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# MODELING OF THE INTERATOMIC INTERACTIONS IN THE COPPER CRYSTAL APPLIED IN THE STRUCTURE (111)Cu||(0001)$Al_2O_3$

# MODELOWANIE MIĘDZYATOMOWYCH ODDZIAŁYWAŃ W KRYSZTALE MIEDZI ZNAJDUJĄCYM SIĘ W UKŁADZIE (111) Cu||(0001)$Al_2O_3$

Atomistic model developed by Rosato-Guillopé-Legrand (RGL) [1] in the application to the copper crystal applied in the metal/oxide system (111)Cu||(0001)$Al_2O_3$ was studied. The parameters of the model were identified with use of the concept of elastic eigen – states proposed originally in [8]. To test the studied RGL potential, the own program, which uses the code of the package for quantum-mechanical calculations (CASTEP [10]) was written. It is shown that due to suitable selection of the parameters the model predicts adequate behaviour within the range of small strains, while for finite deformations the results are not correct. Therefore, the possibility of the replacement of the studied RGL potential is discussed.

Zbadano zastosowanie potencjału opracowanego przez Rosato-Guillopé-Legranda (RGL) [1] do modelowania oddziaływań międzyatomowych w krysztale miedzi znajdującym się w układzie metal/ tlenek: (111)Cu||(0001)$Al_2O_3$. Parametry modelu zidentyfikowano za pomocą koncepcji sprężystych stanów własnych zaproponowaną w sposób oryginalny przez J. Rychlewskiego [8]. Aby zweryfikować badany model opracowano własny program wykorzystujący kod pakietu do obliczeń kwantowo – mechanicznych (CASTEP [10]). Wykazano, że z uwagi na odpowiedni dobór parametrów, model poprawnie opisuje zachowanie kryształu w zakresie małych odkształceń, natomiast w przypadku skończonych deformacji wyniki nie są prawidłowe. W związku z tym rozważono zastosowanie nowego potencjału.

## 1. Introduction

The aim of the paper is to investigate the atomistic model developed by Rosato-Guillopé-Legrand (RGL) [1] in the application to the copper crystal applied in the metal/oxide system (111)Cu||(0001)$Al_2O_3$. Such a model was used by Dimitriev et al. in a series of papers concerning the interatomic interactions across the copper/sapphire interface [2], [3], [4]. Similarly to Dimitriev the coherent interface assumption is employed [5], [6]. In such a case Cu crystal is subjected to the complex trigonal deformation defined by the Green strain tensor (fig.1a,b):

$$T_\varepsilon = \begin{bmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad (1.1)$$

where $\varepsilon_{xx} = \varepsilon_{yy} = \frac{1}{2}\left[\left(\frac{a}{a_o}\right)^2 - 1\right]$.

If the variable $a$ takes the value of the sapphire lattice constant $a_s$, Cu atoms of the interface will be placed atop of the oxygen sites (fig1c) and the considered Cu structure in the metal/oxide system will be obtained. Within the frame of the applied model, the interatomic interactions are described by RGL potential. Accordingly, the potential energy per atom is a sum of the repulsive energy $E_{rep}$, and the binding energy $E_b$:

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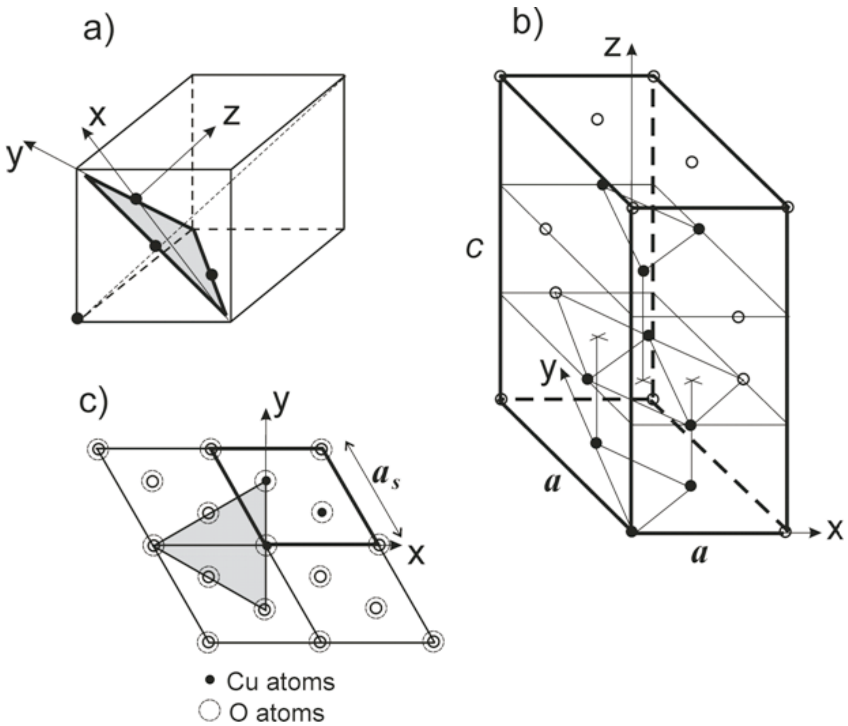

Fig. 1. Periodic cell of Cu crystal in the metal/ oxide system (111)Cu || (0001)$Al_2O_3$: a) the close – packed plane of Cu with assumed coordination system, b) periodic cell of Cu crystal assumed in ab initio calculations for the complex trigonal deformation path controlled by the variable $a$. For $a = a_0 = 4.428$Å fcc structure, for $a = a_s = 4.763$Å Cu structure in the metal oxide system c) the base of the periodic cell of Cu crystal spanned on the oxygen atoms

$$E_{rep} = A \sum_i \exp\left(-p\left(\frac{r_i}{r_0} - 1\right)\right) \tag{1.2}$$

$$E_b = -\xi \sqrt{\sum_i \exp\left(-2q\left(\frac{r_i}{r_0} - 1\right)\right)}, \tag{1.3}$$

where $r_0$ is the distance between nearest neighbors at zero temperature and $r_i$ is the distance of $i$ atom from the considered central one. The first summand (1.2) is a pair wise term, while the second one (1.3) is a many body term. The binding energy is assumed as proportional to the d band width. Thus the bond is formed by d electrons without participation of s electrons, though s wave functions localized in different lattice points overlap each other. Therefore, s electrons as well as d electrons are present in common inter-node space fig.2.

