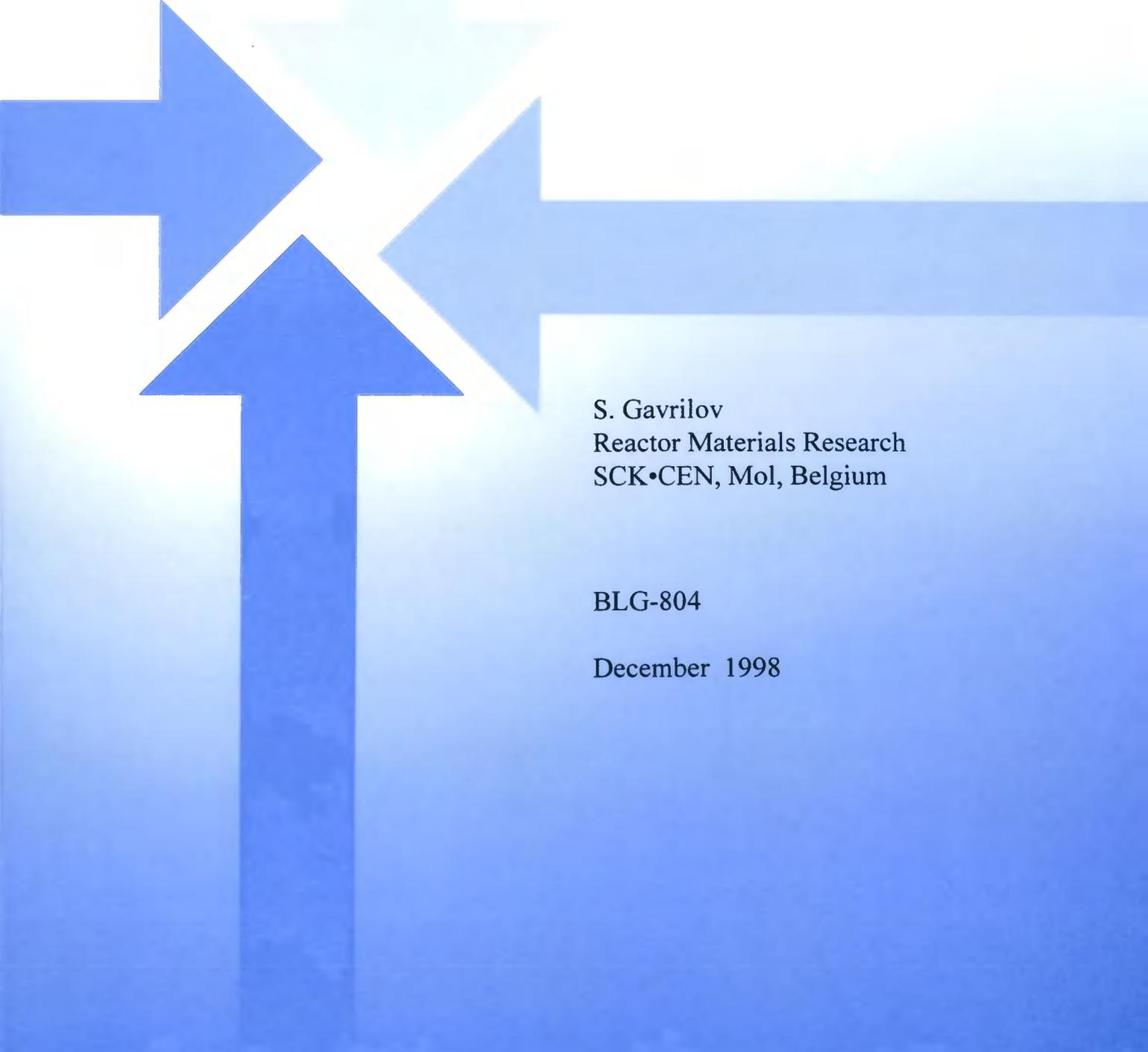


Simulation of helium behaviour in beryllium

FINAL REPORT
ASSOCIATION EURATOM-BELGIAN
STATE FOR FUSION.
Underlying Technology.



S. Gavrilov
Reactor Materials Research
SCK•CEN, Mol, Belgium

BLG-804

December 1998

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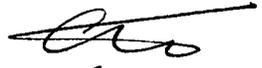
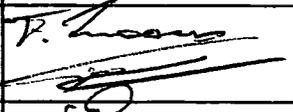
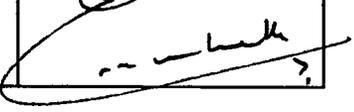
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ABSTRACT

Production of helium is a damaging neutronic effect on the properties of beryllium. It is a problem for the continued safe operation of fission and fusion reactors, which have beryllium components. The damage results from a complex interaction of helium atoms with the crystal structure of beryllium. Thus far it has not been attributed to specific key variables and has been the object of numerous experiments. Because experiments are difficult and expensive, the helium behaviour in beryllium should be simulated by computer modelling. As part of SCK•CEN's ongoing effort to develop fusion technologies, I therefore analysed the initial steps of the helium behaviour in beryllium. Using Molecular Dynamics calculations, I estimated the possible migration mechanisms of helium atoms, the behaviour and the properties of the helium-vacancy clusters, and the formation mechanisms of the helium-bubbles embryos. This report presents my first modelling results.

The analysis shows that vacancy assisted diffusion is the basic mechanism for helium migration in irradiated beryllium. By this mechanism the simple complexes, consisting of one helium atom and one vacancy are moving to vacancy sinks (grain boundaries, dislocations, precipitates). Near vacancy sinks complexes join in clusters consisting of approximately equal number of helium atoms and vacancies. These big clusters are the origin of helium-bubble embryos. These findings agree well with the experimental data. However, more work is needed to improve the description of helium behaviour in beryllium and to develop accurate mitigation strategies.

KEYWORDS

Fusion, beryllium, helium, Molecular Dynamics, simulation, diffusion

1 Introduction

Beryllium might be used in fusion as neutron multiplier or as a structural material. It is also widely used as moderator and reflector in nuclear fission research reactors. A damaging effect on the properties of beryllium comes from the production of helium inside the material as the result of two nuclear reactions: $(n, 2n)$ and (n, α) .

Experimental data from irradiation experiments are scarce and show a large scatter. Properties such as swelling are very sensitive to structural and fabrication parameters. Therefore computer simulation of beryllium with different structure and with helium impurities could help to correctly interpret experimental data and to predict the behaviour of the material in different circumstances.

