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## RECONFIGURATION OF POINT DEFECTS IN FCC AND HCP METALS AT INITIAL STAGE OF RECOVERY PROCESS

### REKONFIGURACJA STRUKTURY DEFEKTÓW SIECIOWYCH W POCZĄTKOWYM STADIUM ZDROWIENIA METALI O SIECI RSC I HZ

The conducted studies regarded the analysis of change of structure of point defects occurring during initial stage of recovery of FCC (Al, Cu) and HCP (Ti, Mg and Zn) metals at temperature close to  $T_h = 0.5T_m$ . The changes in resistivity of the deformed and later recovered samples were measured. The recovery time was 1, 2, 3, 4 or 5 min. The observed changes were correlated with reorganization of arrangement of lattice defects during annealing.

*Keywords:* FCC metals, HCP metals, point defects, resistivity measurements

Przeprowadzone badania dotyczyły analizy zmian struktury defektów sieciowych, zachodzących w początkowym okresie zdrowienia metali RSC (Al, Cu) oraz HZ (Ti, Mg oraz Zn) w temperaturze zbliżonej do  $T = 0.5 T_m$ . Badano zmiany oporu właściwego odkształconych próbek poddanych zdrowieniu przy czasach 1, 2, 3, 4 lub 5 min. Obserwowane zmiany skorelowano z reorganizacją struktury defektów sieciowych podczas wyżarzania.

Uzyskane wyniki pokazały, że w przypadku metali o sieci RSC spadek oporności właściwej w funkcji czasu zdrowienia maleje monotonicznie, co świadczy o postępującej anihilacji defektów strukturalnych. Dla sieci HZ stwierdzono, że zmiany te mają charakter oscylacyjny z minimum występującym po czasie około 1-2 min. Świadczy to o rekonfiguracji defektów sieciowych i tworzeniu się w początkowym stadium zdrowienia złożonych, niestabilnych termodynamicznie struktur (układy wakancji, pętle, zarodki dyslokacji), które powodują chwilowy efekt oczyszczenia struktury i w konsekwencji spadek oporu właściwego poniżej poziomu właściwego dla struktury całkowicie poddanej zdrowieniu, charakteryzującej się równowagową koncentracją wakancji.

## 1. Introduction

Lattice defects such as vacancies or dislocation are characteristic feature of each metal. Their role in the hardening processes is well known and was a subject of many papers [1-5]. It is also known, that heat treatment of the deformed metal leads to its recovery according to the following scheme:

- Thermally activated migration of interstitial atoms with simultaneous migration of vacancies causing decrease of vacancy concentration
- Rearrangement of dislocations and annihilation of dislocations
- Growth of sub-grains in preferential directions

Not clear, however, is the path leading to the reconfiguration of the lattice defects at the beginning stage of the recovery process in the deformed metal.

Studies performed on zinc and cadmium single crystals deformed at low temperature showed a significant influence of configuration of point defects on the hardening process of the deformed structure. A tendency towards formation of complex vacancy structures such as loops, bi-vacancies, and

tri-vacancies at certain temperature-stress conditions, causes anomalies of mechanical and physical properties. The phenomena are closely connected with crystal lattice and were often observed in hexagonal metals with high c/a ratio [9, 14].

Resistivity of metal or alloy is strongly connected to the concentration of defects in the structure, which limits free path of conducting electrons interacting with phonons and dissipation centers. The interactions occur at an atomic level. Therefore, the number of the scattering centers to the number of atoms forming a crystal lattice of a studied conductor is an essential element having influence on resistivity. Statistical analysis of a typical metal points out, that the most abundant group of defects of the crystal lattice is vacancies. The additional scattering element are the mentioned phonon interactions responsible mainly for existence of thermal component of specific resistance [6,15]. However, conducting measurements at liquid nitrogen allows to keep the thermal component at constant level, thus it is permitted to neglect it in qualitative analyses.

