TEMPERATURE DEPENDENCE OF A PERIOD OF THE MODULATED STRUCTURE IN ATOM–VACANCY SOLID SOLUTION

Olena V. Oliinyk[*], Valentyn A. Tatarenko

G.V. Kurdyumov Institute for Metal Physics, N.A.S.U.,
36 Academician Vernadsky Boulevard, UA-03680, Kyyiv-142, Ukraine

ABSTRACT

The effective vacancy–vacancy interaction is considered. Based on the continuum approximation for the Fourier components of strain-induced vacancy–vacancy interaction energies, approximating expressions for their expansion coefficients are obtained depending on the elasticity moduli, longitudinal and transverse phonon frequencies, and vacancy-concentration-dependent lattice parameter. The behaviour of $\mathbf{k}$-dependent Fourier components of the strain-induced vacancy–vacancy interaction energies near the Brillouin zone centre, $A(\mathbf{n})+B(\mathbf{n})k^2$, is analysed. As shown, $A(\mathbf{n}) < 0$ and $B(\mathbf{n}) > 0$ along all the high-symmetry [100], [110], [111], [½10] directions in reciprocal space for f.c.c. crystals with negative anisotropy factor. The criterion of modulated-structure formation for interacting vacancies in f.c.c. crystals is considered. Dependence of the modulated-structure period on temperature is plotted.

Key words: vacancies, strain-induced interaction, modulated structures

INTRODUCTION

Within the crystals under irradiation, modulated structures can be formed [1]. We consider the case when, due to irradiation, the vacancies were generated in f.c.c. crystal; then the irradiation was stopped. Another way to produce the atom–vacancy solid solution is a high-temperature quenching, which fixes a raised amount of pre-melting vacancies. At the initial stage of an annealing, the average concentration of vacancies is constant until vacancies have time to approach the surface or to disappear in sinks. The vacancy interactions are governing mechanism of formation of the modulated structures in vacancy-containing crystals.

RESULTS AND DISCUSSION

With decreasing temperature, T, or increasing concentration of vacancies (v), c, their interaction-caused drift begins dominating in their random motion, and the damping decrement becomes negative for every values of wave vector,

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[*] e-mail: neutrino@ukr.net, tatar@imp.kiev.ua tel: +380 44 4241221

k, which belongs to the sphere of a radius $k_0(T, c)$ about $\mathbf{k} = \mathbf{0}$, and the modulated structures appear. For $|\mathbf{k}| > k_0(T, c)$, the damping decrement is positive, and the modulated structures disappear [2].

A given paper is based on overrunning continuous approximation for the Fourier components, $\tilde{V}^{vv}(\mathbf{k})$, of the strain-induced vacancy–vacancy interaction energies. Within the finite region near $\mathbf{k} = \mathbf{0}$ [2, 3], the $\tilde{V}^{vv}(\mathbf{k})$ may be represented as follows: $\tilde{V}^{vv}(\mathbf{k}) \cong A(\mathbf{n}) + B(\mathbf{n})|\mathbf{k}|^2 + Q$ $(\mathbf{n} = \mathbf{k}/|\mathbf{k}|)$. Here, the well-known first term is based on long-wave-limit approximation [2]; the second term is a correction to this approximation, and the third term is a gauge, which eliminates strain-induced self-action of vacancies. The transition to the direct-lattice space is defined according to the formula:

$$V^{vv}(\mathbf{r} - \mathbf{r}') = \frac{1}{N} \sum_{\mathbf{k} \in 1^{st} BZ} \tilde{V}^{vv}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}')} ,$$

where summation is carried out over all N **k**-points of quasi-continuum within the 1st Brillouin zone (BZ) of f.c.c. lattice.
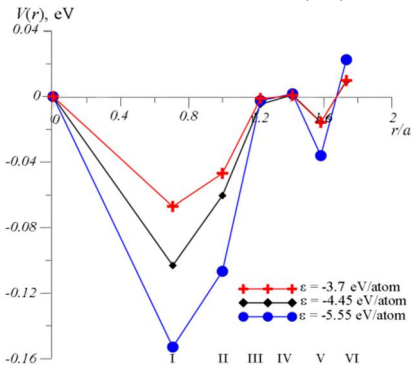

Fig. 1 – The dependence of the strain-induced vacancy–vacancy-interaction energies on the normalized radius of coordination sphere in a crystal with various cohesion energy, ε [3–5], which is used to estimate the concentration-dependent dilatation coefficient, L^v

In the direct-lattice space, the dependence of the strain-induced vacancy–vacancy interaction energy on the normalized radius of coordination sphere is shown in *Fig. 1*. One should pay attention to the quasi-oscillating and long-range character of the strain-induced vacancy–vacancy interaction energies. Thus, its contribution on distant coordination spheres can be dominant.