The present work is part of a project undertaken to understand basic first steps in the process of progressive helium concentration increase during neutron irradiation and to evaluate the influence of the temperature on the process.

2 Interatomic potential calculation method

Interatomic potential is an important part of material calculations at atomic scale. Empirical many-body potentials are replacing pair potentials in atomistic modelling with the possibility to apply these potentials to materials with complex structures. But it is still a problem to develop a correct form for many-body potentials and to parameterize them.

For our simulation we chose N-body potential. The attractive part is taken identical to that used in the cohesion model derived from the second moment approximation of the tight binding scheme. This scheme was adapted to hexagonal closed packed (hcp) metals. The total energy of a system of N interacting particles may be written as:

$$E_{tot} = \frac{1}{2} \sum_{ij} V(R_{ij}) + \sum_i f(\rho_i) \quad (1),$$

where the summation extends over all N atoms. $V(R_{ij})$ is a pair-potential describing a direct interaction between two atoms i and j separated by distance R_{ij} . f is the so-called many-body function. In the tight binding scheme, f is interpreted as a sum of squares of hopping integrals and ρ_i is written as a sum of pair potentials

$$\rho_i = \sum_j \Phi(R_{ij}) \quad (2).$$

In the second moment approximation, f is proportional to the square root of ρ and this form implies that the elastic constant C_{12} is larger than C_{66} . However, $C_{12}-C_{66}$ is negative for beryllium hexagonal close-packed structure. Therefore, the following functional dependence of f on ρ is preferred:

$$f(\rho) = \sqrt{\rho}(1 + A\rho) \quad (3),$$

where A is a constant. We have chosen A to be $(2\rho_0)^{-1}$, where ρ_0 is the value of ρ_i for the ideal lattice. Following Ackland et al. [4] $V(r)$ and $\Phi(r)$ are written as cubic splines:

$$V(r) = \sum_{k=1}^n A_k (R_{ak} - r)^3 H(R_{ak} - r), \quad (4a)$$

$$\Phi(r) = \sum_{k=1}^m B_k (R_{bk} - r)^3 H(R_{bk} - r), \quad (4b)$$

where R_{ak} and R_{bk} are the knot points such that $R_{a1} > R_{a2} > \dots > R_{an}$ and $R_{b1} > R_{b2} > \dots > R_{bm}$; $H(x)=0$ for $x < 0$ and $=1$ for $x > 0$; $n=7$ and $m=5$. Eqs. (4a) and (4b) thus have 24 adjustable parameters which allow a fitting of the potential on macroscopic and microscopic properties of the material.

Calculation of potential parameters for beryllium and other hexagonal close-packed metals was performed by Igarashi et al. [1]. They parameterized potential using equations (1-4) and

fitted to the cohesive energy, unrelaxed vacancy formation energy, five independent second-order elastic constants and two equilibrium conditions. Unfortunately, they estimated the inhomogeneous contribution to the elastic constants (see Appendix 1) as very small and neglected this contribution in equations for elastic constants. Later, van Midden and Sasse [5] developed a method for the analytical estimation of the inhomogeneous contribution. Particularly for beryllium, they calculated the contribution to the elastic constant C_{12} as 60% of the real value. Hou et al. [6] recently found out that the potential of Igarashi et al. (noted IKV) incorrectly describes the vacancy migration energy and gives a negative value for the (0001) surface energy.

For reliable material calculations at atomic scale it is necessary to define as accurately as possible the potential parameters for an adequate description of basic properties of the material. For instance, we need to account for the vacancy mobility in modelling the nucleation of helium-vacancy complexes as well as in modelling the dynamics of dislocation loops. Therefore we started a major effort to improve the IKV potential.

As it was mentioned above, van Midden and Sasse [5] suggested that the sublattice displacements, and thus an inhomogeneous contribution to the elastic constants may play an essential role in the prediction of the properties of the material. To show the influence of an inhomogeneous contribution, they calculated its contribution using IKV potentials. It was concluded that this contribution can reach 6.5% of the C_{11} elastic constant and 65% of the C_{12} elastic constant. Unfortunately, in this estimate, they used the potential parameters given in [1], which were obtained without taking into account the inhomogeneous contribution to the elastic constants.

We used two methods in order to re-evaluate the parameters of the IKV potential when inhomogeneous deformations are taken into account. The first is to use the analytical expressions (see Appendix 2) of the elastic constants as derived from the IKV potential when inhomogeneous deformation are allowed, and then, to use a minimization technique in order to evaluate the parameters entering this potential function. For the second the elastic constants are written down in terms of energies associated with well-defined deformation fields (see Appendix 3) and the IKV parameters are adjusted in such a way that the derived elastic constants match the experimental values. Matching was reached by the same minimization technique as for the analytical method.

First we used both methods independently with identical constraints, namely the matching of the elastic constants, the cohesive energy, the unrelaxed vacancy formation energy, the c/a ratio and the equilibrium atomic volume to experimentally measured values. The results obtained by both methods were perfectly consistent, showing that the approximation applied in the analytical approach are valid. However, the inhomogeneous contribution to the elastic constants vanished and the calculated vacancy migration energy was still unphysically high.

Further, in addition to the previous constraints, we imposed the inhomogeneous contribution to the elastic constants to be consistent with the measured Raman frequency, which is related to the polarization mode in the basal plane of the beryllium lattice. All attempts using the experimental value of the Raman frequency (20THz) as additional characteristic for the fitting procedure give too high values for equilibrium functions making it difficult to perform correct molecular dynamic calculations with the obtained potential parameters. Moreover, all sets of potential parameters, which satisfy the physical characteristics of beryllium mentioned above

give a value for the Raman frequency of about 15 ± 1 THz. This fact supports the assumption that there is a strong correlation between the Raman frequency and other physical characteristics, used for the fitting procedure. We neglected the Raman frequency as material characteristic for the fitting procedure and keep this question for future detailed investigation.

The third strategy was to modify the IKV potential function in order to get a better realistic description of the close atomic interactions, as they occur at the vacancy migration through a saddle point. We modified the set of knot points for equations (4a-b) in such a way that the vacancy migration energy and the (0001) surface energy became comparable to experimental values. The parameters and the knot points of the IKV potential function obtained in our calculations are given in Table 1.

