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Atomic Structure in the Vicinity of Nanovoids and Features of These Defects

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Many properties of metals are determined by the defects, such as point defects, their complexes and nanovoids, whereas properties of these defects are generally related to the changes in atomic structure in the vicinity of these defects. In this work, recently developed approach is applied to simulate vacancy complexes and nanovoids. A developed model on the basis of Molecular Statics is used to investigate the atomic structure peculiarities in the vicinity of vacancy complexes and nanovoids, and the atomic displacements in the elastic medium surrounding the computational cell are determined in a self-consistent manner. The second part of the work is concerned with the study of atomic structure changes under temperature increasing within the new model based on Molecular Dynamics. Within the scope of this model, coordinates of the atoms in the area nearby of vacancy complex or nanovoid surface are averaged, during a simulation. Obtained mean positions of atoms are used for calculation of averaged interatomic distances; that allows determining lattice-parameter temperature dependence and then temperature-determined changes of atomic structure in the defects' vicinity. Simulation is performed for various f.c.c. and b.c.c. metals. For these metals, thermal expansion data are obtained, and the change of atomic structure in the defects' vicinity is determined from temperature increase.

Багато властивостей металів визначаються дефектами, їхніми комплексами і нанопорами, тоді як властивості цих дефектів, взагалі кажучи, пов'язані зі змінами атомної структури поблизу цих дефектів. У даній роботі нещодавно запропонований підхід застосовується для симуляції вакансійних комплексів та нанопор. Нещодавно запропонована модель на основі методи молекулярної статики використовується для дослідження особливостей атомної структури в околі вакансійних комплексів і нано-

пор, а також уможливлює самоузгодженим чином знайти атомні зміщення у пружньому середовищі, яке оточує розрахункову комірку. Другу частину роботи присвячено вивченню змін атомної структури зі зростанням температури, шляхом застосування нової моделі, яка ґрунтується вже на молекулярній динаміці. В рамках даної моделі координати атомів поблизу вакансійних комплексів або поверхні нанопор усереднюються в процесі симуляції. Одержані середні положення атомів використовуються для розрахунку усереднених міжатомних відстаней, що уможливлює спочатку одержати температурну залежність параметра ґратниці, а потім обумовлені температурою зміни атомної структури в околі дефектів. Моделювання проводилося для різних ГЦК- та ОЦК-металів. Для цих металів одержано дані для теплового розширення, а також визначено зміну атомної структури в околі дефектів при зростанні температури.

Многие свойства металлов определяются дефектами, их комплексами и нанопорами, тогда как свойства этих дефектов, вообще говоря, связаны с изменениями атомной структуры вблизи этих дефектов. В данной работе недавно предложенный подход применяется для симуляции вакансионных комплексов и нанопор. Недавно предложенная модель на основе метода молекулярной статики используется для исследования особенностей атомной структуры в окрестности вакансионных комплексов и нанопор, а также позволяет самосогласованным образом найти атомные смещения в упругой среде, окружающей расчётную ячейку. Вторая часть работы посвящена изучению изменений атомной структуры с ростом температуры путём применения новой модели, основанной уже на молекулярной динамике. В рамках данной модели координаты атомов вблизи вакансионных комплексов или поверхности нанопор усредняются в процессе симуляции. Полученные средние положения атомов используются для расчёта усреднённых межатомных расстояний, что позволяет сначала получить температурную зависимость параметра решётки, а затем обусловленные температурой изменения атомной структуры в окрестности дефектов. Моделирование проводилось для различных ГЦК- и ОЦК-металлов. Для этих металлов получены данные для теплового расширения, а также определено изменение атомной структуры в окрестности дефектов при росте температуры.

Key words: point defects, vacancy complexes, nanovoids, b.c.c. metals, f.c.c. metals, Molecular Statics, Molecular Dynamics, simulation.