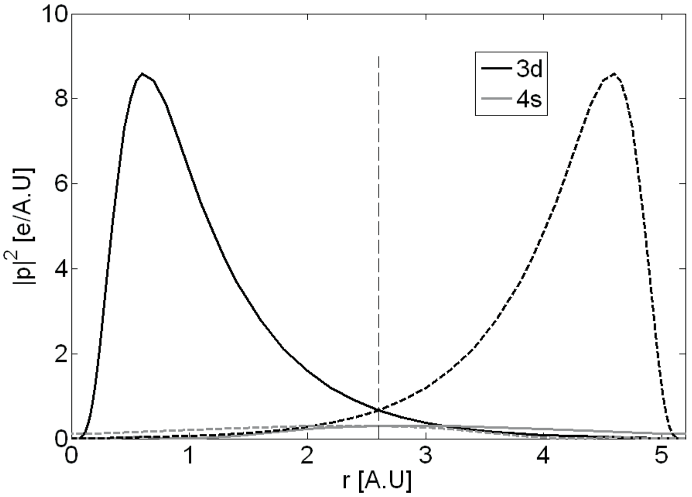

Fig. 2. Radial charge density distributions for 3d and 4s electrons coming from neighboring Cu atoms [7]

The considered model requires to determine four parameters: $A$, $\xi$, $p$, $q$. In the present study, they are obtained assuming that the model behaviour is correct in the range of infinitesimal strains but for arbitrary deformation paths. Thus the proceeding of the strain process $\boldsymbol{\varepsilon}$ is characterized by the function of energy density in the form:

$$\Phi\left(\varepsilon_{ij}\right) = \frac{1}{2} S_{ijkl}\varepsilon_{kl}\varepsilon_{ij} , \tag{1.4}$$

where $S_{ijkl}$ is elastic stiffness tensor.
In chapter 2, there is shown by means of group theory and a direct physical analysis, how the crystal symmetry controls the form of the stiffness tensor $\boldsymbol{S}$ and accordingly uniquely determines the basis of the eigen-subspaces of this tensor. The energy density stored in an arbitrary strain process is a sum of the energy densities belonging to three eigen-subspaces, as it was shown in the less known papers by J. Rychlewski [8], [9]. Accordingly, if the parameters $A$, $\xi$, $p$, $q$ are chosen in such a way that the model subjected to three strain states defined by basis vectors of three eigen-subspaces behaves correctly, the employed assumption will be fulfilled.

To test the studied model the own program which uses the code of the package for quantum-mechanical calculations (Castep [10]) written. Castep is the implementation of Kohn-Sham method [11], which enables to determine the total energy of the system formed by the atoms of given electronic configurations. As a result of application of the created program the dependence of the elastic strain energy density on the parameter controlling the process is obtained. The program enables to carry out the simulations of the finite strain processes in the case of the cubic crystals (chapter 3).The considered atomic model is subjected to the process of tetragonal deformation. As a result two functions $\Phi(\varepsilon)$ are obtained. One of them base on RGL potential determined in the present paper and the second one is used by Dimitriev [12]. The functions of energy density $\Phi(\varepsilon)$ are compared to the results of ab initio calculations obtained by means of the program written by one of the authors [7].

## 2. Influence of the crystal symmetry on the form of RGL potential

Individual atoms of given electron configurations, forming an ideal crystal, arrange themselves in the most energetically advantageous structure. The copper crystal has the face centered cubic structure (fcc). This structure is characterized by the symmetry group $O_h$ (fig.3), in which the inversion center and the four-fold symmetry axes parallel to y, z axes can be assumed as the generator elements [13]. In the three-dimensional space, the following matrices represent them [13]:

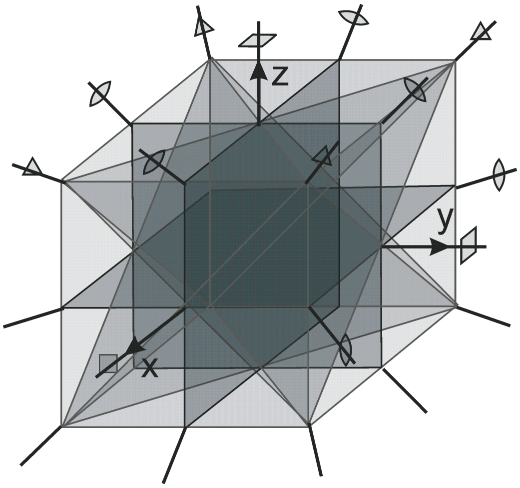

Fig. 3. The symmetry elements of Cu elementary cell (the point group $O_h$)

$$\mathbf{D}(i) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \mathbf{D}\left(C_{4y}\right) = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix}, \quad \mathbf{D}(C_{4z}) = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{2.1}$$

The elastic strain process is described by function Φ (ε), where Φ – the elastic strain energy density. In the range of small strains the harmonic approximation can be used [14]. According to it:

$$\Phi(\varepsilon) = \frac{1}{2} S_{ijkl}\varepsilon_{ij}\varepsilon_{kl} \tag{2.2}$$

$S_{ijkl}$ ($i, j, k, l = 1, 2, 3$) is the stiffness tensor. If the course of the process is considered in the nine-dimensional strain space, ***S*** will take the form of the second rank tensor. According to Neumann's principle a quantity describing a physical property of a crystal remains invariant with respect to the operations belonging to the symmetry group characterizing the given crystal [15]. The representation of the symmetry operator $U$ in the nine-dimensional space can be created on the basis of the representation of the symmetry operator $U$ from the three-dimensional space by means of Cartesian product:

$$\mathbf{D}'(U) = \mathbf{D}(U) \otimes \mathbf{D}(U) \tag{2.3}$$

If ***D*** ($U$) is the unitary operator then ***D***' ($U$) will preserve this property. Thus the stiffness tensor characterizing the elastic behavior of the crystal has to fulfill the following conditions:

$$\mathbf{D}'(U)\,\mathbf{S}\,\mathbf{D}'^{T}(U) = \mathbf{S}, \quad U \in G \tag{2.4}$$