Table 1. Parameters of the many-body potentials for beryllium obtained by Igarashi et al.[1] and in this work.

| Parameter | Igarashi et al.[1] | Modified |
|-----------|--------------------|-------------|
| R_{a1} | 2.0400000 | 2.0234000 |
| R_{a2} | 1.7407111 | 1.7366245 |
| R_{a3} | 1.3816634 | 1.3517570 |
| R_{a4} | 1.2278749 | 1.2169300 |
| R_{a5} | 1.0400000 | 1.0337383 |
| R_{a6} | 0.9735266 | 0.9738500 |
| R_{a7} | 0.9637914 | 0.9513044 |
| A_1 | 0.8975540 | 0.8306150 |
| A_2 | -2.0922508 | -1.9628927 |
| A_3 | -6.9015384 | -6.9545162 |
| A_4 | 18.6591697 | 20.706253 |
| A_5 | 55.5572581 | 45.866237 |
| A_6 | 50.0000000 | 100.000000 |
| A_7 | 100.000000 | 50.000000 |
| R_{b1} | 2.0400000 | 2.0370000 |
| R_{b2} | 1.7233905 | 1.7171990 |
| R_{b3} | 1.4095758 | 1.4138468 |
| R_{b4} | 1.2242095 | 1.2262806 |
| R_{b5} | 1.0408000 | 1.0368327 |
| B_1 | 2.7114616 | 2.6139573 |
| B_2 | -5.9662845 | -6.2203690 |
| B_3 | -19.6955993 | -17.265278 |
| B_4 | 57.1589316 | 59.789590 |
| B_5 | 188.8640451 | 159.38566 |
| A | 0.00638918 | 0.006249515 |

The elastic constants, the cohesive energy, the unrelaxed vacancy formation energy, the c/a ratio and the equilibrium atomic volume calculated using new parameters agree to within 5% with those measured experimentally.

3 Molecular Dynamics calculations

Interatomic potential calculations were performed. Constraint molecular dynamic methods are used to estimate formation energies, helium-vacancy binding energies and migration energies.

3.1 Defects in beryllium lattice

The properties of self-interstitial atoms and vacancies were estimated.

In the present model, the vacancy formation energy is 0.93 eV. Figure 1 shows the lattice relaxation, around a vacancy, obtained by molecular dynamic calculations. The gain of vacancy formation energy due to structural relaxation is 0.04 eV. This value is in good agreement with the value 0.035 eV calculated in the framework of the density functional theory in local density approximation [3]. The binding energy of a di-vacancy in the basal plane was estimated at 0.13 eV.

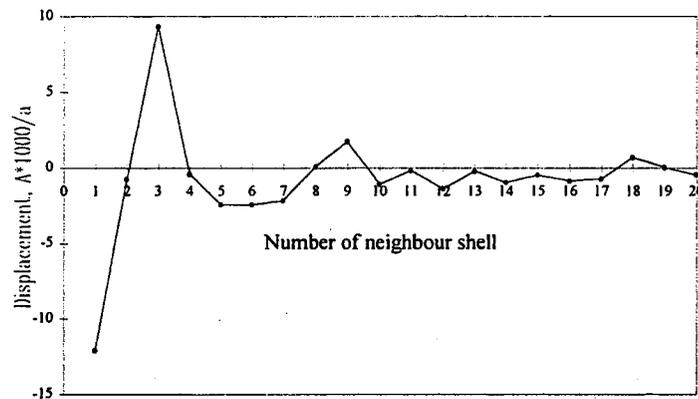


Figure 1. The neighbour shells' displacements around a vacancy from the positions in an ideal beryllium lattice (first neighbour shell - 6 atoms, second - 6, third - 6, fourth - 2, etc).

For the formation energy of a self-interstitial atom 10.5 ± 0.3 eV was also calculated.

The activation energy of self-diffusion is the sum of the vacancy formation energy and the vacancy migration energy. The migration energies were calculated as the difference between the configuration energies of the system with the atom at the potential saddle point between two vacancies and the system with a single vacancy. The values of 0.6 ± 0.3 and 0.7 ± 0.3 eV are found respectively parallel and perpendicular to the c-axis. The resulting activation energies 1.7 ± 0.3 and 1.8 ± 0.3 eV are in slight disagreement with the experimental data 1.71 and 1.61 eV [5].

3.2 Helium atoms in perfect beryllium lattice

The principal energy diagram of helium atoms states in a metal lattice is shown in Figure 2. This diagram shows helium atoms energy in different positions in lattice. The energy E_{He}^f (the formation energy of a helium interstitial) is required to bring helium atoms from the gas phase into an interstitial position in the lattice. Two helium atoms in interstitial positions can create

a stable configuration and decrease their formation energy for the value of binding energy E_{2He}^b . If a helium atom is in a vacancy position, the formation energy E_{He}^f decreases the binding energy of a helium-vacancy complex. The binding energy of a helium atom with a vacancy is:

$$E_{HeV}^b = E_V^f + E_{He}^f - E_{HeV}^f,$$

where E_V^f is the vacancy formation energy and E_{HeV}^f is the formation energy of the helium-vacancy (HeV) complex.

The average dissociation energy of the HeV complex is:

$$E_{HeV}^D = E_{HeV}^b + E_{He}^M,$$

where E_{He}^M is the migration energy of a helium atom from one interstitial position to another through the saddle point. The estimations of all these values obtained by the constraint molecular dynamic method are given in Table 2.

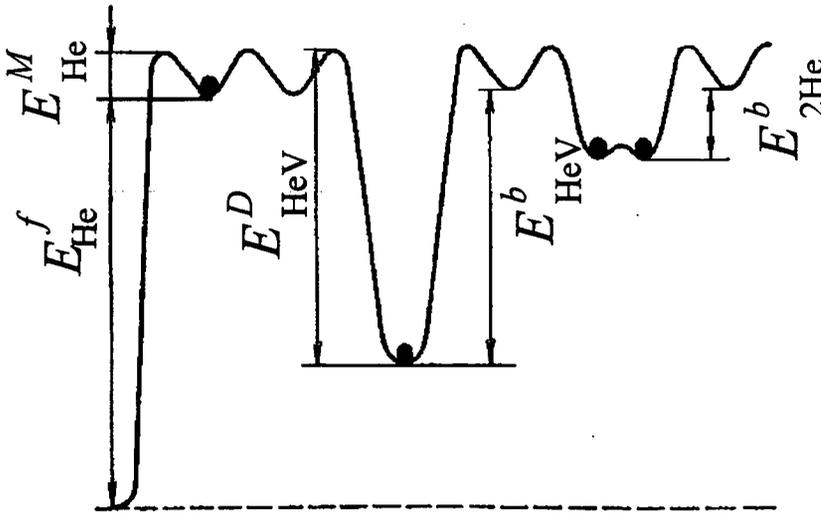


Figure 2. Principal energy diagram of helium atom states in a metal lattice.