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Some electrical and thermodynamic data of the investigated elements [6-7]

Metal	Resistivity at 300K $\times 10^{-8}$ [ $\Omega\text{m}$ ]	Resistivity at 77K $\times 10^{-9}$ [ $\Omega\text{m}$ ]	Self-diffusion coefficient $D_0$ $\times 10^{-4}$ [ $\text{m}^2\text{s}^{-1}$ ]	Diffusion activation energy $Q$ [ $\text{kJ mol}^{-1}$ ]	Single vacancy activation energy * [eV]	Melting point [K]
Al	2.5	2.46	1.7	142	1.47	933
Cu	1.55	2.34	0.2	197.2	2.04	1356
Ti	42	110 **	0.5-0.66	150	1.55	1911
Mg(a)	4.18	9.84	1.5	136.1	1.41	923
Mg(c)	3.48	6.97	1.0	134.8	1.39	923
Zn(a)	5.38	1.1	0.58	101.7	1.05	691
Zn(c)	5.58	1.05	0.13	91.3	0.94	691

\*) single vacancy activation energy contains a sum of two elements: enthalpy of vacancy creation and enthalpy of migration

\*\*) own measurement

The studied samples underwent 50% plastic deformation by rolling. The deformation process caused introduction to material large amount of structural defects such as vacancies and dislocations. Additionally, each metal is characterized by certain amount of vacancies due to thermal instability of the structure. It is to underline, that formation of a single vacancy is connected with formation of interstitial atom. Thus, two types of defects of opposite signs are produced, which mutual interactions leads to structural changes in a material.

Natural feature of structure is pursuit of achieving at certain thermal exposition the equilibrium concentration of vacancies typical for given temperature. The tendency is described by a formula, where the equilibrium concentration of vacancies is given by the ratio of number of nodes  $n$  to the number of atoms  $N$ ; dependency of  $n/N$  from temperature  $T$  and energy of formation of a single vacancy  $E_v$  is given by equation:

$$\frac{n}{N} = \exp\left(-\frac{E_v}{kT}\right) \quad (1)$$

where:  $k$  – is Boltzmann constant

Thus, the amount of vacancies increases exponentially with temperature.

In case of pre-deformed metallic sample followed by annealing the following processes will compete mainly:

- annihilation of vacancies introduced by deformation by recovery process
- formation of thermal vacancies as natural mechanism to receive equilibrium concentration characteristic for given annealing temperature
- formation of nuclei of new grains and dislocation structures
- in some cases: possibility of formation of complex vacancy arrangements such as multi-vacancies and vacancy loops (Fig. 1)

Studies performed at various metals showed, that complex vacancy arrangements appearing in FCC structures have thermodynamically stable character and do not exhibit tendency to reconfiguration. They are also characterized by energy diversification. The results show that the close-packed (111)

surface has the lowest surface energy and the (110) surface has the largest surface energy. There is a significant difference among the vacancy formation energies between the different surfaces. The vacancy formation energy of the (111) surface is the highest, while that of the (110) surface is the lowest [16].

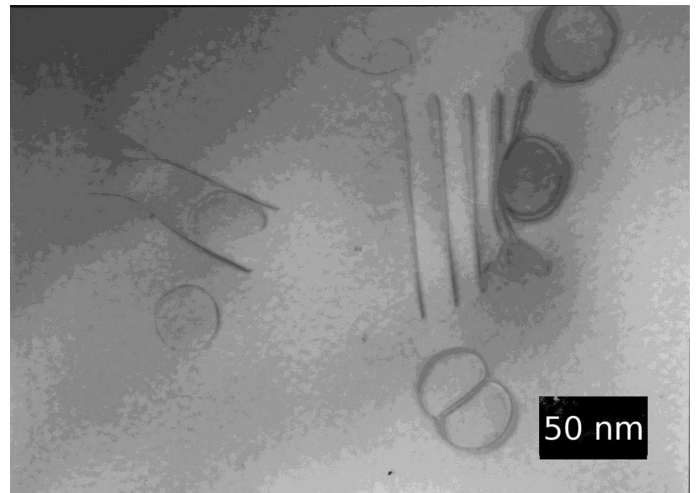


Fig. 1. TEM micrograph of vacancy loops in zinc

On the other hand in the HCP metals, especially in those with high  $c/a$  ratio, the vacancy mechanism play important role in the hardening processes causing phenomena of anomaly of mechanical properties at various temperatures.

The amount of defects in structure affects resistivity and mechanical properties of a metal or alloy. According to Matthiessen rule, the measured value of resistivity includes few components:

$$\rho = \rho_d + \rho_p + \rho_i + \rho_{gb}$$

where

$\rho_d$  – background resistivity from electron scattering at dislocations

$\rho_p$  – background resistivity from electron scattering at phonons

$\rho_i$  – background resistivity from electron scattering at point defects

$\rho_{gb}$  – background resistivity from electron scattering at grain boundaries.