where $G$ is the point group of the considered crystal.
In the case of copper, the stiffness tensor is subjected the restrictions associated with the symmetry elements: $i$, $C_{4y}$, $C_{4z}$. Their representations ***D***' ($U$) can be formulated on the basis of the relationships (2.1), (2.3). Satisfying the conditions (2.4) the stiffness tensor takes the form:

$$\mathbf{S} = \begin{pmatrix} S_{1111} & 0 & 0 & 0 & S_{1122} & 0 & 0 & 0 & S_{1122} \\ 0 & S_{1212} & 0 & S_{1221} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & S_{1212} & 0 & 0 & 0 & S_{1221} & 0 & 0 \\ 0 & S_{1221} & 0 & S_{1212} & 0 & 0 & 0 & 0 & 0 \\ S_{1122} & 0 & 0 & 0 & S_{1111} & 0 & 0 & 0 & S_{1122} \\ 0 & 0 & 0 & 0 & 0 & S_{1212} & 0 & S_{1221} & 0 \\ 0 & 0 & S_{1221} & 0 & 0 & 0 & S_{1212} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{1221} & 0 & S_{1212} & 0 \\ S_{1122} & 0 & 0 & 0 & S_{1122} & 0 & 0 & 0 & S_{1111} \end{pmatrix} \tag{2.5}$$

So the tensor ***S*** has four independent components: $S_{1111}$, $S_{1122}$, $S_{1212}$, $S_{1221}$. Symmetry of the strain tensor and the relationship (2.2) impose on the stiffness tensor additional restrictions:

$$S_{ijkl} = S_{jikl} = S_{ijlk} = S_{klij} \tag{2.6}$$

Thus in the case of the copper crystal three independent components: $S_{1111}$, $S_{1122}$, $S_{1212}$ are obtained.

As it is shown above, the form, which takes the stiffness tensor with regard to the crystal symmetry, can be obtained by means of representation theory. The other way is the analysis of the courses of the appropriate strain processes. According to Neumann's principle, the element belonging to the symmetry group of the considered crystal associates the states, in which the strain processes proceed analogically. Thus the energy density stored in these states is identical. Due to this, the relations between the components of the stiffness tensor are obtained. Let's take into consideration the strain process described by the tensor $\boldsymbol{\varepsilon}$ with one non-zero element $\varepsilon_{11}$ (fig.4a). Under the influence of the symmetry axis $C_{4z}$ the state $\boldsymbol{\varepsilon}$ is transformed into $\boldsymbol{\varepsilon}'$, in which $\varepsilon'_{22} = \varepsilon_{11}$ (fig.4b).

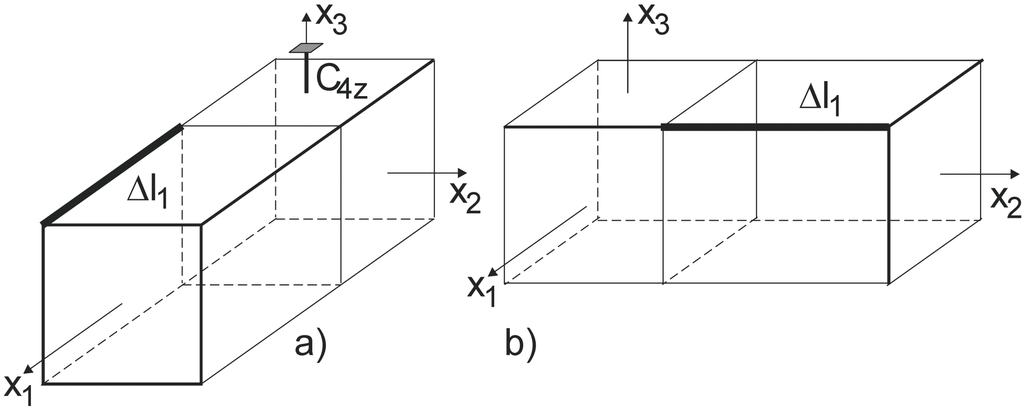

Fig. 4. The elementary cell of the copper crystal subjected to the strain state a) $\boldsymbol{\varepsilon}$ with $\varepsilon_{11} \neq 0$, b) $\boldsymbol{\varepsilon}$', which is the state $\boldsymbol{\varepsilon}$ transformed by the symmetry axis $C_{4z}$

The equality of the energy densities $\Phi(\boldsymbol{\varepsilon})$ and $\Phi(\boldsymbol{\varepsilon}')$ allows obtaining of the following relationship:

$$\frac{1}{2}S_{1111}\varepsilon_{11}^2 = \frac{1}{2}S_{2222}(\varepsilon_{22}^{'})^2 \Rightarrow S_{1111} = S_{2222} \tag{2.7}$$

Likewise one can derive the equalities:

$$S_{1212} = S_{1313}, \quad S_{1122} = S_{1133} \tag{2.8}$$

Using of the symmetry axis $C_{4y}$ gives the following relationships:

$$S_{1111} = S_{3333}, S_{1212} = S_{2323}, S_{1122} = S_{2233} \tag{2.9}$$

To show the vanishing of the stiffness tensor components three strain processes has to be considered simultaneously. As an example, let's take into account the strain state $\boldsymbol{\varepsilon}$ with two non – zero elements: $\varepsilon_{12}$, $\varepsilon_{33}$ (fig. 5a). The symmetry axis $C_{4y}$ transforms it into $\boldsymbol{\varepsilon}$', in which $\varepsilon'_{11} = \varepsilon_{33}$, $\varepsilon'_{23} = \varepsilon_{12}$ (fig. 5b). Applying of $C_{4y}$ axis in the case of $\boldsymbol{\varepsilon}$' introduces the state $\boldsymbol{\varepsilon}$" with $\varepsilon_{33}^{''} = \varepsilon_{33}$, $\varepsilon_{12}^{''} = -\varepsilon_{12}$ (fig.5c).