The modulated structure can be formed along those crystallographic direction, which is parallel to $\mathbf{n}_c = \mathbf{k}_c/|\mathbf{k}_c|$ corresponding to the highest growth rate and has the wave vector with a magnitude of

$$|\mathbf{k}_c| \cong \{-(A(\mathbf{n}_c) + Q + \tilde{\varphi}_{el.chem}(\mathbf{0}) + k_B T/[c(1-c)])/[2(B(\mathbf{n}_c) + \gamma)]\}^{1/2} ;$$

$\tilde{\varphi}_{el.chem}(\mathbf{k})$ is the Fourier component of 'mixing' energies for direct 'electrochemical' interactions in atom–vacancy solid solution, k_B is the Boltzmann constant. Within the wave-length approximation, $\tilde{\varphi}_{el.chem}(\mathbf{k}) \cong \tilde{\varphi}_{el.chem}(\mathbf{0}) + \gamma|\mathbf{k}|^2$.

The 'mixing' energies, $\varphi_{el.chem}(r)$, for a solid solution are calculated with use of the Machlin potential [6] or the Morse potential [7] (*Fig. 2*).
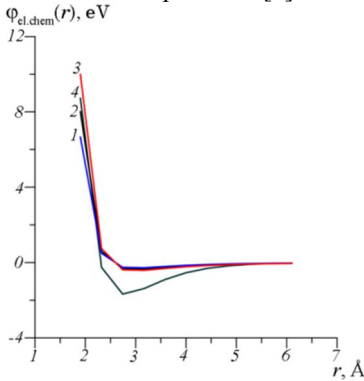
$\varphi_{el.chem}(r)$, eV

Fig. 2 – The 'mixing' energies, $\varphi_{el.chem}(r)$, for direct 'electrochemical' interactions in atom–vacancy solid solution based on a crystal with various cohesion energies, ε: (1) ε = –3.7 eV/atom [4], (2) ε = –4.45 eV/atom [3], and (3) ε = –5.55 eV/atom [5] in Machlin potential [6]; (4) Morse potential [7]

The approximated expansion coefficients for Fourier components of the strain-induced *v–v*-interaction energies are dependent on the elasticity moduli of f.c.c. crystals, C_{11}, C_{12}, C_{44}; *e.g.*,

$$A[100] = -9K^2(L^v)^2 a_0^3 / (4C_{11}) \quad [2, 8],$$

$$B[100] \cong 9K^2 a_0^4 (L^v)^2 M\, \omega_L^2 / (256C_{11}^2),$$

where $K = (C_{11} + 2C_{12})/3$—compressibility modulus, a_0—an f.c.c.-lattice parameter, L^v—concentration coefficient of f.c.c.-lattice dilatation, M—the Ni atom mass, ω_L—the longitudinal-polarized phonon frequency at the high-symmetry X-point of the BZ surface. $B(\mathbf{n})$ is positive along all the high-symmetry [100], [110], [111], [½10] directions in reciprocal space for f.c.c. crystals with anisotropy factor $\xi \equiv (C_{11} - C_{12} - 2C_{44})/C_{44} < 0$. $B(\mathbf{n})$ increases with temperature along the [100], [110], [111] directions (see *Fig.3*, where $L^v = -0.149$, $L^v = -0.124$, $L^v = -0.187$ were calculated using the Machlin potential, and $L^v = -0.0153$ corresponds to the Morse potential).