Different possible helium interstitial positions in the hcp lattice were considered for beryllium. Among geometrically possible helium interstitial sites, only the octahedral sites are found to be stable.

Figure 3 shows the structural relaxation around a helium-vacancy complex. The structural relaxation around a helium atom in the interstitial position was also estimated.

Table 2. The formation (E_{He}^f) and migration (E_{He}^M) energies for a helium atom in an interstitial position, binding energy of two helium atoms in interstitial positions (E_{2He}^b), formation (E_{HeV}^f), binding (E_{HeV}^b) and dissociation (E_{HeV}^D) energy of helium-vacancy complex, all in eV.

| E_{He}^f | E_{He}^M | E_{2He}^b | E_{HeV}^f | E_{HeV}^b | E_{HeV}^D |
|------------|------------|-------------|-------------|-------------|-------------|
| 8.4 | 0.6 | 1.0 | 5.0 | 4.3 | 4.9 |

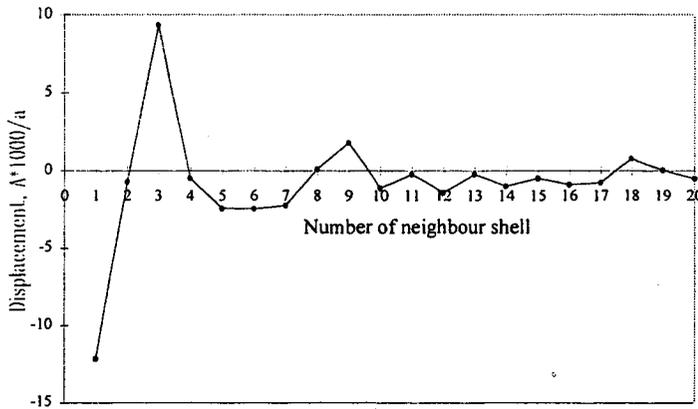


Figure 3. The neighbour shells displacements around a helium-vacancy complex.

3.3 Clusters of helium atoms in interstitial positions and in combination with vacancies

Formation and binding energies were computed for mono-vacancies, di-vacancies, three-vacancies and helium interstitials at different geometrically plausible equilibrium sites.

The binding energy of a defect cluster formed by n helium atoms and m -vacancies may be written as

$$E^b(He_n-V_m) = mE^f(V_m) + nE^f(He) - E^f(He_n-V_m).$$

Similarly, the binding energy of one helium atom to a cluster formed by n helium atoms and m -vacancies may be written as

$$E^b(He) = E^f(He_{n-1}-V_m) + E^f(He) - E^f(He_n-V_m).$$

The binding energy of one vacancy to a cluster formed by n helium atoms and m -vacancies may be written as

$$E^b(V) = E^f(He_n-V_{m-1}) + E^f(V) - E^f(He_n-V_m).$$

The binding energy of a defect cluster formed by n helium atoms in interstitial positions may be written as

$$E^b(nHe) = nE^f(He) - E^f(nHe).$$

Formation and binding energies obtained with the model potential described above are given in Table 3.

Table 3. Formation (E^f), binding (E^b) energies of vacancy(V), di-vacancy(V_2), three-vacancy(V_3), helium clusters in interstitial position(He_n) and He_n - V_m clusters, all in eV.

| Type of defect | E^f | E^b (defect) | E^b (He) | E^b (V) |
|-------------------|----------|----------------|------------|-----------|
| V | 0.90 | - | - | - |
| V_2 | 1.68 | 0.13 | - | - |
| V_3 | 2.37 | 0.34 | - | - |
| He | 8.4 | - | - | - |
| He_2 | 15.8 | 1.0 | - | - |
| He_3 | 22.6 | 2.6 | - | - |
| He_4 | 31.2 | 2.5 | - | - |
| He_5 | 40.7 | 1.3 | - | - |
| He_6 | unstable | | | |
| He-V | 5.0 | 4.3 | 4.3 | 4.3 |
| He_2 -V | 12.5 | 5.2 | 0.9 | 4.2 |
| He_3 -V | 20.1 | 6.0 | 0.8 | 3.4 |
| He_4 -V | 27.7 | 6.8 | 0.8 | 4.3 |
| He_5 -V | 35.6 | 7.3 | 0.5 | 6.0 |
| He_6 -V | unstable | | | |
| He- V_2 | 5.7 | 4.5 | 4.4 | 0.2 |
| He_2 - V_2 | 10.2 | 8.5 | 4.0 | 3.3 |
| He_3 - V_2 | 15.2 | 11.8 | 3.4 | 5.8 |
| He_4 - V_2 | 21.8 | 13.6 | 1.8 | 6.8 |
| He_5 - V_2 | 28.6 | 15.3 | 1.7 | 8.0 |
| He_6 - V_2 | 35.6 | 16.7 | 1.4 | - |
| He_7 - V_2 | 43.6 | 17.1 | 0.4 | - |
| He_8 - V_2 | unstable | | | |
| He- V_3 | 7.5 | 3.6 | 3.3 | -0.9 |
| He_2 - V_3 | 11.0 | 8.6 | 4.9 | 0.1 |
| He_3 - V_3 | 14.5 | 13.4 | 4.9 | 1.6 |
| He_4 - V_3 | 20.2 | 16.2 | 2.8 | 2.6 |
| He_5 - V_3 | 27.5 | 17.2 | 1.0 | 1.9 |
| He_6 - V_3 | 35.0 | 18.1 | 0.9 | 1.4 |
| He_7 - V_3 | 42.7 | 18.9 | 0.8 | 1.8 |
| He_8 - V_3 | 50.5 | 19.5 | 0.6 | 2.1 |
| He_9 - V_3 | 58.6 | 19.8 | 0.3 | - |
| He_{10} - V_3 | 66.9 | 19.9 | 0.1 | - |

4 Discussion of the result

This section discusses the first stages in the model, which describes the behaviour of helium in the beryllium lattice.