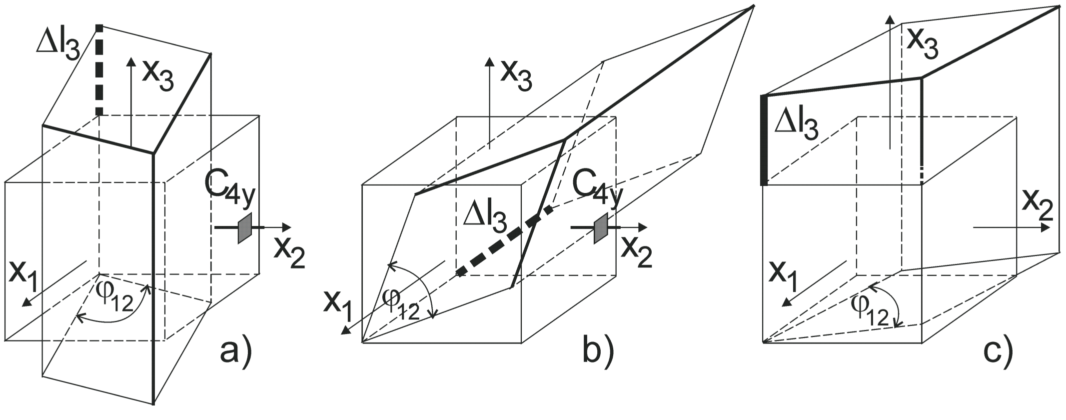

Fig. 5. The elementary cell of the copper crystal subjected to the strain state a) $\boldsymbol{\varepsilon}$ with $\varepsilon_{12} \neq 0$, $\varepsilon_{33} \neq 0$, b) $\boldsymbol{\varepsilon}$', which is the state $\boldsymbol{\varepsilon}$ transformed by the symmetry axis $C_{4y}$, c) $\boldsymbol{\varepsilon}$" which is the state $\boldsymbol{\varepsilon}$' transformed by the symmetry axis $C_{4y}$

The appropriate energy densities are assigned to these states:

$$\Phi(\boldsymbol{\varepsilon}) = \frac{1}{2}\left[S_{3333}\varepsilon_{33}^2 + 4S_{1212}\varepsilon_{12}^2 + 4S_{1233}\varepsilon_{12}\varepsilon_{33}\right] \tag{2.10}$$

$$\Phi(\boldsymbol{\varepsilon}') = \frac{1}{2}\left[S_{1111}\varepsilon_{33}^2 + 4S_{2323}\varepsilon_{12}^2 + 4S_{1123}\varepsilon_{12}\varepsilon_{33}\right] \tag{2.11}$$

$$\Phi(\boldsymbol{\varepsilon}'') = \frac{1}{2}\left[S_{3333}\varepsilon_{33}^2 + 4S_{1212}\varepsilon_{12}^2 - 4S_{1233}\varepsilon_{12}\varepsilon_{33}\right] \tag{2.12}$$

If the relationships (2.9) are taken into account, on the basis of the equalities of the respective energy densities, one will obtain:

$$\left.\begin{array}{l}\Phi(\varepsilon) = \Phi(\varepsilon') \Rightarrow S_{1123} = S_{1233} \\ \Phi(\varepsilon') = \Phi(\varepsilon'') \Rightarrow S_{1123} = -S_{1233}\end{array}\right| \Rightarrow S_{1123} = S_{1233} = 0 \tag{2.13}$$

The both discussed above approaches: application of the representation theory to study the influence of the crystal symmetry on the form of stiffness tensor $\boldsymbol{S}$ and application of the energy density in physical approach was not considered in such a way by other authors and, according to authors opinion, is rather new.

The symmetry of the copper crystal is so high that determines the eigen – states (vectors) of the stiffness tensor independently. The values of the components of the tensor $\boldsymbol{S}$ do not have influence on their form. In the case of fcc structure one can distinguish three significant eigen-subspaces characterized by the eigen-values, so called Kelvin moduli [8], [9] which can be calculated from (2.5) after taking into account (2.6). Thus:

$$\lambda_I = S_{1111} + 2S_{1122}, \quad \lambda_{II} = S_{1111} - S_{1122}, \quad \lambda_{III} = 2S_{1212} \tag{2.14}$$

The base of each of the subspaces is formed by the appropriate set of eigen – vectors:

$$\omega_{\text{I}} = \frac{1}{\sqrt{3}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \omega_{\text{II.1}} = \frac{1}{\sqrt{6}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix}, \quad \omega_{\text{II.2}} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{2.15}$$

$$\omega_{\text{III.1}} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \omega_{\text{III.2}} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad \omega_{\text{III.3}} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{2.16}$$

Using the parameter $\varepsilon$ the strain processes can be assigned to the particular eigen-states:

$$\varepsilon_{\text{I}} = \varepsilon\omega_{\text{I}}, \quad \varepsilon_{\text{II.1}} = \varepsilon\omega_{\text{II.1}}, \quad \varepsilon_{\text{II.2}} = \varepsilon\omega_{\text{II.2}} \tag{2.17}$$

$$\varepsilon_{\text{III.1}} = \varepsilon\omega_{\text{III.1}}, \quad \varepsilon_{\text{III.2}} = \varepsilon\omega_{\text{III.2}}, \quad \varepsilon_{\text{III.3}} = \varepsilon\omega_{\text{III.3}} \tag{2.18}$$

The energy densities stored in the processes belonging to one of the subspace I, II, III are identical. Therefore each of the subspaces is characterized by the appropriate function [8], [9]:

$$\Phi_i(\varepsilon) = \frac{1}{2}\lambda_i\varepsilon^2, \quad i = \text{I}, \text{II}, \text{III} \tag{2.19}$$

An arbitrary strain process can be presented as a linear combination of the elementary processes related with three elastic eigen – states (2.17), (2.18). In the same way the density of elastic energy is decomposed (2.19). The discussed results show how the crystal symmetry controls the elastic energy distribution into three additive terms.

On the basis of above considerations the parameters of the studied model can be identified from the following conditions:

$$\frac{d^2\Phi_j(\varepsilon)}{d\varepsilon^2} = \lambda_j\,, \tag{2.20}$$

where $\lambda_j$ are the experimental values of Kelvin moduli and $\Phi_j(\varepsilon)$, $j = 1, 2, 3$ are the energy densities stored in three elementary processes: $\varepsilon_I = \varepsilon\omega_1$, $\varepsilon_2 = \varepsilon\omega_{II,I}$, $\varepsilon_3 = \varepsilon(\omega_{\text{III.1}} + \omega_{\text{III.2}} + \omega_{\text{III.3}})$. Using RGL model (1.2), (1.3) the energy densities take the following form:

$$\Phi_j(\varepsilon) = \left(A\sum_i \exp\left(-p\left(\frac{r_i^{(j)}(\varepsilon)}{r_0} - 1\right)\right) - \xi\sqrt{\sum_i \exp\left(-2q\left(\frac{r_i^{(j)}(\varepsilon)}{r_0} - 1\right)\right)}\right)\Bigg/\Omega, \tag{2.21}$$

where $r_i^{(j)}$ is the distance of the $i$ atom from the considered central one in the deformed crystal subjected to the $j$ deformation path, while $\Omega$ is the volume of the crystal unit cell. Then the atomic model behaves correctly when is subjected arbitrary infinite small strains. Additionally the equilibrium conditions is introduced:

$$\left.\frac{d\Phi_1(\varepsilon)}{d\varepsilon}\right|_{\varepsilon=0} = 0 \tag{2.22}$$

The identified atomic RGL model behaves correctly if the aforementioned conditions are satisfied.

