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RADIATION-INDUCED FORMATION OF "HEAVY" CLUSTERS IN BINARY CRYSTALS

Radiation-induced formation of defects in binary crystals with significantly different atomic masses has been studied. The classical molecular dynamics method is used for a modified model that is an alternative for that with pair collisions. A computer program realizing the Verlet algorithm in the framework of the molecular dynamics approach is developed. The results obtained testify to the existence of a certain interval of incident particle energies, at which the so-called "heavy" clusters, i.e. clusters composed of heavier atoms, can be formed.

K e y w o r d s: radiation-induced defect formation, binary crystals, molecular dynamics, computer simulation.

1. Introduction

The study of radiation-induced defects in substances at the fundamental level requires *ab initio* calculations. Therefore, the obtaining of results that can be used in practice following this way is a too complicated task, even if large computational facilities are engaged. Hence, a further search of methods for the creation of radiation-resistant materials is inevitably associated with the results of computer simulation and their comparison with experimental data [1].

Using the method of molecular dynamics (MD) simulation, we have analyzed the specific features of the defect formation that takes place owing to elastic collisions in binary crystals composed of atoms with considerably different masses, e.g., U–Al compounds. The mass of an Al atom, m_{Al}, is approximately nine times lighter than that of U, m_{U}. Therefore, this example corresponds well to the formulated problem. Radiation-stimulated processes in such materials have their own specificity, which is important to be taken into account in the case of radiation processing of materials for electronic equipment [2], under the neutron irradiation of reactor materials [3], and so forth.

An atom in the crystal lattice shifts, if it obtains an energy higher than the energy of displacement E_{d} [4]. The threshold energy of an incident particle, E_{thr}, is defined as its minimum energy that provides the transfer of the displacement energy E_{d} to the lattice atom at their elastic collision. In turn, E_{d} is the minimum energy that is required for a lattice atom to transit into an interstitial position. The threshold energy of incident particles, E_{thr}, is determined by the formula

$$E_{\mathrm{d}} = \frac{m_{\mathrm{ion}}}{M} E_{\mathrm{thr}}, \tag{1}$$

where E_{d} is the energy of an atom displacement from the site into an interstice, m_{ion} the mass of a bombarding particle, and M the mass of an atom in the crystal lattice. If we accept the average value of $E_{\mathrm{d}} \approx 25$ eV and assume that the irradiation is carried out, e.g., only with nitrogen ions (N^+), the threshold displacement energies in the case of U–Al alloy are equal to about 48 eV for the Al atom and about 425 eV for the U one. This means that only Al atoms can be displaced from their sites in the crystal lattice of U–Al alloy using N^+ ions with energies within an interval of about 48–425 eV.

This work was aimed at studying the specific features in the emergence of defects induced by radiation

in binary crystals consisting of atoms with considerably different masses and at finding the dependence of the formation probability for the so-called "heavy" clusters on the energy of bombarding particles and the ratio between the atomic masses in the binary crystal.

2. Simulation of the Process of "Heavy"-Cluster Formation in Binary Crystals

Let us begin the simulation procedure from the kinetic energy values that correspond to the threshold displacement energy of "light" atoms. In our case, these are Al atoms, so that $E_{\rm thr} \geq 48$ eV. When $E_{\rm thr}$ increases in the energy interval of about 48–425 eV, the displacements of Al atoms are observed, and, as a result, the environment of U atoms becomes disordered. We may expect that the U atoms will approach one another at that to form the so-called "heavy" clusters. The results of computer simulation confirm this assumption. The consideration of the formation of "heavy" clusters, i.e. the clusters consisting of "heavy" atoms, is important for the solution of various problems in radiation physics.

2.1. Model of radiation-induced defect formation

In the MD method, the motion of atoms in a crystal is described by the equations of motion taken from classical mechanics with a given interaction potential [5, 6]. In a system consisting of N particles, the force that acts on the i-th atom, F_i , is calculated as the vector sum of forces acting from other $N-1$ atoms. Then, the equation of motion for the i-th atom acquires the form

$$m\frac{d^2\mathbf{r}_i(t)}{dt^2} = \sum_{i\neq j}^{N-1} \mathbf{F}(r_{ij}), \tag{2}$$

where

$$\mathbf{F}(r_{ij}) = -\sum \frac{\partial U(\mathbf{r}_{ij})}{\partial x_i} \tag{3}$$

is the force acting on the i-th atom from other j atoms, m is the atomic mass, $\mathbf{r}_i(t)$ the radius vector of the i-th atom, and r_{ij} the distance between atoms i and j.