Helium atoms, generated in a beryllium lattice by nuclear reactions, migrate fast by jumping along interstitial positions up to capture in traps. The reason for the high mobility of helium atoms is their low migration energy. This is the energy needed to transport a helium atom from one interstitial position to an other. The calculated value of this migration energy is 0.6 eV and agrees well with experimentally determined values, 0.6 eV [10] and 0.41 eV [11]. Such a low value for the migration energy means that helium migration already takes place at room temperature.

Another helium migration mechanism is vacancy assisted diffusion. Here, a helium atom migrates by jumping into a vacancy. At low temperature, this mechanism is only possible in beryllium with high vacancy concentration, for instance in irradiated beryllium. The activation energy of vacancy assisted diffusion in an ideal crystal lattice is the sum of three energies: the vacancy formation energy, the vacancy migration energy, and the energy needed to transport a helium atom from the interstitial position to its neighbouring vacancy. The latter energy is very small, hence the activation energy of vacancy assisted diffusion is in practice equal to the sum of the vacancy formation energy and the vacancy migration energy. This sum is the self-diffusion activation energy. The self-diffusion activation energy can be obtained by molecular dynamics calculation and equals 1.8 eV. This calculated value agrees well with the experimentally determined value 1.71 eV [12]. The value indicates that vacancy assisted diffusion of helium atoms in an ideal beryllium lattice is possible from temperatures higher than 700 K. Neutron irradiation makes vacancy assisted diffusion possible at lower temperatures, since it produces a large number of vacancies (considerably higher than the thermal equilibrium concentration). In irradiated beryllium the activation energy of vacancy assisted diffusion of helium becomes equal to the vacancy migration energy. The calculated vacancy migration energy is 0.6 eV. Note that the activation energy of vacancy assisted diffusion is the same as the activation energy for the interstitial migration of helium. Although they are equal, vacancy assisted diffusion predominates in irradiated beryllium, since vacancies are high binding energy traps for helium atoms (3.1 eV) and soon after the generation in the beryllium lattice most of these atoms are captured in vacancies.

The helium atoms in a beryllium lattice interact with each other. This interaction manifests itself in the formation of helium and helium-vacancy clusters. Molecular Dynamics (MD) calculations show that these clusters have following features:

- He_n clusters (n helium atoms in interstitial positions) are stable (have positive binding energies) when $n \leq 5$;
- He_nV clusters (n helium atoms decorating one vacancy) are stable when $n \leq 5$;
- He_nV_2 clusters (n helium atoms decorating di-vacancy) are stable when $n \leq 7$;
- He_nV_3 clusters (n helium atoms decorating three adjacent vacancies) are stable when $n \leq 10$.

Note that above calculations only deal with helium atoms in the associated Wigner-Seitz cells. Other helium atoms, sitting in the neighbouring interstitial sites, could also bind to the same cluster and these are not taken into consideration in the present calculation. The binding-energy analysis of the considered clusters shows the following peculiarities:

- the binding energy of a helium atom to a cluster also drops with the number of helium atoms in the cluster. When this number is equal to some critical value, the cluster becomes unstable;
- the binding energy of vacancy to cluster increase with the number of helium atoms.

Therefore helium and helium-vacancy clusters are able to bind a limited number of helium atoms. After the incorporation of a critical number of helium atoms to the cluster, it will only continue to grow after addition of another vacancy. This new vacancy can form by displacing a beryllium atom from its lattice position in to an interstitial position. The latter is based on the result of Molecular Dynamics calculations of configurations where a beryllium atom occupies an interstitial position nearest to the helium-vacancy cluster. The mechanism becomes energetically preferable when :

- $n > 5$ in He_n clusters;
- $n > 6$ in He_nV clusters;
- $n > 7$ in He_nV_2 clusters.

The opposite process, the recombination of a cluster vacancy with an interstitial beryllium atom, is also possible. This process takes place spontaneously and decreases the energy of the system. The recombination is possible when an interstitial atom appears near a He_nV cluster and $n < 5$. When $n \geq 5$ recombination does not take place.

The vacancy concentration affects the growth mechanism of helium-vacancy clusters. In beryllium with an equilibrium vacancy concentration, the clusters will grow by capture of migrated vacancies. More probably though they grow by displacing a beryllium atom into an interstitial position. Afterwards they can be incorporated into the cluster which in turn can displace additional beryllium atoms. When the clusters reach a critical size, they are able to squeeze out a group of beryllium atoms which has the form of a dislocation loop. When the vacancy concentration is considerably higher than the equilibrium concentration, clusters with an approximately equal number of helium atoms and vacancies form. These clusters are the most stable clusters, because the sum of the vacancy binding energies of vacancy to cluster and helium atom to cluster is maximum. The binding energy inside these clusters is high which makes the cluster stable, even at high temperatures. This is the reason why almost no helium is released from irradiated beryllium up to 900 K in thermal desorption experiment [13].

A great number of vacancies and interstitial atoms form in beryllium under neutron irradiation. Microstructural examinations of irradiated beryllium show a markedly higher concentration of dislocation loops as compared to unirradiated beryllium. Hence interstitial beryllium atoms (formed during irradiation) are preferably captured on dislocations. As a result, the vacancies, which are formed as part of a Frenkel pair, avoid recombination with the interstitial atoms and supersaturates the lattice. Then, simple HeV clusters form when the vacancy captures a migrated helium atom. These clusters are very mobile and migrate fast in the beryllium lattice. They interact and form large clusters. The mobility of the large clusters is smaller and decreases strongly with their size. Hence they stop and grow by further capturing smaller clusters. In conclusion, vacancy sinks (grain boundaries, dislocation loops, precipitates etc.) are prime locations for the formation of large clusters.

CONCLUSION

Once helium is generated in beryllium by the nuclear reaction, it quickly supersaturates the lattice and joins to vacancies. Then helium and vacancy migrate together to vacancy sinks/nucleation centres (i.e. dislocation loops, grain boundaries, precipitates etc.) where they precipitate to form embryonic intragranular and intergranular bubbles. This process lies at the origin of the high bubble concentration found along grain boundaries by microstructural examination of irradiated beryllium under annealing [13]. A large amount of pores, probably resulting from helium-induced swelling, is found next to the regions of intergranular fracture of the broken tensile samples [14] by scanning electron microscopy.

Pore-depleted areas are observed adjacent to the grain boundaries and to some types of precipitates [13]. The reason for this spatial distribution is the non-uniform distribution of oxide particles in the beryllium structure due to the fabrication process [13,15]. The oxide particles create a stress field and make HeV migration and cluster nucleation difficult. This nonuniformity in the distribution of the pores constitutes a danger for the material: build up of high residual stresses due to unhomogeneous swelling. Irradiated beryllium components can be demolished at high annealing temperatures, even without applying external forces.