The presented way of the parameters identification with use of the energy densities (2.21), related with three eigen-spaces of the stiffness tensor $\boldsymbol{S}$, gives the possibility of parameter calculation with controlled relative error. The advantage of the elastic eigen-states approach is that it provides the high symmetry of deformed crystal, what enables obtaining of the analytic formulae for $r_i^{(j)}(\varepsilon)$. The symbolic and numerical calculations were carried out with use of MATLAB. An example of calculated parameter values for $i = 5$ are given as follows: $A$=0.0855 eV, $\xi$=1.224 eV, $p$=10.960, q=2.278. They are different from the values assumed by Dimitriev et al. [2], [3]. He used RGL potential identified by Hecquet et al. [12], where the parameters are determined according to assumption that: cohesive energy and lattice parameter take the experimental values, while the elastic constants are as near experimental ones as possible.

## 3. Verification of RGL atomistic model by means of ab initio simulations of strain processes

The functions of the energy density stored during different strain processes $\Phi\ (\varepsilon)$ obtained by means of ab initio calculations are the base of verification of created atomic models. Accordingly, the own program has been written, which calling the commercial program CASTEP (Cambridge Serial Total Energy Package) [10] performs the simulation of an arbitrary homogeneous strain process for ideal metal crystals of the cubic symmetry [7]. The strain process is defined by Green tensor, which diagonal elements determine the relative elongations (stretches) of the edges of the elementary cell and the off-diagonal elements correspond to the changes of the angles between the edges (shears). As regards the homogeneity, each elementary cell is subjected to an identical deformation. Accordingly, the homogeneously strained ideal crystal can be still represented by Bravais lattice. On the basis of Green strain tensor, in the given iteration step, the created program defines geometry of the elementary cell with its symmetry and together with the other parameters determined by user the program introduces them as the input data into CASTEP code. The additional parameters are: the cutoff energy $E_{cut}$, the density of Monkhorst-Pack mesh and the type of the exchange-correlation functional. In the performed simulations the functional in a form proposed by J.P. Perdew and Y.A. Wang (PW91) [16] obtained by the generalized gradient approximation (GGA) is used. Because of the way of operation of CASTEP software the own code is the Linux shell script written in bash. As a result of the program application one obtains the set of the total energies per the elementary cell volume $E_c$ corresponding to the successive stages of the strain process. On the basis of the calculated $E_c$ one gets the strain energy density according to the formula [17]:

$$\Phi(\varepsilon) = \frac{E_c(\varepsilon) - E_c\left(\boldsymbol{\varepsilon}_{\mathbf{eq}}\right)}{V_{eq}} \tag{3.1}$$

where $E_c(\boldsymbol{\varepsilon}_{eq})$ is the total energy of the ideal crystal in the equilibrium state per the elementary cell of volume $V_{eq}$.

The developed method of the strain process simulation was used to characterize the elastic behaviour of Cu crystal in the range of small strains. In this aim, the ideal Cu crystal has been subjected to the strain processes belonging to the particular eigen-subspaces of the stiffness tensor. As a result the relations $\Phi\ (\varepsilon_i)$, $i$=I, II, III were obtained. Approximating them by parabolas, according to the formulas (2.19), Kelvin moduli $\lambda_I$, $\lambda_{II}$, $\lambda_{III}$ were determined. The calculation parameters: $E_{cut}$, density of Monkhorst-Pack mesh were selected in such a way to get the total energies $E_c(\varepsilon)$ converged to less than 0.1 meV/atom. The comparison of the obtained results to the experimental data [18] enabled to verify the developed program.

In the case of the first eigen-state the parameter $\varepsilon$ (2.17) is associated with the relative elongation of three perpendicular edges of the elementary cell $\Delta a_{z.I} / a_{z.eq}$ by the following formula:

$$\varepsilon = \frac{\sqrt{3}}{2}\left[\left(\frac{\Delta a_{z.I}}{a_{z.eq}} + 1\right)^2 - 1\right] \tag{3.2}$$

During the strain process $\Delta a_{z.I} = \langle -0.04 \quad 0.03 \rangle$ Å with the iteration step $h = 0.001$Å. The symmetry of the elementary cell doesn't change and it is determined by the symmetry elements shown at the fig.3 The cutoff energy $E_{cut}$=400eV and Monkhorst – Pack mesh density 13x13x13 were assumed for the calculations. The total energy of the crystal per the elementary cell $E_c$ reaches the minimum at the equilibrium configuration. Thus using the relation $E_c\ (a_{z.I})$ obtained from the simulation, the equilibrium lattice constant $a_{z.eq} = 3.604$Å was determined. This result differs from experimental one of 0.3%. The obtained equilibrium lattice constant enables to present the simulation results in the form of the relation $\Phi\ (\varepsilon_I)$. Applying the least-squares method $\Phi\ (\varepsilon_I)$ has been approximated by a parabola, the doubled coefficient of which is Kelvin modulus $\lambda_I$ (fig.6). The simulation results reveal very good agreement with the experiment [18]. The square of the correlation coefficient $R^2$=0.9981 and Kelvin modulus $\lambda_I$=424.4 GPa differs from the experimental one of 0.4%.