A key issue in the MD simulation is the selection of the interaction potential between atoms. Its choice depends on the origin of the examined material and the research task. The simplest case supposes a pair interaction between the particles in the crystal [7]. In this approximation, the total potential energy of a system of N particles can be written as the sum of all interaction energies U_{ij} between the i-th and j-th particles. Designating the distance between the i-th and j-th atoms as $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, we obtain

$$U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \sum_{i=1}^{N} \sum_{j=1, j>i}^{N} U_{ij}(r_{ij}). \tag{4}$$

One of the most popular potentials that are used at the MD simulation of atomic processes in crystals is the Lennard-Jones potential [8–10]

$$U(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}, \tag{5}$$

where $A = 4\varepsilon\sigma^{12}$, $B = 4\varepsilon\sigma^{6}$, r is the interatomic distance, e the potential well depth, and σ the distance, at which the interatomic potential equals zero. As a rule, this potential is used in researches, where the basic attention is focused on obtaining the qualitative results, rather than on calculating the quantitative parameters of the material.

In the case of our model lattice, the parameters of the interaction between different atoms were determined as the average values of the corresponding parameters for both potentials between the same atoms. It should be noted that the model lattice does not correspond to the real lattice of the U–Al compound, and the introduced notations are conditional:

1. First, a lattice consisting of only U atoms was simulated, and the corresponding values of potential parameters that provided the lattice stability were determined.

2. A model lattice for Al atoms was also constructed, and the corresponding potential parameters were also determined.

3. The parameters of the potential between different atoms were obtained as the average values

$$X_{ij} = \frac{X_{ii} + X_{jj}}{2}, \tag{6}$$

where X_{ij} are the parameter values for the interaction potential between the Al and U atoms, X_{ii} the parameter values for the interaction potential between

Table 1. **Parameters of model lattice potentials**

No.	A_1	B_1	A_2	B_2	A_3	B_3
1	3.7×10^{-12}	0.16×10^{-6}	2.7×10^{-12}	0.017×10^{-6}	3.2×10^{-12}	0.09×10^{-6}
2	3.5×10^{-12}	0.12×10^{-6}	2.5×10^{-12}	0.012×10^{-6}	3.0×10^{-12}	0.066×10^{-6}
3	3.1×10^{-12}	0.09×10^{-6}	2.1×10^{-12}	0.01×10^{-6}	2.6×10^{-12}	0.05×10^{-6}

Al atoms, and X_{jj} the parameter values for the interaction potential between U atoms.

It should be emphasized that the computer experiment was carried out, by using a model binary lattice, the characteristic feature of which was the large difference between the atomic masses. The influence of this lattice feature on the radiation-induced defect formation had to be studied. Therefore, when constructing the model lattice, we used the real parameters for the potentials between Al ($\sigma = 1.1646$ Å and $\varepsilon = 0.2703$ eV) and Pb ($\sigma = 1.1836$ Å and $\varepsilon = 0.2348$ eV) atoms [11]. In the paper, we consider U–Al compounds, because they are related to important reactor materials. But actually we are interested in a result that is determined by a large difference between the atomic masses.

In Table 1, the potential parameters for a model cubic lattice are presented. Here, A_1 and B_1 are the potential parameter values for the model lattice with light (Al) atoms, A_2 and B_2 the corresponding parameter values for the model lattice with heavy (U) atoms, and A_3 and B_3 are the potential parameters for different atoms. The rows in Table 1 correspond to the variations of potential parameters, which were carried out in order to test their influence on the results obtained.

A computer program was developed to simulate the process of radiation-induced defect formation in binary crystals. It is based on the MD method and uses the Verlet algorithm [12]. According to the latter, the locations of the particles and their velocities at each time step were determined from the equations

$$\mathbf{r}_i^n = \mathbf{r}_i^{n-1} + \Delta t \mathbf{v}_i^{n-1} + \frac{(\Delta t)^2}{2m}\mathbf{F}_i^{n-1}, \qquad \mathbf{v}_i^n = \mathbf{v}_i^{n-1} + \frac{\Delta t}{2m}(\mathbf{F}_i^n + \mathbf{F}_i^{n-1}), \tag{7}$$

$$\mathbf{F}_i^n = -\sum_{j,j\neq i}^{N} \frac{\partial U_{ij}^n}{\partial x_i}, \tag{8}$$

where i is the particle number ($i = 1, ..., N$), n the number of an integration step, Δt the magnitude of an integration step, and $\mathbf{F}_i^n$ the force acting on the i-th atom from other j atoms. The computer program was written in the C# language under the .NET Framework [13, 14], by using the capabilities of the powerful Unity 3D graphic engine [15]. The program has a graphic interface, which displays the dynamics of atoms, additional windows with the program parameters, and information about the chosen atoms. The program has two basic classes. One of them realizes the calculation of the atomic dynamics, by using the Verlet algorithm. The other is responsible for extracting results in the real-time mode.