In frame of this work following methods and software were developed:

Methods:

- Development of the interatomic potentials for metals with hexagonal close-packed structures
- Numerical calculations of the elastic constants for material with complex structures
- Analytical and numerical estimations of inhomogeneous contribution to the elastic constants
- Energetic calculations of helium and helium-vacancies complexes in beryllium

Software:

- Minimization kit for beryllium potential (on base of "MERLIN" minimization kit)
- Visualization program for structure analysis of clusters (projections of 3D structures on computer screen)
- Animation program to analysis of dynamic processes in lattice
- Program for analysis of lattice deformations around distinct defects
- Program for simulation of helium-vacancies complexes

RECOMMENDATIONS AND SUGGESTIONS FOR FUTURE WORK

As a result of my work I suggest the following approaches to decrease the effects of irradiation on beryllium:

- to create a uniform distribution of sinks for vacancies(precipitations, dislocations) in the grains
and/or
- to introduce impurities which reduce the rate of vacancy and HeV migration.

The first approach results in a network of small helium clusters(bubbles) with a small total volume in comparison with the heterogeneous distribution of big helium bubbles. The second approach reduces the swelling rate.

Post-irradiation of beryllium can not be performed for extracting helium from beryllium without critical changes to the structure: helium is not released at temperatures below 1000 K due to the high stability (high binding energy) of the helium-vacancy clusters with an equal number of helium atoms and vacancies (which are created under irradiation).

The interaction of helium atoms with extended lattice defects (dislocations, grain boundaries) has not been simulated yet. Such calculations are very important for a full understanding of the behaviour of helium in beryllium. Hence, it is necessary to perform a more advanced study of these phenomenon. The change of the structure of irradiated beryllium with temperature should be a also subject for future investigations.

I suggest to perform the following tasks:

Experimental

1. Microstructure examinations (Transmission Electron Microscopy) of beryllium:
 - estimation of dislocation and dislocation loops concentrations in irradiated and unirradiated specimens
 - comparison of structure evaluation of irradiated beryllium under annealing with helium release.
2. Estimation of the point defects concentration in irradiated beryllium by Positron Annihilation method.

Molecular Dynamics simulation:

1. Interaction of helium atoms with extended defects of crystal lattice (dislocation, dislocation loop, grain boundaries, precipitation) particularly:
 - calculation of formation and binding energies of helium-vacancy clusters in stress fields created by extended defects;
 - simulation of migration of helium atoms along dislocations;
 - estimation of extended defects as sinks for vacancies, interstitial helium atoms and HeV clusters.
2. Estimation properties of large helium-vacancy clusters with equal number of vacancies and helium atoms (dissociation energies, configurations et. al.).
3. Simulation of beryllium structure modification during neutron irradiation:
 - estimation of interstitials capture processes on dislocation and dislocation loops;
 - estimation of equilibrium vacancy concentration under irradiation.

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APPENDIX 1. Inhomogeneous contribution in the elastic constants: definition and calculations

In the process of developing an interatomic potential for a particular material, elastic constants are commonly used as experimental input. But with the decreasing symmetry in the lattices studied, the relations for the elastic constants become more and more complicated. The equations for elastic constants, which were derived using the method of homogeneous deformation, do not hold. Born and Huang [8] pointed out that in noncentrosymmetric lattices (for instance a hexagonal close-packed beryllium lattice) the elastic constants are composed of two terms. The first term $C_{ij}^{(1)}$ is related to a homogeneous strain in the system, while the second term $C_{ij}^{(2)}$ arises due to possible relative displacement of different sublattices when a macroscopic homogeneous strain is applied. Two sublattices of hexagonal close-packed lattice and possible relative displacement of one of them are shown in Figure A1.1.

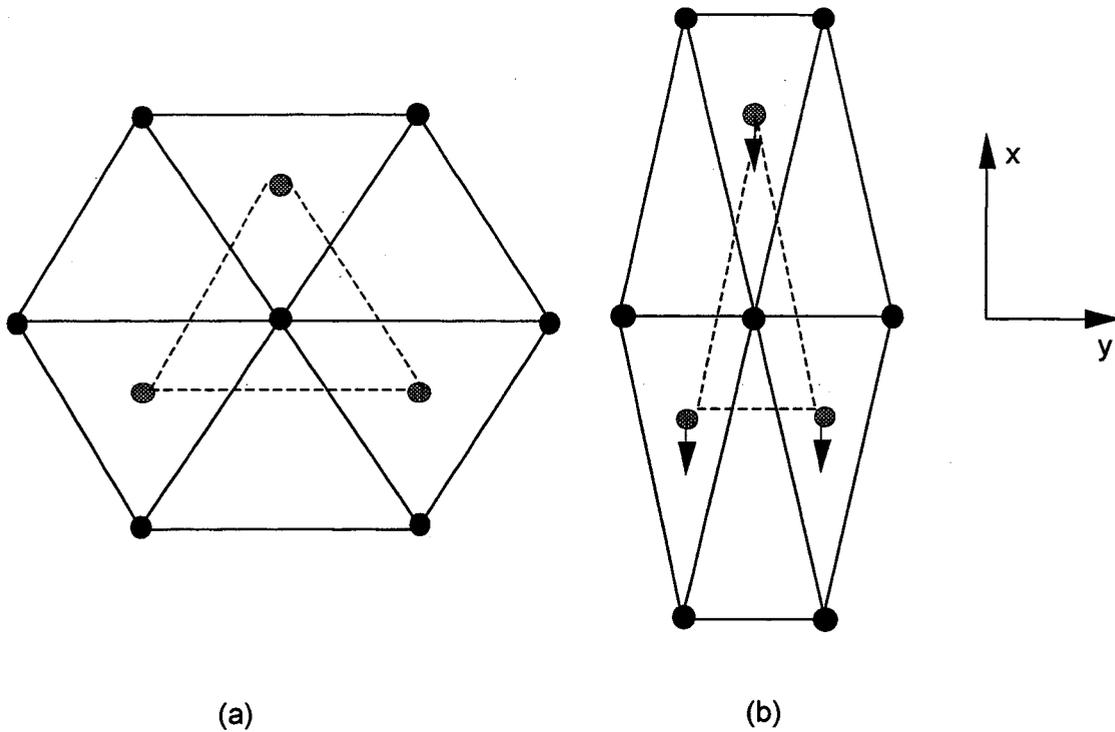


Figure A1.1 View along the c axis of a hexagonal close-packed lattice. The solid and dashed lines indicate the two sublattice planes, displaced a distance $\pm c/2$ along c axis. a) and b) lattices without and with applied strain respectively.