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1. INTRODUCTION

A considerable amount of micro- and nanovoids is generated in systems under extreme conditions such as irradiation. The defects play a significant role in the processes of material structure forming, diffusion phase transformations, swelling, *etc*. Therefore, it is necessary to develop the methods of determining the defects characteristics. It is ob-

vious that defect characteristics are determined by the atomic structure. Atoms surrounding defect shift from the sites of ideal lattice, *e.g.* defect atomic structure changes with respect to an ideal one; that, in turn, leads to changes in interaction energy of neighbour atoms and results in modification of defect energy characteristics and other features. In general, displacement fields in the vicinity of voids and nanovoids were determined by the solution of equations from the classical theory of elasticity. However, the validity of the theory of elasticity in the case of nanovoids appears to be doubtful as for this kind of defects, as well as for point defects, the usual usability condition does not meet the conditions of the above-mentioned theory $R >> a$, where R is the nanovoid radius and a is the lattice parameter. In other words, a description of displacement fields near the nanovoids in the framework of the theory of elasticity appears to be problematic, as it does not take into account the discrete atomic structure of materials.

For the better understanding of the arising problem, let us look at the results of the works that dealt with the determination of the displacement fields near point defects. In the work of Dederichs and Pollmann [1], the general equations for the displacement field of point defects in cubic crystals are given and some exact results are presented on the basis of anisotropic elasticity theory. One from these exact results, which concerns the displacement field of point defects in cubic crystals in the direction (100), coincides with one for the cubic axes:

$$S_1(100) = \frac{P}{4\pi r^2}\frac{1}{c_{11}+c_{12}}\left(\frac{d}{c_{44}} + 2\frac{(c_{11}-c_{12})(c_{12}+c_{44})}{c_{11}c_{44}(c_{11}-c_{12})(c_{11}+c_{12}+2c_{44})}\right), \qquad (1)$$

where c_{ij} are the elastic constants, $d = c_{11} - c_{12} - 2c_{44}$, P is the spur of the dipole forces tensor P_{ij}.

In another work [2], the atomic structure in the vicinity of monovacancy is determined, using the model [3, 4], which takes into account the atomic displacements in the elastic continuum surrounding the computational cell.

In Figure 1, the simulation results for displacements of atoms in the vicinity of vacancy in the directions (100), (110), (111) are presented. In this figure, the values for displacements in the direction (100) are shown as a dashed line, another curve shows the displacements being calculated by Eq. (1), given in article [1] by Dederichs.

From Figure 1, it can be seen, that the magnitudes of atomic displacements, obtained by Molecular Statics (MS), differ significantly from the predictions of the anisotropic theory of elasticity. It should be emphasized that the displacement fields in the vicinity of vacancy obtained from the computer simulation take into account anisotropy of media as well as its discreteness, and these results lead us to the conclusion that the discreteness factor for this problem is more vital than the influence of anisotropy.

The main aim of displacement field investigation in the vicinity of

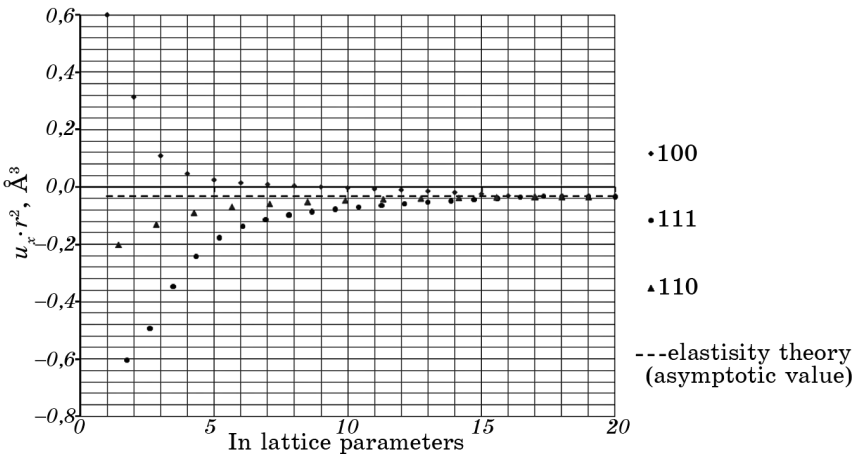

Fig. 1. The displacement field for the vacancy in case of the simulation data for the directions (markers) and calculated from the Eq. (1).