The radiation-induced defect formation was simulated in three stages [16].

1. Initialization of the model system. The atoms are located at the sites of a model cubic lattice. The choice of the model lattice type should not affect the qualitative results in our case. The boundary conditions are given in terms of quasielastic forces. The model lattice contains 1000 atoms.

2. Relaxation of the model lattice to an equilibrium state. The latter is reached by integrating the differential equations, by following the Verlet algorithm. The model lattice temperature is introduced in the framework of the standard MD approach [17].

3. Research of the radiation-induced defect formation.

Unlike calculations, in which elastic collisions between the incident particles and the lattice atoms are simulated, e.g., using the Born–Mayer potential [18–20], our model includes the so-called random external forces, F_R. The latter simulate impacts of the atoms in the model lattice with a certain frequency by external particles with a certain kinetic energy.

As was mentioned above, the external force F_R was introduced to simulate the action of an incident particle on an atom in the model lattice. This force corresponds to the transfer of a certain piece of the kinetic energy to the atom. The formula

$$\frac{(F_R t)^2}{2M} = 25 \text{ eV}, \tag{9}$$

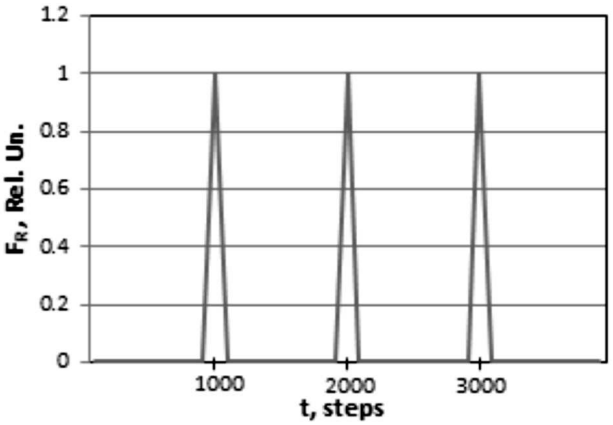

Fig. 1. Illustration of the external force F_R acting with an average frequency determined by the average interval between the peaks. The pulse duration does not correspond to the scale of Fig. 1 and is equal to 5–10 steps

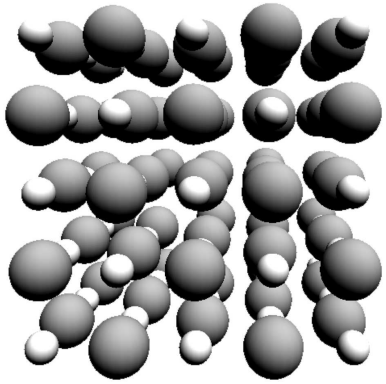

Fig. 2. Fragment of a model lattice composed of atoms of two types with different masses

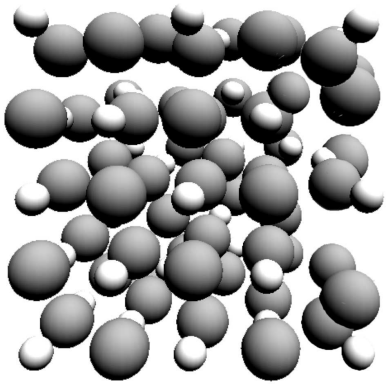

Fig. 3. Fragment of the model lattice with "heavy" clusters (in particular, in the upper right and lower right corners)

where t is the pulse duration, and M the mass of model particle, was used for the quantity F_R in the computer experiment corresponding to a certain energy. In so doing, we assumed that the average displacement energy was equal to $E_{\rm d} = 25$ eV. During the computer experiment, the magnitude of F_R was gradually increased until the atoms started to irreversibly quit their sites. Of course, this value of F_R corresponded to an energy of 25 eV. The quantities t (see Fig. 1) and M were also known. Hence, with the help of formula (9), a relation between the kinetic energy transferred to the atom and the quantity F_R was established. In particular, in Figs. 5 and 6 (see below), the corresponding values of energy are related to F_R by this expression.