Energy needed to produce a single vacancy in a pure metal is in the range  $\Delta H = 0.5$  to  $1$  eV and depends mainly on the strength of interatomic bonds. This is a value much lower than the one necessary to produce a single dislocation in the pure metal. Therefore, the quantitative domination of point defects in the structure is noted. The analogical situation takes place in case of ability of a vacancy to migrate. The energy needed to move a vacancy is much lower than energy needed to move a dislocation. Thus, the changes in resistivity observed in first minutes of the recovery process should be connected with reorganization of the point-defect structure in crystal lattice. Dislocations and grain boundaries as features of a bigger scale and significantly less abundant, express much smaller effect on the electrical parameters of a metal.

The differences in specific conductivity of chosen metals should be also taken into consideration, i.e. resistivity of titanium and copper at 300K differs by about 20 times, what causes differences in sensitivity of described method for particular metals. The same quantitative change in relation to scattering centers caused in various metals will translate to other scale of changes in electrical properties. Despite this, the method of analysis of structural changes by means of measurements of the electrical properties allows to perform qualitative evaluation of processes undergoing in a material and may make up for a starting point for further studies.

Basing on the above information a respective experiment was designed and conducted.

## 2. Methods

Five metals with various crystal lattice and lattice parameters given in table 1 were chosen: Al (99.97 wt.%), Cu (99.97 wt.%), Ti (99.95 wt.%), Mg (99.7 wt.%) and Zn (99.995 wt.%). Aluminum and copper represent face-centered-cubic (FCC) lattice while titanium, magnesium and zinc the hexagonal-closed-packed (HCP) one. The FCC and HCP lattices were chosen due to their structural similarity: both lattices are constructed from closed packed planes with highest density of atoms varying only in the stacking sequence (ABCABC in case of FCC and ABAB in case of HCP lattice). Aluminum and copper were chosen for their relatively low melting temperature and extremely different densities. The hexagonal metals were chosen with respect of their different  $c/a$  ratio:

- $c/a$  of titanium equals 1.587, which is much below the ideal, which is 1.633
- $c/a$  of magnesium equals 1.623, which is the closest value to the ideal one
- $c/a$  of zinc equals 1.856, much higher from the ideal one.

The above metals were deformed by cold-rolling by 50%. Next, samples were cut out as shown in Figure 2. The samples underwent annealing at temperature about  $0.5T_m$  at times of 1 to 5 min. The duration of the process was determined experimentally and reflect the range of the biggest structural changes occurring in the initial stage of annealing. For refer-

ence, samples directly after deformation were used (in Figs. 3-7,  $t = 0$ min) and samples after 1h of annealing (dashed line). In order to minimize time of heating the samples to a given temperature and obtaining the most stable annealing conditions, salt bath was applied. After taking the samples out from the bath, they were cooled in water (supersaturated) and mounted to four-point head to measure resistivity. All the measurements were performed at liquid nitrogen (77K), what allowed to decrease the influence of thermal component of resistivity and keeping it at constant level.

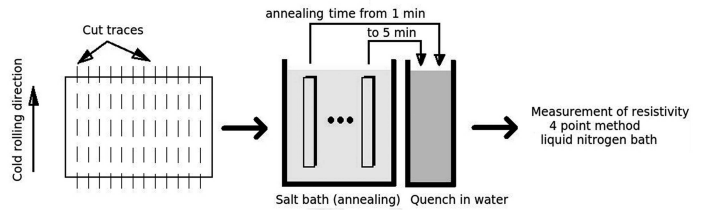


Fig. 2. Preparation of samples: Samples were cut out of the sheet of metal. Next each sample was annealed in salt bath, followed by quenching in water and measurement of resistivity

The following devices were applied for measuring purposes: nanomultimeter KEITHLEY 2182A, power pack with current efficiency of 10A, polarization switch and reference resistor of  $0.22\Omega$  with power loss of 100W. Current in a measuring circuit was  $I = 2$  A, time interval between polarization switches was 3 s. A single measurement point in the characteristic in Figures 3 to 7 consisted of average of 20 measurements. Repeatability of the results was at the level of  $10^{-12}\Omega m$ , what is a value 3 to 4 times lower than the measured one, thus it was not necessary to introduce range of errors on the characteristics (Figs. 3-7)

The results of the test cannot be interpreted quantitatively but they enable for comparison of conductivity of the discussed samples and allow for determination of structural changes after various annealing times.