Following the strain-expansion formalism, Van Midden and Sasse [5] have shown that in the hexagonal close-packed structure there is only one independent $C_{ij}^{(2)}$ component, namely:

$$-C_{11}^{(2)} = -C_{22}^{(2)} = C_{12}^{(2)} = -C_{66}^{(2)} = C^{(2)} \quad (\text{A1.1}).$$

Martin, in his "inner elasticity theory" [9], has obtained that

$$C^{(2)} = D_{y,xx}^2 / E_{xx} \quad (\text{A1.2}),$$

where $D_{y,xx}$ and E_{xx} are so-called inner elastic constants. According to Martin we can define these constants as

$$\begin{aligned} D_{ij} &= -\frac{1}{\Omega} \left(\frac{\partial^2 E_{coh}}{\partial \zeta_i \partial \eta_j} \right) \\ E_{ij} &= -\frac{1}{\Omega} \left(\frac{\partial^2 E_{coh}}{\partial \zeta_i \partial \zeta_j} \right) \end{aligned} \quad (\text{A1.3})$$

where Ω is the atomic volume, E_{coh} is the cohesive energy per atom, ζ is the inner displacement vector, and η is the Lagrangian strain matrix. The symmetry of the hexagonal close-packed structure reduces the D tensor to only one independent component, namely

$$D_{x,xy} = D_{y,xx} = -D_{y,yy} \quad (\text{A1.4}).$$

Similarly, there are only two independent components of the E tensor namely E_{zz} , which is not involved in the relaxation contribution, and

$$E_{xx} = E_{yy} = \frac{1}{4} \rho \omega_R^2 \quad (\text{A1.5}),$$

where ρ is the density of the crystal and ω_R is the frequency of the Raman mode polarized in the basal plane.

APPENDIX 2. Analytical calculation of the elastic constants

The second elastic constants, $C_{\alpha\beta\gamma\delta}$, can be evaluated by expanding the energy of the system to the second order with respect to an infinitesimal strain applied to the system. As already was shown in Appendix 1 that in noncentrosymmetrical lattices, such as the hexagonal close-packed lattice, the elastic constants are composed of two terms: homogeneous and inhomogeneous. Using the terminology described in section 2.1 of this report we can write the following equation for the homogeneous term:

$$\begin{aligned} \Omega_0 C_{\alpha\beta\gamma\delta} = & \frac{1}{2} \sum_j \left\{ \frac{R_{j\alpha} R_{j\beta} R_{j\gamma} R_{j\delta}}{R_j^2} \left(V''(R_j) - \frac{V'(R_j)}{R_j} \right) \right\} \\ & - f'(\rho) \sum_j \left[\frac{R_{j\alpha} R_{j\beta} R_{j\gamma} R_{j\delta}}{R_j^2} \left(\Phi''(R_j) - \frac{\Phi'(R_j)}{R_j} \right) \right] \\ & - f''(\rho) \sum_j \frac{R_{j\alpha} R_{j\beta}}{R_j} \Phi'(R_j) \sum_j \frac{R_{j\gamma} R_{j\delta}}{R_j} \Phi'(R_j) \end{aligned} \quad (\text{A2.1}),$$

where $R_{j\alpha}$ is the α th component of the vector \mathbf{R}_j connecting the atom j to the atom chosen as origin, and the Ω_0 is the equilibrium atomic volume.

The second "inhomogeneous" term is a combination of two inner elastic constants(see Appendix 1). The inner elastic constants we can write in the same terms as the previous equation

$$\begin{aligned} E_{\alpha\beta} = & \sum_j \left\{ 2f'(\rho) \Phi''(R_j) + V''(R_j) \right\} \frac{R_{j\alpha} R_{j\beta}}{R_j^2} \\ & + \sum_j \frac{1}{R_j} \left\{ 2f'(\rho) \Phi'(R_j) + V'(R_j) \right\} \left(1 - \frac{R_{j\alpha} R_{j\beta}}{R_j^2} \right) \end{aligned} \quad (\text{A2.2a}),$$

$$\begin{aligned} D_{\alpha,\beta\gamma} = & \sum_j \left\{ 2f'(\rho) \Phi''(R_j) + V''(R_j) \right\} \frac{R_{j\alpha} R_{j\beta} R_{j\gamma}}{R_j^2} \\ & - \sum_j \left\{ 2f'(\rho) \Phi'(R_j) + V'(R_j) \right\} \left(\delta_{\alpha\beta} - \frac{R_{j\alpha} R_{j\beta}}{R_j^2} \right) \frac{R_{j\gamma}}{R_j} \end{aligned} \quad (\text{A2.2b}).$$

APPENDIX 3. Numerical calculation of the elastic constants

The homogeneous parts of the elastic constants $C_{\alpha\beta\gamma\delta}$ are defined by means of a Taylor expansion of the total energy for the system, $E(V, \varepsilon)$, with respect to a small strain ε of the lattice (V is the volume). The letters α , β , γ and δ refer to Cartesian components. In the present work we considered the hexagonal close-packed structure, which is spanned by the three vectors $\left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\right)$, $(0, 1, 0)$ and $\left(0, 0, \frac{c}{a}\right)$. The Bravais lattice vectors are normally written in a matrix form, i.e.

$$\mathbf{R} = \begin{pmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{c}{a} \end{pmatrix}. \quad (\text{A3.1})$$

The distortion of the lattice is expressed by a multiplying equation (A3.1) with a symmetric ($\varepsilon_{xy} = \varepsilon_{yx}$) distortion matrix \mathbf{e} , which is written as

$$\mathbf{e} = \begin{pmatrix} 1 + \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1 + \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1 + \varepsilon_{zz} \end{pmatrix} \quad (\text{A3.2}).$$

As mentioned above, we express the energy of the strain system by means of a Taylor expansion in the distortion parameters

$$E(V, \alpha) = E(V_0, 0) + V_0 \left(\sum_{\alpha, \beta} \tau_{\alpha\beta} \varepsilon_{\alpha\beta} + \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta} C_{\alpha\beta\gamma\delta} \varepsilon_{\alpha\beta} \varepsilon_{\gamma\delta} \right) \quad (\text{A3.3})$$

The volume of the unstrained system is denoted V_0 and $E(V_0, 0)$ is the corresponding total energy. In the equation above, we have introduced the parameter $\tau_{\alpha\beta}$ which is an element in the stress tensor, and $C_{\alpha\beta\gamma\delta}$, which is a second order elastic constant. Since the matrix in equation (A3.2) is symmetric, it contains only six different parameters. It is often convenient to change to the Voight notation in order to reduce the number of indices.

