opposite side. This allows us to maintain a constant concentration of divacancies in the system.

In order not to restrict the migration of the traced atom, the concept of the tracking cube proposed earlier and realized in [5, 6] is applied. If the atom reaches the inner boundary of the cube, then the cube is shifted by $\Delta x = L / 4$ so that the atom is again in the middle of the cube. (L is the length of the edge of the cube).

An illustration of this algorithm for a planar system is shown in **Figure 2**. The square moves from ABCD to A'B'C'D', and if the divacancy is in the zone AA'D'D, then it appears at a random place in the region BB'C'C.
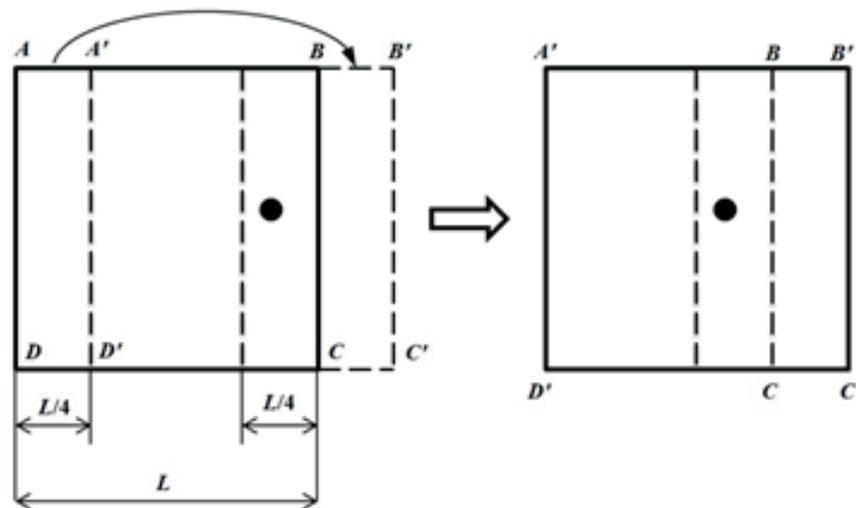

Figure 3: Schematic representation of the displacement of the tracking square when the traced atom approaches the inner boundary of the tracking square.

3. Results and discussion

When simulation of the migration of atoms, the basic activation barriers assume the values equal to 0.9 eV and 0.6 eV, after which the barrier size of the A atom was

simultaneously increase and decrease for the B type atom so that their average value is remained equal to 0.9 or 0.6 eV. The experiments are carried out for temperatures from 500 K to 1900 K (step is 50 K).

As a result of the simulation, the dependences of the self-diffusion coefficients on the temperature are obtained. The Arrhenius dependencies are plotted for the logarithm of the self-diffusion coefficient versus the reciprocal temperature (an example of such a graph is shown in **Figure 4**) and the effective energy of atom migration and the pre-exponential factors are calculated.
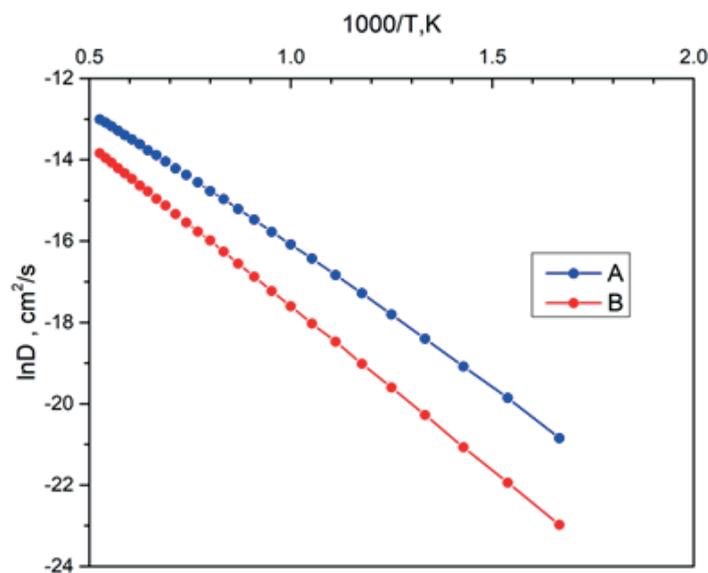

Figure 4: Arrhenius dependencies of the self-diffusion coefficients of atoms of type A and B in the case of the difference in the activation barrier values for the jumps of these atoms to vacancies 0.2 eV.