## 3. Discussion

The experiment regards three aspects of defects of crystal lattice of metal:

- The initial material is strongly defected. Annealing causes recovery what results in reduction of point defects.
- Characteristic material feature depending on the temperature is equilibrium concentration of the vacancies, which rises strongly with an increase of the temperature.
- Large density of the vacancies in the structure leads to a formation of conglomerates (bi-vacancies etc.), which migration energy and lifetime are different than that of a single vacancy.

Short times of annealing at temperature of  $T = 0.5 T_m$  cause overlapping of the four processes mentioned in the introduction. The key aspect of the problem is amount of the energy necessary to produce a vacancy. This is an individual quantity for each metal depending to large extend on its structure and purity. In case of pure metal of crystal lattice of FCC (Al, Cu) or HCP (Mg) lattice with  $c/a$  ratio  $\sim 1.633$ , the energies are much alike. However, for many HCP metals with

c/a ratio different from ideal one, the energies are much lower. Besides, purity of the metal is an important factor; alloying additions decrease the energy of the vacancy formation: in case of copper (0.85eV) the addition of 35% of Zn decreases the energy to 0.30eV.

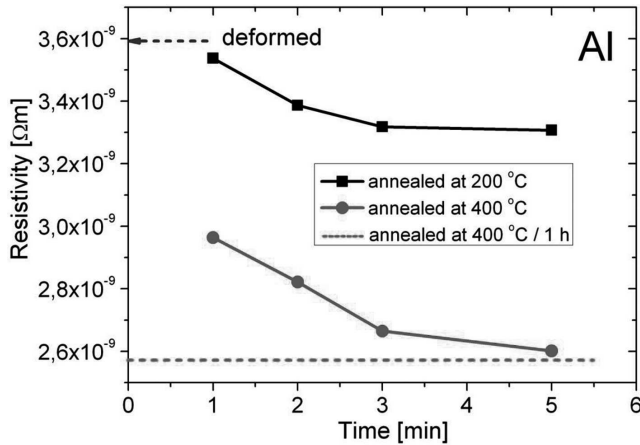


Fig. 3. Characteristics of resistivity in time for as deformed aluminum sample, samples annealed at 200 and 400°C and fully recovered sample (dashed line)

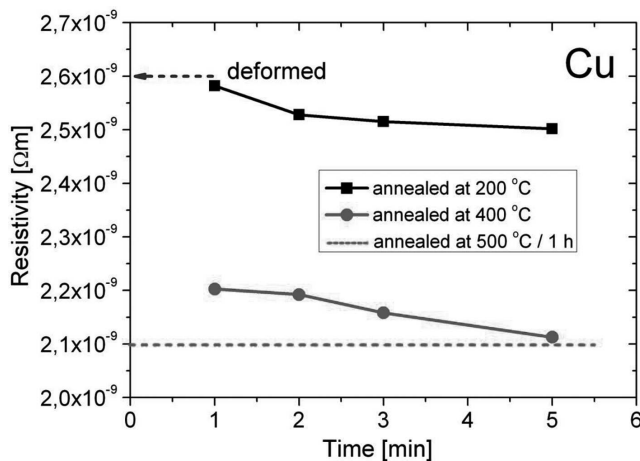


Fig. 4. Characteristics of resistivity in time for as deformed copper sample, samples annealed at 200 and 400°C and fully recovered sample (dashed line)

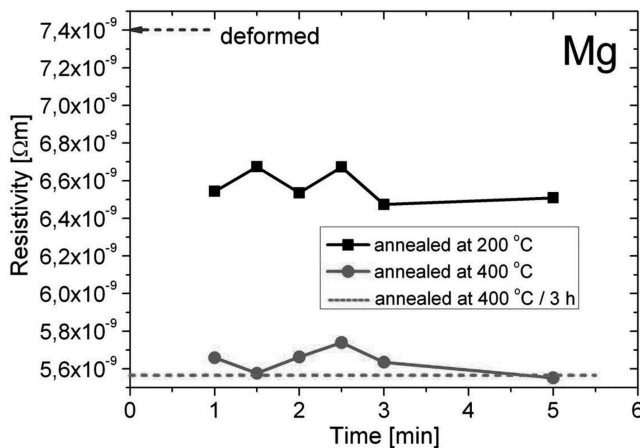


Fig. 5. Characteristics of resistivity in time for as deformed magnesium sample, samples annealed at 200 and 400°C and fully recovered sample (dashed line)