nanovoids is related to the evaluation of displacement field influence on the void growth rate (the kinetic equations for the growth rate of the voids in cubic metals are obtained, taking into consideration the elastic strains arising from voids in [5], based on the general equations for the vacancy fluxes under strain obtained in [6]), and, therefore, there is a vital necessity to know displacements at the surface and within the thin surface layer. That is why the information about displacement fields, which can be obtained with the help of anisotropic elasticity theory, does not allow to solve the specified problem.

In our recent works [2–4], a new approach was developed. In particular, in this approach an iterative procedure is used, in which the atomic structure in the vicinity of point defect and C_1 constant, determining the displacement of atoms embedded into an elastic continuum, are obtained in a self-consistent manner. The vacancy features (including formation volumes and migration volumes) obtained for a number of cubic metals agree well with experimental values [2]. In this work, we use our approach for direct investigation of the atomic structure in the vicinity of vacancy complexes and nanovoids. Molecular Dynamics is used in the second part to investigate the changes of atomic structure with the temperature increase. Thus, the obtained atoms positions give us the possibility to determine these defects characteristics and to perform more advanced level simulation of nanovoid growth in materials, supersaturated with vacancies, in particular under irradiation.

2. SIMULATION OF MOLECULAR STATICS OF ATOMIC STRUCTURE

The equilibrium positions of atoms in the computational cell are simulated using a variational procedure, which is usually employed in the

molecular statics method [2, 3].

The computational cell (zone I, Fig. 2) is a sphere containing more than 60000 atoms. It is surrounded by atoms embedded into an elastic medium (zone II, Fig. 2). The displacements **u** of these atoms, connected with the disturbances caused by a pore, are found on the basis of the first term of the static isotropic elastic equation solution [2–4]:

$$\mathbf{u} = C_1 \mathbf{r}/r^3. \tag{2}$$

In this model, a self-consistent iterative procedure is introduced to calculate the C_1 constant as well as the atomic structure simulation in the crystal with a defect. The constant C_1 is calculated according to Eq. (2) using the results of atomic displacements simulation in the computational cell for the atoms in the coordination shells that are located in a spherical layer III. The constant C_1 calculated at the previous step of the iterative procedure is used to determine atomic displacements of the elastic medium II. Then, the relaxation of the atoms of zone I is carried out anew, and the constant C_1 is calculated again.

Thus, obtained atomic structure in the vicinity of pores is compared with the displacement field from the solution of equations from the theory of elasticity. According to classical theory of elasticity, displacements fields in a spherical layer G in region near void of radius R [7]:

$$\begin{gathered} u_x = C_0 x + C_1 \frac{x}{r^3}, \; u_y = C_0 y + C_1 \frac{y}{r^3}, \\ C_0 = \frac{1-2\nu}{E} \frac{(p - 2\gamma/R)R^3}{R_G^3 - R^3}, \; C_1 = \frac{1+\nu}{2E} \frac{(p - 2\gamma/R)R^3 R_G^3}{R_G^3 - R^3}, \end{gathered} \tag{3}$$

where ν is the Poisson ratio, E is the Young modulus, γ is the specific surface energy, p is the internal pressure, R_G is the radius of the sphere

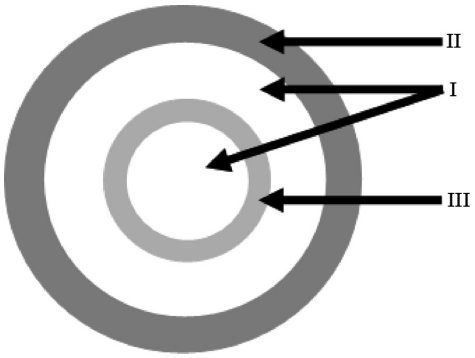

Fig. 2. Scheme of computational cell: I—directly computational cell, II—atoms embedded in an elastic continuum, III—atoms for C_1 calculation.

which volume equals to the average volume per void. In our calculations, only one void is taken into account and C_0 equals to zero.