The action of the force F_R upon atoms is governed by a stochastic function, which determines the corresponding average frequency of impacts (Fig. 1) and the distribution of impact directions. In the standard platform .NET Framework, random numbers are produced by an additive generator of random numbers [21]. This generator forms a random number according to the formula

$$x_{n+1} = (x_n + x_{n-k}) \bmod l, \tag{10}$$

where the order k and the modulus l are fixed positive integers, and $x_1, ..., x_n$ are arbitrary numbers. Every $(n+1)$-th term of the sequence depends on the previous n-th one.

With regard for the external force F_R and expression (8), the total force acting on the i-th atom can be presented in the form [22]

$$\mathbf{F}_i^n = -\sum_{j,j\neq i}^{N} \frac{\partial U_{ij}^n}{\partial x_i} + F_R. \tag{11}$$

In Fig. 2, a fragment of the model lattice consisting of 125 atoms is shown. Figure 3 demonstrates the effect of "heavy" cluster formation in it.

2.2. Results and their discussion

"Heavy" clusters emerge as a result of the disordering in the initial lattice under the influence of fast ions. The interatomic distances in the initial model lattice have definite values: $a = 5.3$ Å between the atoms with different masses and $2a = 10.6$ Å between the atoms with identical masses. As was indicated above, the bombarding is carried out using ions with energies at which only "light" atoms can

be displaced. The computer program determines the coordinates of all atoms and the distances between the nearest atoms, Δx, at any time moment in the course of model lattice bombardment. A criterion of the cluster creation is the emergence of a configuration of atoms with identical masses, in which the distance Δx is equal to a. The computer experiment made it possible to reveal the accumulation kinetics for "heavy" clusters with 2, 3, and larger numbers of atoms (see Fig. 4). Region I in Fig. 4 corresponds to the transformation of two-atom "heavy" clusters into three-atom ones.

The dependence of τ_i on the ratio between the atomic masses in the crystal, $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$, for various irradiation energies is shown in Fig. 5. Certainly, the value of τ_i is reciprocal to the formation probability for a certain "heavy" cluster. Model computer experiments with atomic mass values quoted in Table 2 were performed. Sources of monoenergetic ions were supposed to be used. The energies of ions bombarding the crystal were chosen to fall within the intervals corresponding to the displacement of only lighter atoms. Namely,

1) for the mass ratio $m_{\mathrm{Al}}/m_{\mathrm{U}_1}$, the selected energies amounted to 70, 85, 107, 150, 205, 300, 350, and 425 eV;

2) for the mass ratio $m_{\mathrm{Al}}/m_{\mathrm{U}_2}$, the selected energies amounted to 70, 85, 107, 150, and 205 eV; and

3) for the mass ratio $m_{\mathrm{Al}}/m_{\mathrm{U}_3}$, the selected energies amounted to 70, 85, and 107 eV.

Underlined are the threshold energies of bombarding ions for three mass ratios, which are quoted in Table 2.

In Fig. 6, the energy dependences of τ_i are depicted for various mass ratios $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$.

The results, which are illustrated in Figs. 5 and 6, point to certain features in the formation of "heavy" clusters, which depend on the mass ratio of atoms in the binary lattice and the ion beam energy. It is natural that the interval of energies, in which "heavy" clusters can be formed, becomes narrower for smaller ra-

Table 2. **Masses of atoms in the model lattices examined in the computer experiment and the corresponding threshold energies of bombarding ions, E_{thr}**

No.	m_{Al}, a.m.u.	m_{U_i}, a.m.u.	E_{thr} for Al atoms, eV	E_{thr} for U_i atoms, eV
1	27	238	48	425
2	27	115	48	205
3	27	60	48	107