As already mentioned, there are five independent elastic constants for a hexagonal material, called C_{11} , C_{12} , C_{13} , C_{33} and C_{55} . Since we have five independent constants, we need five different strains to determine these. We will obtain an expression only for sum $(C_{11} + C_{12})$, for the combinations of other elastic constants we will adduce only distortion matrixes and the expression itself.

Lets consider following distortion matrix:

$$\mathbf{e} = \begin{pmatrix} 1 + \varepsilon_{xx} & 0 & 0 \\ 0 & 1 + \varepsilon_{yy} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (\text{A3.4})$$

it changes the size of the basal plane, while keeping the z axis constant. The Taylor expansion of the total energy can be written

$$E(V, \alpha) = E(V_0, 0) + V_0 \left[(\tau_{xx} \varepsilon_{xx} + \tau_{yy} \varepsilon_{yy}) + \frac{1}{2} (\varepsilon_{xx} \varepsilon_{xx} C_{xxxx} + \varepsilon_{xx} \varepsilon_{yy} C_{xxyy} + \varepsilon_{yy} \varepsilon_{xx} C_{yyxx} + \varepsilon_{yy} \varepsilon_{yy} C_{yyyy}) \right]$$

if $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon$, and introducing the Voight notation, we have

$$E(V, \varepsilon) = E(V_0, 0) + V_0 \left[(\tau_1 + \tau_2) \alpha + \frac{1}{2} (\alpha^2 C_{11} + \alpha^2 C_{12} + \alpha^2 C_{21} + \alpha^2 C_{22}) \right].$$

Due to $C_{11} = C_{22}$ and $C_{12} = C_{21}$ we obtain

$$E(V, \varepsilon) = E(V_0, 0) + V_0 \left[(\tau_1 + \tau_2) \varepsilon + \varepsilon^2 (C_{11} + C_{12}) \right] \quad (\text{A3.5}).$$

If we sum up equation (A3.4) for positive and negative distortions ε then we obtain

$$C_{11} + C_{12} = \frac{E(V, +\varepsilon) + E(V, -\varepsilon) - 2E(V, 0)}{2V_0 \varepsilon^2} \quad (\text{A3.6}).$$

Using the same routine and other distortions matrixes we can derive the expressions for other elastic constants combinations. But the common expression for all these combinations will be:

$$C = \frac{E^+ + E^- - 2E^0}{KV_0 \varepsilon^2} \quad (\text{A3.7}),$$

where C is an elastic constants combination, E^0 is the energy per atom with no displacement field (cohesive energy), E^+/E^- is the energy with a field given by ε positive/negative and K is a constant, which depend on an elastic constants combination. The elastic constants combination which was used in this work, the displacement fields and the K constants corresponding to these combinations are given in Table A3.1.

Table A3.1 Displacement fields for numerical calculation of the elastic constants.

| | X' | Y' | Z' | K |
|-------------------|----------------------|----------------------|----------------------|-----|
| $C_{11} + C_{12}$ | $X(1 + \varepsilon)$ | $Y(1 + \varepsilon)$ | Z | 2 |
| $C_{11} - C_{12}$ | $X(1 + \varepsilon)$ | $Y(1 - \varepsilon)$ | Z | 2 |
| C_{33} | X | Y | $Z(1 + \varepsilon)$ | 1 |
| C_{44} | $X + \varepsilon Z$ | Y | $Z + \varepsilon X$ | 4 |
| B | $X(1 + \varepsilon)$ | $Y(1 + \varepsilon)$ | $Z(1 + \varepsilon)$ | 9 |

Two distinct methods for numerical calculation of the inhomogeneous part of the elastic constants are used in our work:

- The numerical calculation of the inner elastic constants D_{ij} and E_{ij} , and after the direct calculation of $C^{(2)}$ by the equation (A1.2)
- Search of the lattice inhomogeneous relaxation, by addition one more distortion field for one of the two sublattices.

For the numerical calculation of the inner elastic constants we use the method of the displacements fields. This method is analogous to the method described in this Appendix for the numerical calculation of the usual elastic constants. The displacement fields are given in Table A3.2.

Table A3.2 Displacements for the calculation of inner elastic constants D_{ij} and E_{ij}

| Inner elastic constants | X' | Y' |
|-------------------------|-------------------------|------------------------|
| $D_{x,xy}$ | $X+\varepsilon Y/2+S^*$ | $Y+\varepsilon X/2$ |
| $D_{y,xx}$ | $X(1+\varepsilon)$ | $Y+S^*$ |
| $D_{y,yy}$ | X | $Y(1+\varepsilon)+S^*$ |
| E_{xx} | $X+S^*$ | Y |

* - the internal displacement S is applied to only one of the two sublattices.

Second method for numerical calculation of the inhomogeneous part of elastic constants is based on "self" lattice relaxation. The internal displacement S has been chosen to minimize the total energy of lattice. The displacement fields for this method are given in Table A3.3.

Table A3.3 Displacement fields for numerical calculation of the elastic constants with taking into account the inhomogeneous contribution to these constants

| | X' | Y' | Z' | K |
|-----------------|------------------------|--------------------|--------------------|-----|
| $C_{11}+C_{12}$ | $X(1+\varepsilon)$ | $Y(1+\varepsilon)$ | Z | 2 |
| $C_{11}-C_{12}$ | $X(1+\varepsilon)+S^*$ | $Y(1-\varepsilon)$ | Z | 2 |
| C_{33} | X | Y | $Z(1+\varepsilon)$ | 1 |
| C_{44} | $X+\varepsilon Z$ | Y | $Z+\varepsilon X$ | 4 |
| B | $X(1+\varepsilon)$ | $Y(1+\varepsilon)$ | $Z(1+\varepsilon)$ | 9 |

* - the internal displacement S is applied to only one of the two sublattices and the energy minimized as a function of S .

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