3. RESULTS OF MS SIMULATION

The simulation is done for vacancy complex of 15 vacancies (we may consider it as nanovoid of $r = 5.72$ Å) and for nanovoid of size $r = 8.08$ Å that has atoms of up to 2 and 10 coordination shells deleted. The pairwise potential for b.c.c. iron is used [8].

The results for displacement fields u_x at $z = 0$ obtained using MS simulation and equations from the theory of elasticity (Eq. (3)) for two pores are presented in Fig. 3 and Fig. 4. From the symmetry considerations, it is clear that the displacement fields obtained for u_y are similar to u_x and differ just by a 90 degrees rotation over z-axis. Predicted by the MS simulation, displacement fields as a function of coordinates in the vicinity of nanovoids have functionally complex non-monotonic character, unlike the results from the theory of elasticity. Their shapes are more complicated, include several differently localized maximums and minimums, absolute value of which is larger in comparison with the results, given by equations from the classical theory of elasticity. These peculiarities of displacement fields should be taken into consideration, when simulating void growth rate takes into account elastic fields, generated by nanovoids.

From elastic theory, it is known that volume change connected with lattice relaxation during defect formation linearly depends on C_1 constant [2, 3]:

$$\Delta V = 4\pi C_1. \tag{4}$$

It should be emphasized that the results of self-consistent calculation

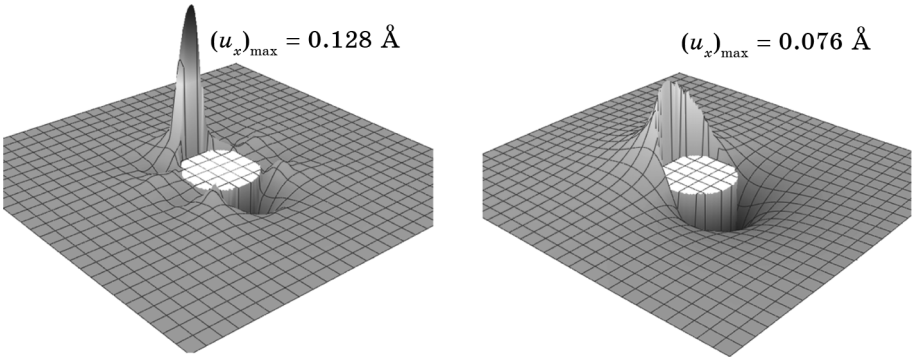

Fig. 3. The displacement field for the vacancy complex of 15 vacancies (nanovoid with radius $r = 2a = 5.72$ Å) as obtained, using MS simulation (left) and using equation from the theory of elasticity (right).