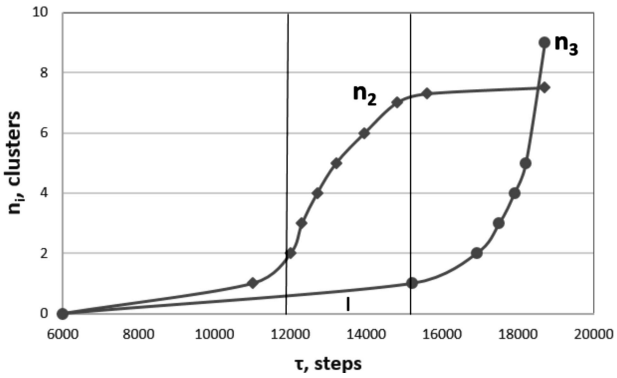

Fig. 4. Accumulation kinetics for "heavy" clusters with 2 and 3 atoms

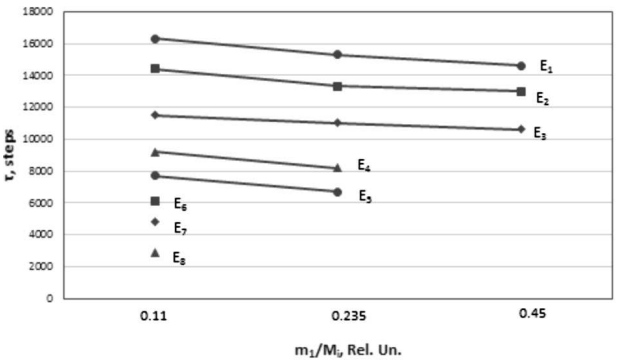

Fig. 5. Dependences of τ on the mass ratio $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$ for atoms in the crystal for various energies of bombarding ions: $E_1 = 70$ eV, $E_2 = 85$ eV, $E_3 = 107$ eV, $E_4 = 150$ eV, $E_5 = 205$ eV, $E_6 = 300$ eV, $E_7 = 350$ eV, and $E_8 = 425$ eV

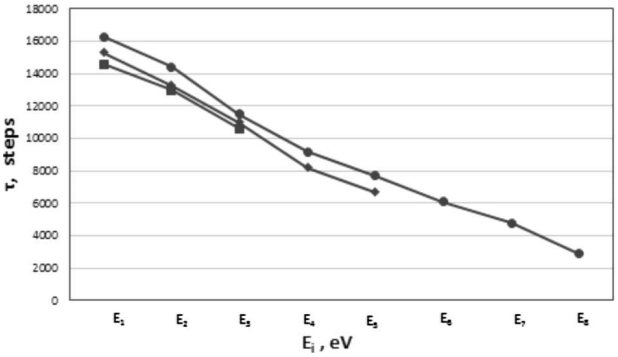

Fig. 6. Energy dependence of τ_i for various atomic mass ratios $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$ (see Fig. 5)

tios $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$. From Fig. 5, one can see that "heavy" clusters are not formed at $E > E_5$. The simulation results showed that in case where the "heavy" atoms undergo a substantial displacement simultaneously with the "light" ones, the formation probability for "heavy" clusters drastically decreases. In Fig. 6, one can see a symbatic energy dependence of the formation probability for "heavy" clusters in the energy intervals that correspond to certain mass ratios $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$. It is remarkable that the probabilities of "heavy" cluster formation at $E = E_3$ differ insignificantly for all examined $m_{\mathrm{Al}}/m_{\mathrm{U}_i}$ ratios.

3. Conclusions

The processes of radiation-induced defect formation in binary crystals with a considerable difference between the atomic masses have been studied. A modified model is applied to research the formation of radiation-induced damages in the crystals using the MD method, and a corresponding computer program is developed. It is found that the so-called "heavy" clusters are formed in binary crystals with substantially different atomic masses of their components, which are subjected to the ionic irradiation. The probability of "heavy" cluster formation is found to depend on the atomic mass ratio between different atoms and the ionic radiation energy; the corresponding energy dependences are determined. It is important to consider the phenomenon of radiation-induced formation of "heavy" clusters, when using radiation methods in electronics, as well as when solving other technical problems.

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РАДІАЦІЙНО-СТИМУЛЬОВАНЕ ФОРМУВАННЯ "ВАЖКИХ КЛАСТЕРІВ" В БІНАРНИХ КРИСТАЛАХ

Р е з ю м е

Робота присвячена дослідженню особливостей радіаційного дефектоутворення в бінарних кристалах, що складаються з атомів з масами, які значно розрізняються. Використовувався класичний метод молекулярної динаміки, але в модифікованій моделі, яка є альтернативою моделі парних зіткнень. Розроблена комп'ютерна програма, яка реалізує молекулярно-динамічний підхід з алгоритмом Верле. Результати роботи свідчать про те, що існує певний інтервал енергій інцидентних частинок, в якому можливе формування так званих "важких" кластерів, тобто кластерів, які складаються з більш важких атомів.