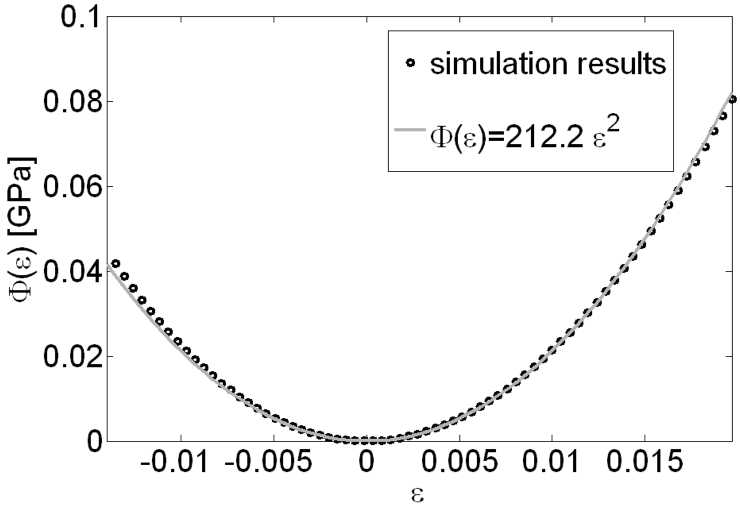

Fig. 6. The elastic strain energy density $\Phi$ as a function of the parameter $\varepsilon$ controlling the course of the process belonging to the first eigen-subspace of the stiffness tensor

Let's take into account the first of the considered states belonging to the second eigen-subspace of the stiffness tensor (2.15). The parameter (2.17) can be replaced by the relative elongation of one of the edges lying in the base of the elementary cell $\Delta a_{z.II} / a_{z.eq}$ fig.3. The two quantities are related as follows:

$$\varepsilon = \frac{\sqrt{6}}{2}\left[\left(\frac{\Delta a_{z.II}}{a_{z.eq}} + 1\right)^2 - 1\right] \qquad ((3.3)$$

The course of the strain process is determined by $\Delta a_{z.II}$ changing in the range $\langle -0.024 \quad 0.025 \rangle \mathring{A}$ with the iteration step $h = 0.001\mathring{A}$. According to Green strain tensor $\boldsymbol{\varepsilon}_{II.1}$ (2.17) the elongation of the edge of the elementary cell base induces appropriate shortening of the perpendicular edge. Thus, the elementary cell takes the form (fig.7), which symmetry is characterized by the group $D_{4h}$. In the considered range of changes of $\Delta a_{z.II}$ it can be assumed that the elongation induces double shortening. The simulation of the described strain process has been carried out at the following parameters: $E_{cut}$=500eV and Monhhorst-Pack mesh density 14x14x14. As a result one has obtained Kelvin modulus $\lambda_{II}$=51.98GPa (fig.8). Comparing to the experimental value the error amounts to 1.3%. The square of the correlation coefficient $R^2$=0.9975.

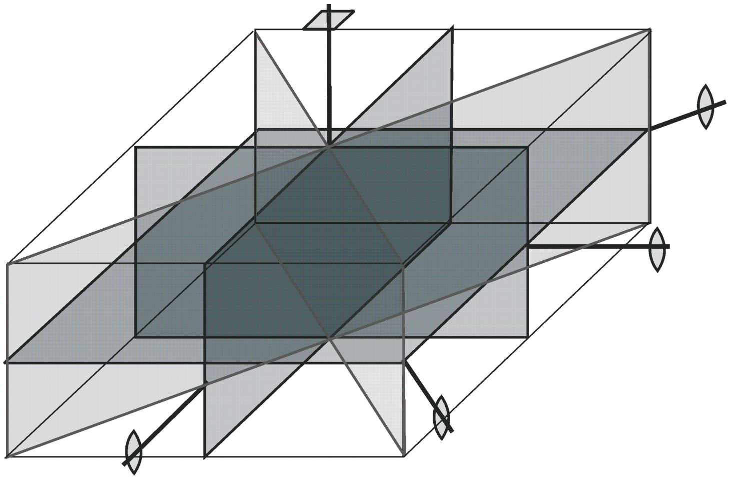

Fig. 7. The symmetry elements of Cu elementary cell subjected to the strain process $\boldsymbol{\varepsilon}_{II.1}$ belonging to the second eigen-subspace (the point group $D_{4h}$)

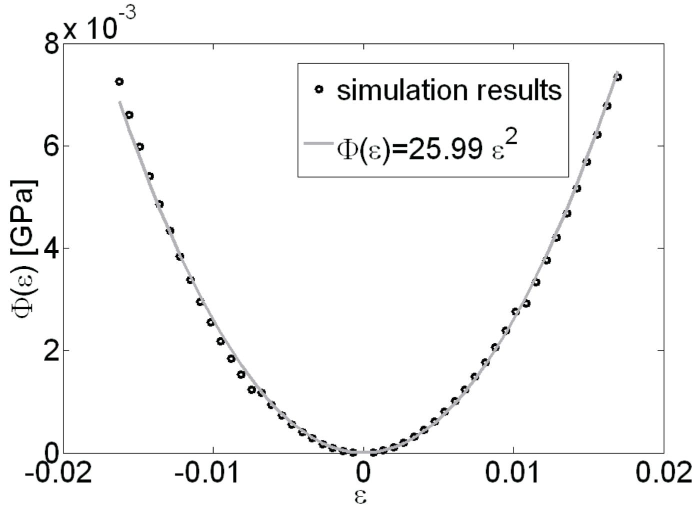

Fig. 8. The elastic strain energy density $\Phi$ as a function of the parameter $\varepsilon$ controlling the course of the process $\boldsymbol{\varepsilon}_{II.1}$ belonging to the second eigen-subspace of the stiffness tensor

In the strain process determined by the first of three distinguished states belonging to the third eigen-subspace of the stiffness tensor (2.16), there occurs only change of the angle between two edges in the base of elementary cell $\Delta\varphi_{12} = 90° - \varphi_{12}$ (fig.9) Thus, one can relate the parameter $\varepsilon$ (2.18) to $\cos(\varphi_{12})$ as follows:

$$\varepsilon = \frac{\sqrt{2}}{2} \sin \Delta\varphi_{12} \tag{3.4}$$

The quantity is varied in the range $\langle -1.2°, 1.2° \rangle$ with the iteration step $h = 0.1°$. During the strain process, the elementary cell takes the form of much lower symmetry characterized by group $C_{2h}$ (fig.9).