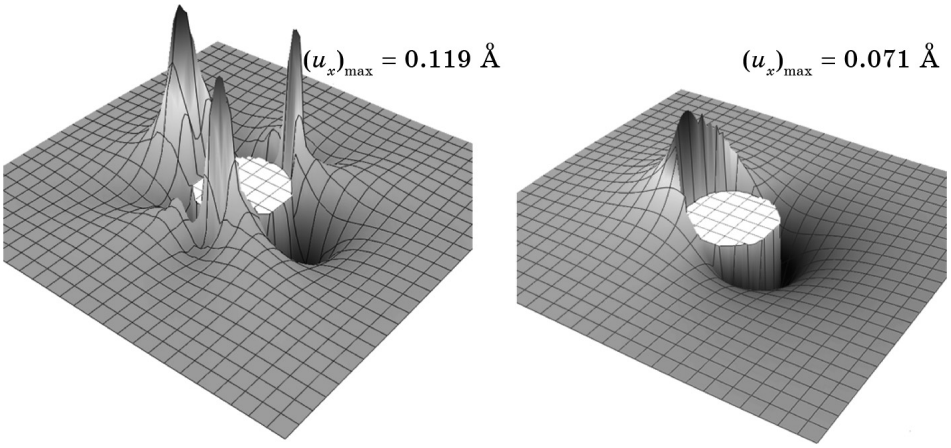

Fig. 4. The displacement field for the nanovoid with radius $r = (3^{3/2}/2)a$ = = 7.43 Å as obtained, using MS simulation (left) and using equation from the theory of elasticity (right).

for atomic structure in the vicinity of vacancy complexes and nanovoids point out a non-monotonic character of size dependence of the relaxation volume, unlike the results from the theory of elasticity (Eq. (3)).

3.1. Molecular Dynamics Simulation of Thermal Expansion and Atomic Structure in the Vicinity of Vacancies, Vacancy Complexes, and Nanovoids

Some time ago, we suggested a new model to simulate atomic structure changes caused by temperature [12, 13]. At first, we describe main features of the model in a short paragraph, and then simulation results concerned with a thermal expansion of some metals and an atomic structure in the vicinity of vacancies at finite temperatures are presented to illustrate abilities of our model. Last, results of simulation for vacancy complexes and nanovoids are presented.

3.2. Model for Atomic Structure Simulation at Finite Temperature

Atomic structure of defectless crystal is studied by Molecular Dynamics (MD) using velocity Verlet algorithm. The computational cell has free-boundary conditions and a spherical shape and contains up to 50000 atoms. Coordinates of the central atom and its neighbours inside the nearest shells are averaged during a simulation run that lasts for large number of vibrations of the atom on the lattice site (up to 1000 vibration periods) (Fig. 5).

This procedure of getting interatomic distances from averaged posi-

tions of atom in the centre of MD cell is applied to lattice of defectless crystal. Using interatomic distances and geometry of f.c.c. and b.c.c. structures, we directly get lattice parameter. Thus, lattice parameter is determined in the nearly the same way as it is done in X-Ray measurements: in experiment, lattice parameter is obtained directly from such structure characteristics as interplanar spacing, whereas in our simulation lattice parameter is directly obtained from interatomic positions. Repeating this simulation at different increasing temperatures, we get the temperature dependence of the lattice parameter. These thermal expansion curves for f.c.c. and b.c.c. metals are shown on Fig. 6 (for iron in the range from 1185 K to 1667 K the data are shown for metastable b.c.c. lattice).

The simulation data show good agreement with the results of experiments (X-ray lattice parameter determination) [14]. As our model gives reliable results concerning changes of interatomic distances and lattice parameters with temperature in defectless lattice, *i.e.* describes temperature changes in distances between atoms, therefore, this model is expected to describe the changes of atomic structure in the presence of defects.

3.2.1. Atomic Structure in the Vicinity of Vacancies at Finite Temperatures

Further, the method of getting lattice parameter via obtained interatomic distances from mean positions of atoms is applied for vacancies. In this case, the atom in centre of computational cell is deleted and distances between atoms in the nearest neighbour shells to the defect are calculated (Fig. 5).

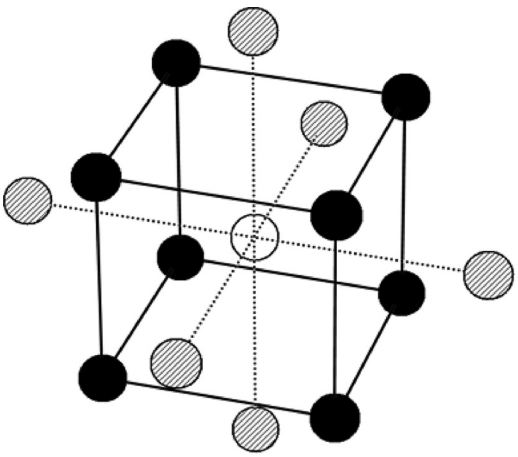

Fig. 5. B.c.c. structure with atoms of two nearest-neighbour shells: hollow—atom in the centre of computational cell (site of the deleted atom in case of vacancy), filled—nearest-neighbour atoms, striped—next-nearest neighbour atoms.