From the obtained data, effective migration energies are calculated for different barrier values and a plot of the migration energies of A and B for the difference of the activation barriers is shown in **Figure 5**. It is shown that at different activation barriers for a given mechanism of diffusion, the migration energies of atoms of both kinds are close between themselves and differ by no more than 0.1 eV, which is impossible, for example, with a single vacation mechanism in which an atom jumps to a neighboring vacancy, since under such a mechanism the effective energy of migration would coincide with the values indicated by the dashed lines, which show the values of the activation barriers.

In the next part of the work, a system is simulated, the values of the parameters being close to the intermetallide NiAl. The values of the activation barriers are taken from [4]. Since in our model a constant concentration of divacancies is maintained, on Arrhenius plots only one point corresponds to real values, since the concentration of divacancies also depends on temperature. Therefore, the values of the coefficient
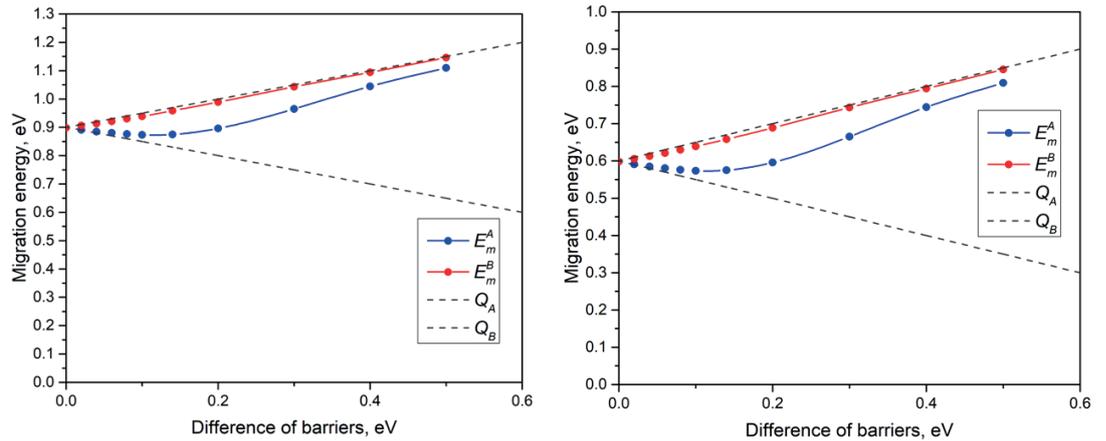
Figure 5: Dependence of the effective energy of migration of atoms of type A and B on the difference in the values of the activation barriers for the jumps of these atoms to vacancies with basic activation barriers of 0.9 and 0.6 eV.

of self-diffusion were recalculated taking into account the energy of formation of the divacancy taken from [12]. Based on the data presented in **Figure 6**, the activation energies of self-diffusion for atoms of both kinds and the pre-exponential factors are calculated.
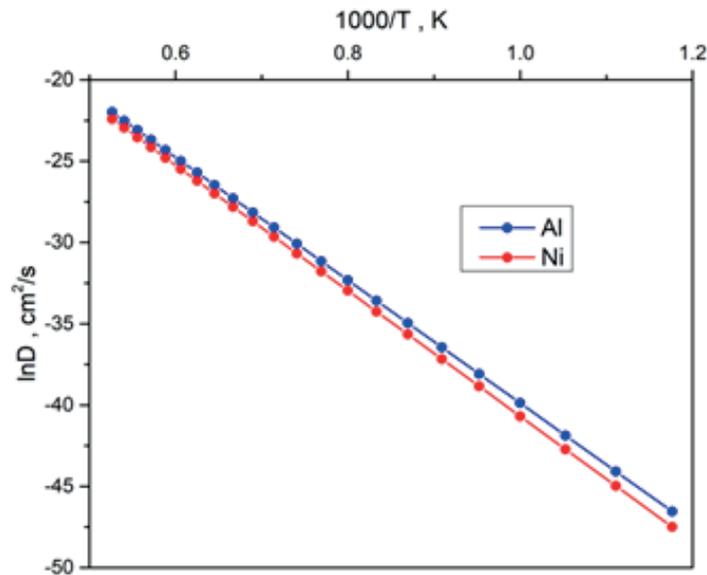

Figure 6: Arrhenius dependences of self-diffusion coefficients of atoms in a system close in parameters to NiAl.