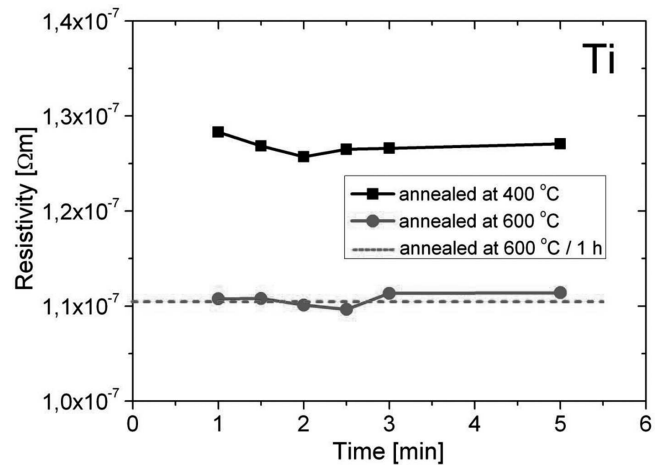


Fig. 6. Characteristics of resistivity in time for as deformed titanium sample, samples annealed at 200 and 400°C and fully recovered sample (dashed line)

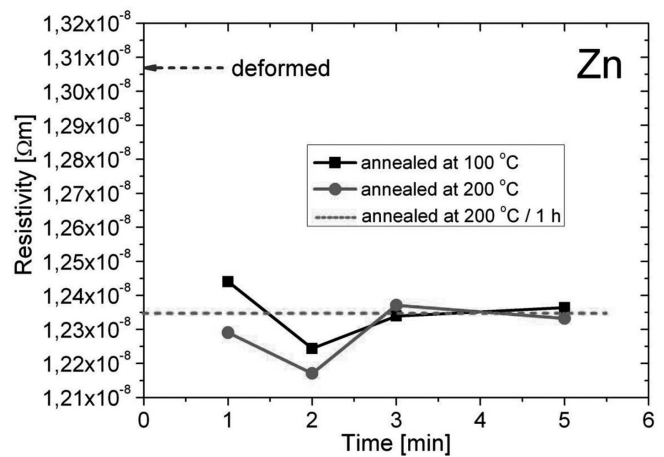


Fig. 7. Characteristics of resistivity in time for as deformed zinc sample, samples annealed at 200 and 400°C and fully recovered sample (dashed line)

Analysis of characteristics of resistivity in annealing time shows, that in some cases they exhibit exponential character, what supports a concept of domination of one process or similar progress of two overlapping processes (Figs. 3 and 4: Al and Cu, curves for annealing at 200°C). The previously-mentioned processes include: on one side, natural annihilation of point defects produced during deformation and as thermal defects due to decrease of temperature leading eventually to equilibrium concentration of defects at given temperature, and on the other side, decomposition of complex vacancy structures such as multi-vacancies and vacancy loops. The second type of the observed dependencies shows also decreasing monotonic character. This may be caused by activation or rapid growth of participation of another process. The effect is present in FCC metals annealed at higher temperatures (Figure 3, 4: Al and Cu, the curves with marked circles, annealed at 400°C). The third case presented in Figures 5-7, regards HCP metals with low energy of vacancy formation (Zn, Mg, Ti). The characteristics of resistivity after determined recovery time is oscillatory, what proves large dynamics of undergoing processes. In previously described cases presented in Figure 3 and 4 for Al and Cu, the relatively high



vacancy formation energy of 0.8 eV does not allow for too big increase of the lattice defects. The amount of vacancies produced in the structure can be significantly higher in case of HCP metals than FCC ones. Large amount of vacancies causes activation of another phenomenon consisting in joining of vacancies into conglomerates of two or more vacancies. Such a system shows much higher mobility (lower migration energy) than a single vacancy [6]. Overlapping of the following processes of: annihilation, growth of the amount of the vacancies to the equilibrium concentration and formation of the vacancy conglomerates results in the observed oscillations on the characteristics.

After certain time, the complex vacancy structures undergo decomposition to single point defects causing an increase of scattering centers by means of conductance electrons in the structure. Thus, the free path of conductance electrons associated by increase of resistivity of metal. The next stage is annihilation of individual vacancies giving the effect of cleaning the structure, and consequently small decrease of resistivity until equilibrium concentration of vacancies is reached.