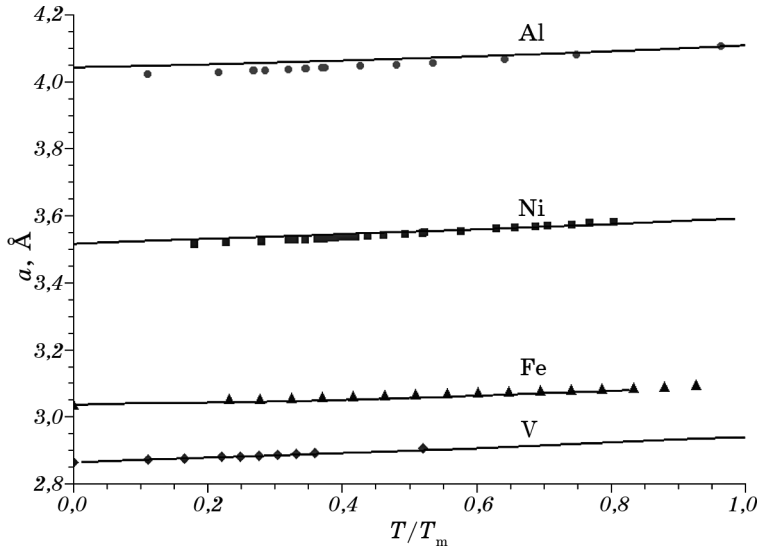

Fig. 6. Thermal expansion of b.c.c and f.c.c. metals: Fe (potential [9]), V (potential [10]), Al, Ni (potentials [11, 12]).

Using the results for perfect crystal and for crystal with vacancy, we get the temperature dependence of the ratio of distances for some nearest shells in the system with vacancy to lattice parameter obtained in perfect lattice (Fig. 7).

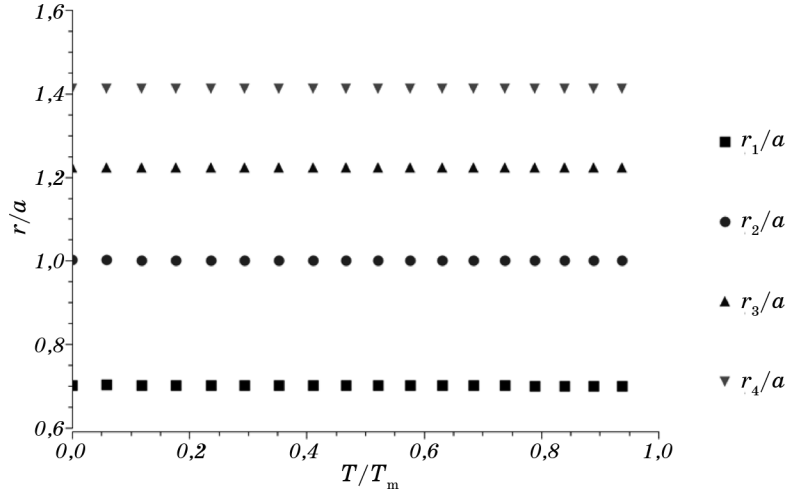

Fig. 7. Temperature dependence of ratio of distances between the centre of empty site (vacancy) and atoms in its nearest shells to lattice parameter for f.c.c. Ni (potential [11]).

We obtain a rather not obvious result that, for the whole temperature range beginning with fifth nearest shells, the ratio under study remains constant with temperature (see Fig. 7).