The values of the diffusion parameters for such a system:

$$D_0^{Ni} = 0.1256 \ \frac{\text{см}^2}{c}, \quad D_0^{Al} = 0.1246 \ \frac{\text{см}^2}{c}$$

$$E_{Ni}^{SD} = 3.25 \ \text{эB}, \quad E_{Al}^{SD} = 3.32 \ \text{эB}$$

Table 1 presents experimental data on the activation energy of self-diffusion for some systems.

TABLE 1: Experimental data on activation energies of self-diffusion in systems with B2 structure [1, 9–11].

Alloy	E^{SD}, эВ	
NiAl	Ni 3.16	—
	Ni 3.01	Al 3.22
NiGa	Ni 1.79	Ga 1.52
CoGa	Co 3.12	Ga 3.12
CuZn	Cu 1.56	Zn 1.58
AuCd	Au 1.21	Cd 1.22

Analysis of this data shows that the activation energies of self-diffusion in all systems, with the exception of NiGa, are close to each other or even equal. The simulation results for the realized diffusion mechanism also confirm similar patterns (see **Figure 5**). Therefore, it can be asserted that, with a high probability, at least in a number of systems with the B2 structure, the diffusion mechanism proposed by us is realized. We also note that the activation energies of self-diffusion obtained by modeling in a system with parameters close to the NiAl intermetallide are also very close to the experimental data for this intermetallic compound.

In addition to the data mentioned, the count of the jump numbers of labeled atoms of type A and B for various barriers is made. **Figure 7** depicts the dependence of the fraction of jumps of a faster atom on temperature at different activation barriers, with an increase in the difference in barrier values.

Atoms with a smaller barrier perform a large number of jumps, but these jumps do not make a significant contribution to the displacement of the di-vacancy. At the last stages of the simulation, with the difference in the barrier values Q = 0.3 eV, the fraction of the jumps of the A-type atom reached values close to 100%.

4. Conclusion

The model of atom migration in B2 structures is developed in the realization of the di-vacancy mechanism 2. Dependences of the migration energies of atoms on the activation barrier values are determined. It is shown that at different activation barriers for the rate of atomic jumps to vacancies from the second coordination sphere and the location of vacancies at the minimum possible distance, the migration energies of atoms of both kind are close to each other and differ by no more than 0.1 eV. The
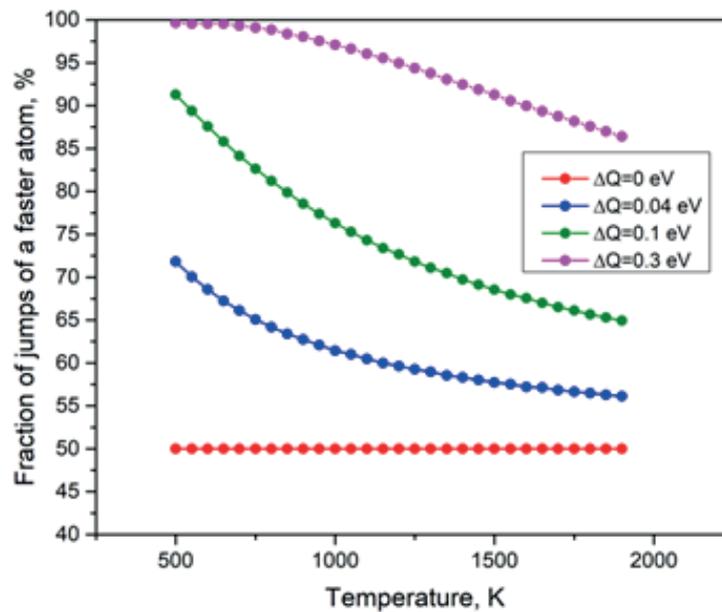
Figure 7: The fraction of jumps of a faster atom from temperature.

values of activation energies of self-diffusion and the pre-exponential factor for atoms of type A and B are obtained in a system that is close in parameters to the NiAl. The self-diffusion activation energies obtained are very close to the experimental data for the activation energy of self-diffusion of Ni and Al.

Comparison of experimental data and modeling results suggests that the di-vacancy mechanism 2 is dominant in B2 structures.

Acknowledgements

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