The analysis of the observed phenomena shows interesting correlation with literature data. According to a model of vacancy diffusion, the value of activation diffusion  $Q$  includes both enthalpy of movement  $\Delta H_w$  as well as enthalpy of formation  $\Delta H_f$  of a vacancy:

$$Q = \Delta H_w + \Delta H_f$$

In case of pure metals,  $\Delta H_w$  and  $\Delta H_f$  exhibit similar proportions, therefore energy of formation of a vacancy of given metal can be compared. Elements with HCP lattice (Ti, Mg and Zn) show the smallest values of diffusion activation energy  $Q$ . Relatively high value of  $Q$  for titanium is due to the highest melting temperature among the studied elements. Therefore, it is characterized by the strongest interatomic bonds. Energy balance confirms possibility of occurring of the discussed phenomena during initial stage of recovery of HCP metals.

#### 4. Conclusions

The obtained results showed in case of FCC metals, a decrease of resistivity in time of recovery decreases monotonically, what attests to progressive annihilation of structural defects. In case of HCP metals, it was observed that the changes exhibit oscillatory characteristics with minimum occurring at time of about 1 to 2 min. Thus, the lattice defects must reconfigure and thermodynamically unstable structures (multi-vacancies, loops) form at the initial stage of the recovery, which are responsible for a cleaning effect of the structure and momentary decrease of the resistivity below the level natural for the fully-recovered structure characterized by equilibrium vacancy concentration.

- In case of FCC metals, the decrease of resistivity in time of annealing show monotonic tendency, what proves progressing annihilation of structural defects.
- In case of HCP metals it was observed, that changes in resistivity in time of annealing exhibit oscillatory charac-

ter with minimum occurring after time of about 2 min. The noted changes support the thesis of reconfiguration of lattice defects and formation of vacancy clusters during initial stage of recovery. Thus, the cleaning process of the structure and momentary drop of resistivity take place. After certain time, the structures decompose, what is associated by increase of resistivity, followed by annihilation of individual vacancies and decrease of resistivity until the equilibrium concentration of vacancies at given temperature is reached.

- Energy balance of vacancy phenomena in discussed types of crystal structure confirms that HCP structures, especially those with large deviation of  $c/a$  ratio from ideal one, are susceptible for operation of vacancy mechanisms.

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#### REFERENCES

- [1] M. Zehetbauer, B. Mikułowski, Archives of Metallurgy **46**, 65 (2001).
- [2] R. Swiatek, M. Zehetbauer, B. Mikułowski, Materials Science and Engineering A **234-236**, 441 (1997).
- [3] R.K.W. Marceau, R. Ferragut, A. Dupasquier, M.M. Iglesias, S.P. Ringer, Materials Science Forum **519-521**, 197 (2006).
- [4] F. Lukác, J. Cizek, I. Procházka, Y. Jirásková, D. Janickovic, W. Anwand, G. Brauer, 16th International Conference on Positron Annihilation (ICPA-16), Journal of Physics: Conference Series **443** (2013).
- [5] J. Galligan, J. Washburn, Philosophical Magazine **8**, 1455 (1963).
- [6] G.E.R. Schulze, Metallphysik, Akademie-Verlag, Berlin, 1974.
- [7] [http://en.wikipedia.org/wiki/Electrical\\_resistivities\\_of\\_the\\_elements\\_\(data\\_page\)](http://en.wikipedia.org/wiki/Electrical_resistivities_of_the_elements_(data_page)).
- [8] <http://engineering.dartmouth.edu/defmech/>
- [9] B. Mikułowski, B. Wielke, Czech. J. Phys. B **35**, 286 (1985).
- [10] B. Wielke, Phys. Stat. Sol. A **33**, 241 (1976).
- [11] B. Mikułowski, G. Boczkal, Archives of Metallurgy and Materials **54**, 1, 197-203 (2009).
- [12] G. Boczkal, B. Mikułowski, Archives of Metallurgy and Materials **48**, 1, 11-19 (2003).
- [13] G. Boczkal, B. Mikułowski, C.-G. Oertel, W. Skrotzki, Crystal Research and Technology **45**, 2, 111-114 (2010).
- [14] G. Boczkal, Archives of Metallurgy and Materials **58**, 4, 1019-1022 (2013).
- [15] H. Ibach, H. Luth, Solid-State Physics, Springer-Verlag, 1991.
- [16] R. Li, Y. Zhong, C. Huang, X. Tao, Y. Ouyang, Physica B: Physics of Condensed Matter **422**, 51 (2013).