Our simulation is performed for the shells nearest to the vacancy. Because quantity of atomic displacements decreases significantly with the distance from vacant site increasing in comparison with the nearest shells, it should be expected that for shells having larger radius the ratio of these shells radius to the lattice parameter conserves as well. Then, we may conclude that geometrical similarity of atomic structure in the vicinity of vacancies beginning with fifth nearest shells preserves as the temperature increases. Whence an interesting and vital effect follows: ground state atomic structure from the Molecular Statics and thermal expansion data both give the possibility to calculate the atomic structure in the vicinity of vacancy for any temperature and, consequently, to calculate the temperature dependence of vacancy formation characteristics such as relaxation volumes and formation volumes [13].

3.2.2. Results of Simulation for Vacancy Complexes and Nanovoids

The same procedure is applied for vacancy complexes and nanovoids. Similarly to the case of vacancy, the atoms in the centre of the computational cell are deleted to create a vacancy complex or a nanovoid. From average atomic positions (Fig. 8), we calculate interatomic dis-

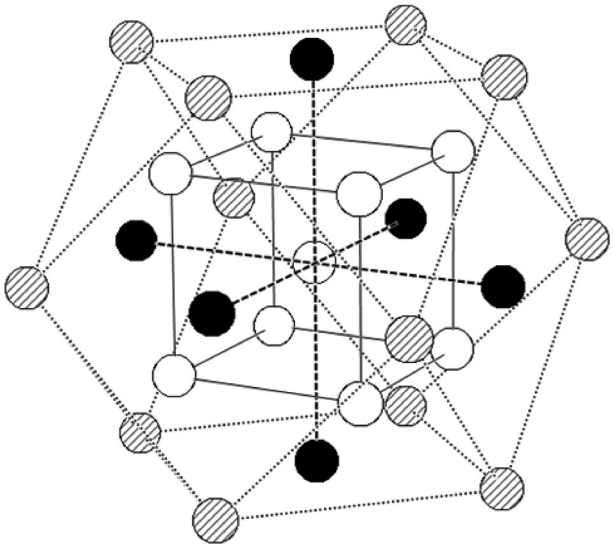

Fig. 8. Void representation: hollow—sites of deleted atoms, filled—nearest-neighbour atoms, and striped—next-nearest neighbour atoms.

tances in the nearest shell to the void border.

The simulation is done for vacancy complexes and nanovoids of the same size as in MS simulation. The results of simulation for nanovoids are shown in Fig. 9.

The ratio of distances between nearest neighbour atoms and centre of defect to lattice parameter beginning with fifth nearest shells remains constant. As a result, we can state that in the case of vacancy complexes as well as in the case of nanovoids the same regularities that were held true for vacancies are satisfied. This fact and its very significant conclusions should be further investigated concerning the studies of void growth in the presence of elastic fields.

Then, it is shown that the ratio of relaxation volume to the atomic volume (or in the units of atomic volume Ω) remains constant as the