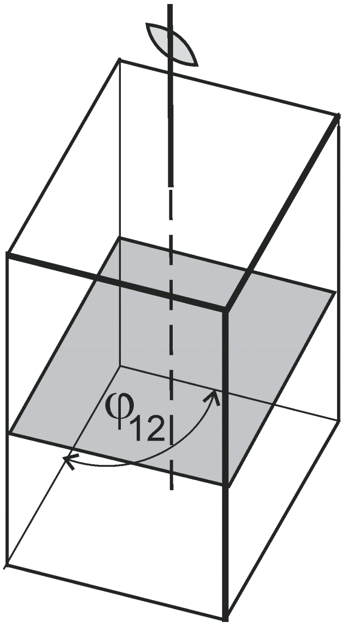

Fig. 9. The symmetry elements of Cu elementary cell subjected to the strain process $\boldsymbol{\varepsilon}_{III.1}$ belonging to the third eigen-subspace (the point group $C_{2h}$)

Performing the simulation of the described process analogically as in the case of the second eigen-subspace one has obtained the results shown in fig.10 and so $\lambda_{III}$=151.52 GPa. The error of determination of Kelvin modulus amounts to 7.4% and $R^2$=0.9999. Thus, despite the low symmetry of the system in the current configuration and so lowered accuracy of the quantum – mechanical calculations, the obtained results are highly consistent with the experiment.

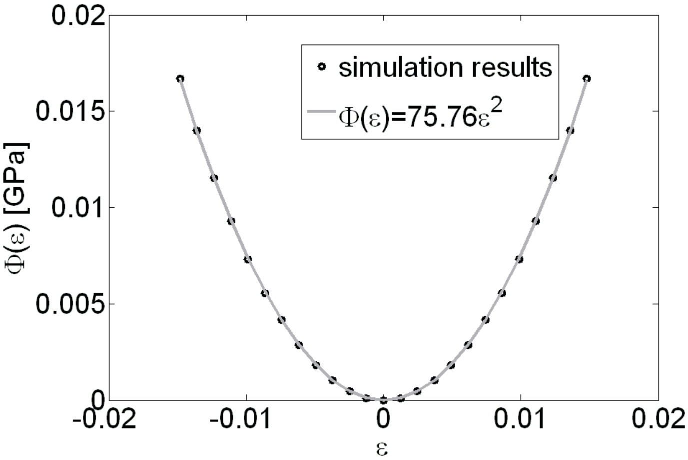

Fig. 10. The elastic strain energy density Φ as a function of the parameter $\varepsilon$ controlling the course of the process $\boldsymbol{\varepsilon}_{III.1}$ belonging to the third eigen-subspace of the stiffness tensor

Let's take into account another process belonging to the third subspace. This process is defined by Green strain tensor $\varepsilon_{trig}$ being the linear combination of the states presented in chapter 2:

$$\varepsilon_{\mathbf{trig}} = \frac{\varepsilon}{\sqrt{6}} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \tag{3.5}$$

According to the tensor $\boldsymbol{\varepsilon}_{trig}$ there occurs an identical change of the angles between three perpendicular edges of the elementary cell $\Delta\varphi$. The parameter $\varepsilon$ is related to $\Delta\varphi$ as follows:

$$\varepsilon = \frac{\sqrt{6}}{2} \sin \Delta\varphi \tag{3.6}$$

$\Delta\varphi$ undergoes changes in the range $\langle -2°,\ 2° \rangle$ with the iteration step $h = 0.1°$.

Thus, during the process the cuboid is being replaced by the rhombohedron. Accordingly, one obtains the elementary cell of much higher symmetry ($D_{3d}$ - fig.11) then in the early considered process of change of one angle.

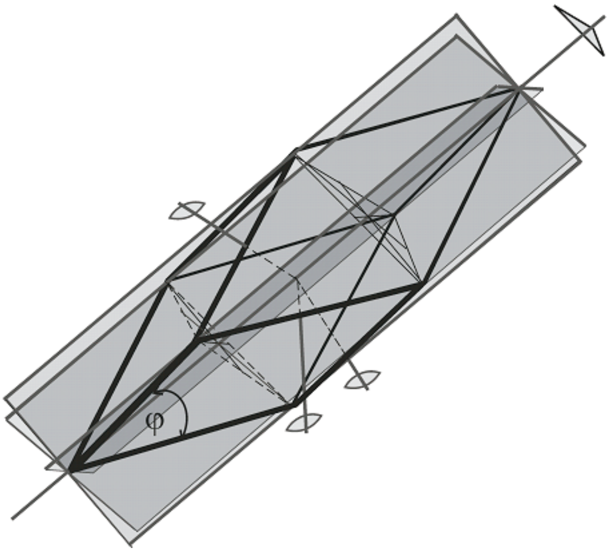

Fig. 11. The symmetry elements of Cu elementary cell subjected to the strain process $\boldsymbol{\varepsilon}_{trig}$ belonging to the third eigen-subspace (the point group $D_{3d}$)

Due to this fact, performing the simulation analogical as previously, one can expect much better results. According to this one has obtained Kelvin modulus $\lambda_{III}$=158.3 GPa (fig.12) differing from the experimental value only of 3.5%.

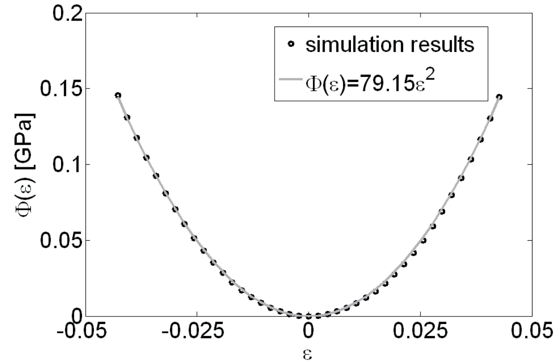

Fig. 12. The elastic strain energy density Φ as a function of the parameter $\varepsilon$ controlling the course of the process $\boldsymbol{\varepsilon}_{trig}$ belonging to the third eigen-subspace of the stiffness tensor