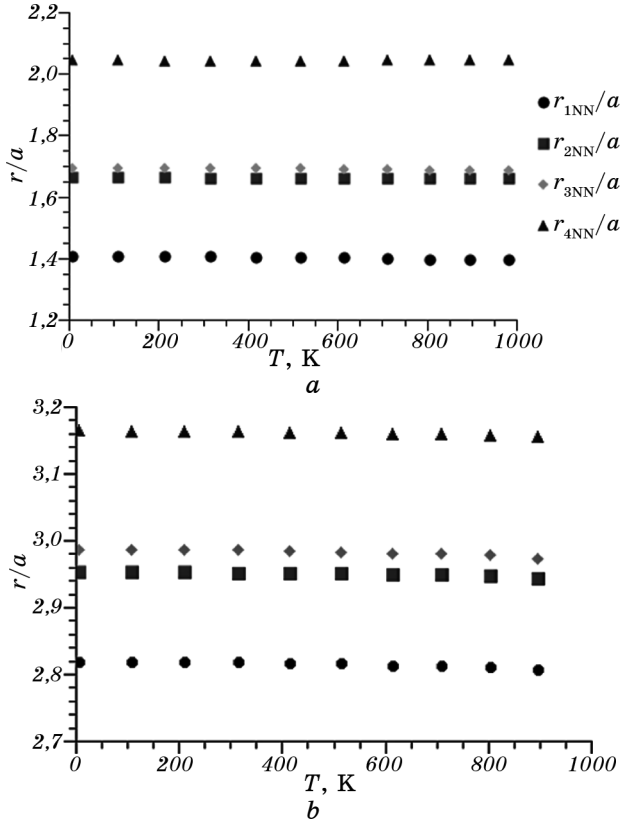

Fig. 9. Temperature dependence of ratio of distances between defect centre and atoms in its nearest shells to lattice parameter for b.c.c. Fe [8]: vacancy complex of 15 vacancies ($r_{void} = 2a$) (*a*); nanovoid of radius 7.43 Å ($r_{void} = (3^{3/2}/2)a$) (*b*).

temperature changes. Therefore, the C_1 value is temperature dependent:

$$C_1(T) = u(T)r^2(T) = [u(0)(1 + \alpha T)][r(0)(1 + \alpha T)]^2 = u(0)r^2(0)(1 + \alpha T)^3 \quad (5)$$

and

$$C_1(T) = C_1(0)(1 + \alpha T)^3.$$

Therefore, all the quantities entering in the definition of C_1 may also depend on temperature.

4. CONCLUSION

A model based on Molecular Dynamics and Molecular Statics is introduced which allows to determine atomic structure in the vicinity of aggregate defects, such as vacancy complexes and nanovoids. More thorough investigation of atomic structure using Molecular Statics permits to find qualitatively new peculiarities in displacement fields from nanovoids that cannot be correctly obtained with the use of equations from the theory of elasticity, because they cannot be applied to the atomic scale. The fields of displacements in the vicinity of nanovoids are significantly more complicated and with much bigger magnitudes of displacements than in the vicinity of vacancies. The displacement fields from our calculations should be taken into account in void growth simulations with the effects of elastic fields, generated by nanovoids.

The results concerning geometrical similarity preservation of the atomic structure beginning with the fifth nearest shells in the vicinity of vacancy during the temperature changes in metals are shown to be correct in the case of nanovoids as well. As the surface curvature for voids of larger radius will decrease, we may suggest that the preservation of geometrical similarity in atomic structure will hold true.

REFERENCES

1. P. H. Dederichs and J. Pollmann, *Z. Phys.*, **255**, No. 4: 315 (1972).
2. I. V. Valikova and A. V. Nazarov, *Phys. Met. Metallogr.*, **109**, No. 3: 220 (2010).
3. I. Valikova and A. Nazarov, *Defect Diffus. Forum*, **277**: 125 (2008).
4. I. V. Valikova and A. V. Nazarov, *Phys. Met. Metallogr.*, **105**: 544 (2008).
5. A. Nazarov, A. Mikheev, I. Valikova, and A. Zaluzhnyi, *Solid State Phenom.*, **172–174**: 1156 (2011).
6. A. V. Nazarov and A. A. Mikheev, *J. Phys.: Condens. Matter*, **20**: 485203 (2008).
7. L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Oxford: Elsevier: 1986).
8. R. A. Johnson, *Phys. Rev.*, **134**, No. 5A: 1329 (1964).
9. M. I. Mendelev, S. Han, D. J. Srolovitz et al., *Philos. Mag.*, **83**: 3977 (2003).
10. P. M. Derlet, D. Nguyen-Manh, and S. L. Dudarev, *Phys. Rev. B*, **76**: 054107 (2007).

11. Y. Mishin, D. Farkas, M. J. Mehl, and D. A. Papaconstantopoulos, *Phys. Rev. B*, **59**: 3393 (1999).
12. E. Reshetnikova, A. Germanov, I. Valikova, and A. Nazarov, *Proc. of International Conference 'Diffusion Fundamentals III' (August 23–26, 2009)* (Athens: 2009), p. 324.
13. Presented for publication.
14. W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Franklin Book Co: 1964).