The results obtained in the case of the process belonging to the second subspace were used to verify the considered RGL atomistic model. In this aim the model was subjected to the tetragonal deformation. The calculations were carried out for two sets of parameters: $A$, $\xi$, $p$, $q$. As a result the functions $\Phi(\varepsilon)$ depicted in fig. 13 were obtained. Their comparison to the ab initio simulation enables to draw the conclusion that the atomistic model behaves correctly in the range of small strains. However the potential RGL formulated in the present work gives the better results. Unfortunately applying the considered model in the range of large strains one is not able to obtain the metastable phase (bcc) [19], which should appear at $\varepsilon \sqrt{6}/10$. According to LCAO method which allows to formulate the considered model the interatomic bond should be created by d electrons as well as s- electrons (fig.2). The RGL potential neglects the last ones. The considered model behaves correctly in the range of small strains only with regard to suitable selection of parameters, what was shown in the present paper. In the range of finite strains the interatomic bond should base on s-d hybridization. Such a model is the better approximation of interatomic interactions across copper crystal and gives a chance for the correct description of Cu – Cu interactions between interfacial copper monolayer and bulk copper in the case of Cu/$Al_2O_3$ system. The other solution is the application of RGL potential identified in the present paper restricting oneself to small strains. Dimitriev et al, in the case of bulk Cu, used parameters arranged by Hecquet et al. [12] and describing the interaction between the interfacial Cu monolayer and the rest of Cu crystal identified the parameters by means of the rigid tensile test, where the strain reached to 3.6 [3]. They did not obtain satisfied results [4].

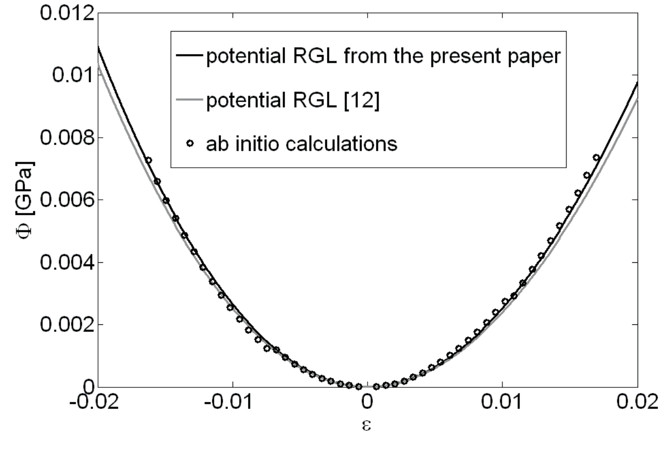

Fig. 13. Functions of the energy density $\Phi(\varepsilon)$ characterizing proceedings of the tetragonal strain processes. They are obtained by means of the atomistic models and ab initio calculations, respectively

## 4. Conclusions

Using crystal symmetry the parameters of RGL potential in the case of copper crystal were identified. One showed that the formulated model behaved correctly in the range of small strains. Accordingly it can describe the interactions across bulk copper being a part of the system: (111)Cu——(0001)$Al_2O_3$ if the system is subjected to small deformations. The data for the model verifications were obtained by means of own program, which using the commercial program CASTEP performs the simulations of homogenous strain processes. In the paper, there was shown that consideration of finite deformations requires developing of a new model in which the interatomic bond bases on s – d hybridization. This will be the subject of further study. Similarly to the present paper, in the new model, there will be taken into account crystal symmetry by means of the representation of the point group operating in the nine dimensional space of strains. To formulate and test this model the developed program for simulations of strain processes will be used.

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### REFERENCES

[1] V. Rosato, M. Guillope, B. Legrand, Thermodynamical and structural properties of f.c.c transition metals using a simple tight-binding model, Phil. Mag. **59**, 321, (1989).

[2] S. V. Dimitriev, N. Yoshikawa, Y. Kagawa, Misfit accommodation at the Cu(111)/$\alpha$-$Al_2O_3$ (0001) interface studied by atomistic simulation, Comp. Mater. Sci. **29**, 95, (2004).

[3] S. V. Dimitriev et al., Atomistic structure of the Cu(111)/$\alpha$-$Al_2O_3$ (0001) interface in terms of interatomic potentials fitted to ab initio results, Acta Mater **52**, 1959 (2004).

[4] S. V. Dimitriev et al., Modeling interatomic interactions across Cu/$\alpha$-$Al_2O_3$ interface, Comp. Mater. Sci. **36**, 281 2006.

[5] I. G. Batyrev, L. Kleinman, In-plane relaxation of Cu(111) and Al(111)/$\alpha$-$Al_2O_3$ (0001) interfaces, phys revb **64**, 033410 (2001).

[6] W. Zhang, J. R. Smith, A. G. Evans, The connection between ab initio calculation and interface adhesion measurements on metal/ oxide systems: Ni/$Al_2O_3$ and Cu/$Al_2O_3$, Acta Mater. **50**, 3803 (2002).

[7] K. Nalepka, Physical foundations of energy-based criterion of material effort for anisotropic solids on the example of a single cupper crystal, 2005 (in Polish) – doctor thesis, supervisor: prof. R.B. Pęcherski.

[8] J. Rychlewski, On Hooke's law, PMM **48**, 420-432, 1984 (in Russian) – Prikl. Matem. Mekhan. **48**, 303-314, 1984 (English translation)

[9] J. Rychlewski, Unconventional approach to linear elasticity,Arch. Mech. **47**, 159-171 (1995).

[10] Quantum Mechanics Physics – CASTEP, ESOCS, FASTSTRUCTURE, Molecular Simulation inc., San Diego 1997.

[11] M. C. Payne et al., Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients, Rev. Mod. Phys. **64**, 1045-1096 (1992).

[12] P. Hecquet, B. Salanon, B. Legrand, Energetics of surface defects: toward a simplified model, surf. Sci. **459**, 23-32 (2000).

[13] International Tables for Crystallography, Volume A, Space-group symmetry, Kluwer Academic Publishers, Dordrecht, 2002.

[14] N. W. Ashcroft, N. D. Mermin, Fizyka Ciała Stałego, PWN, Warszawa, 1986.

[15] J. F. Nye, Physical properties of crystals: their representation by tensors and matrices, clarendon press, oxford, 1957.

[16] J. P. Perdew, Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, Phys. Rev. B **45**, 13244-13249 (1992).

[17] R. Phillips, Crystals, Defects and Microstructures, Modeling Across Scales, Cambridge University Press, 2001.

[18] C. Kittel, Wstęp do Fizyki Ciała Stałego, PWN, Warszawa, 1976.

[19] T. Kraft, P. M. Marcus, Elastic constants and the instability of its bcc structure, Phys. Rev. B **48**, 5886-5890 (1993).

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