If $\xi < 0$, $\tilde{V}^{vv}(\mathbf{k})$ has a one-sided minimum along the [100] direction, but it is greater than $\tilde{V}^{vv}(\mathbf{0})$ as a result of the long-range nature of strain-induced interaction. Besides, there are inequalities as follow:

$$\tilde{V}^{vv}(\mathbf{k}_{\|\overline{X\Gamma}} \to \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\|\overline{W\Gamma}} \to \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\|\overline{K\Gamma}} \to \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\|\overline{L\Gamma}} \to \mathbf{0}).$$

If $(A[100] + Q + \tilde{\varphi}_{el.chem}(\mathbf{0}) + k_B T / [c(1-c)]) / [2(B[100] + \gamma)] < 0$, where, *e.g.*, within the scope of the Debye approximation,

$$Q \cong 9K^2(L^v)^2 (a_0^3/4) \left\langle (1 + 2\xi X + 3\xi^2 Y) / D(\mathbf{n}) \right\rangle_{\mathbf{n}},$$

$$D(\mathbf{n}) = C_{11} + \xi(C_{11} + C_{12})X + \xi^2(C_{11} + 2C_{12} + C_{44})Y,$$

$X = n_x^2 n_y^2 + n_x^2 n_z^2 + n_z^2 n_y^2$, $Y = n_x^2 n_y^2 n_z^2$, the modulated structure can appear along the $[100]$ direction.

Dependence of the modulated-structure period on T is plotted in *Fig. 4*. With increasing temperature, the period of modulated structures increases.
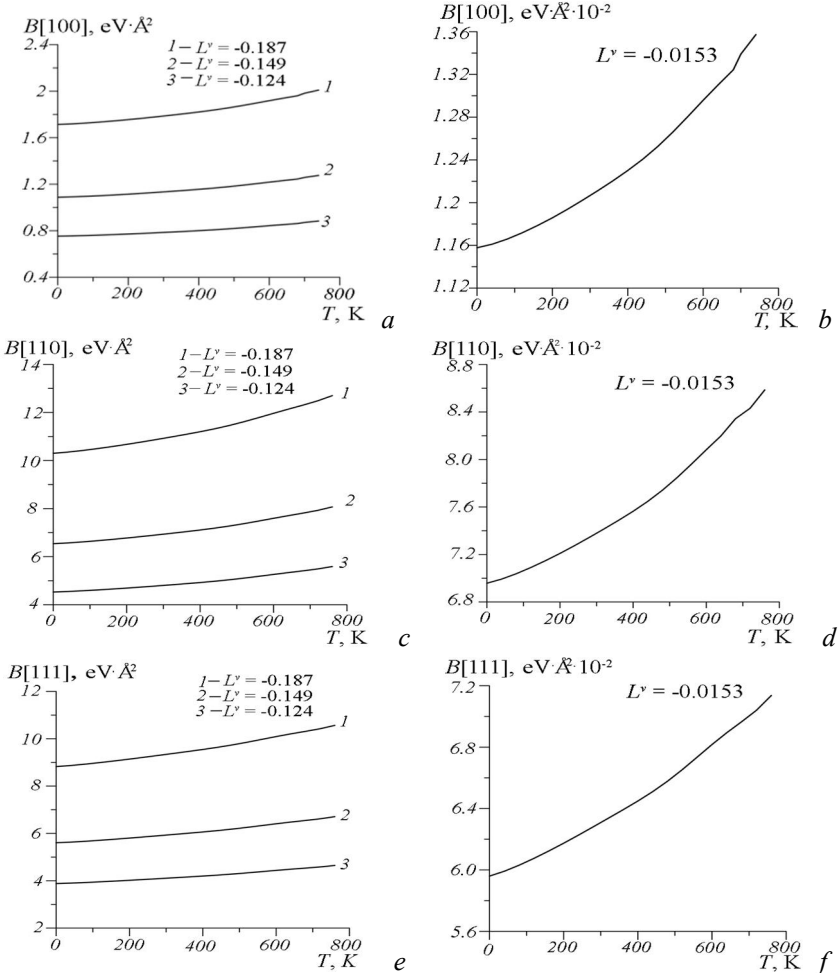

Fig. 3 – The temperature dependence of $B(\mathbf{n})$: *a, b*—$B[1\,0\,0]$, *c, d*—$B[1\,1\,0]$, *e, f*—$B[1\,1\,1]$
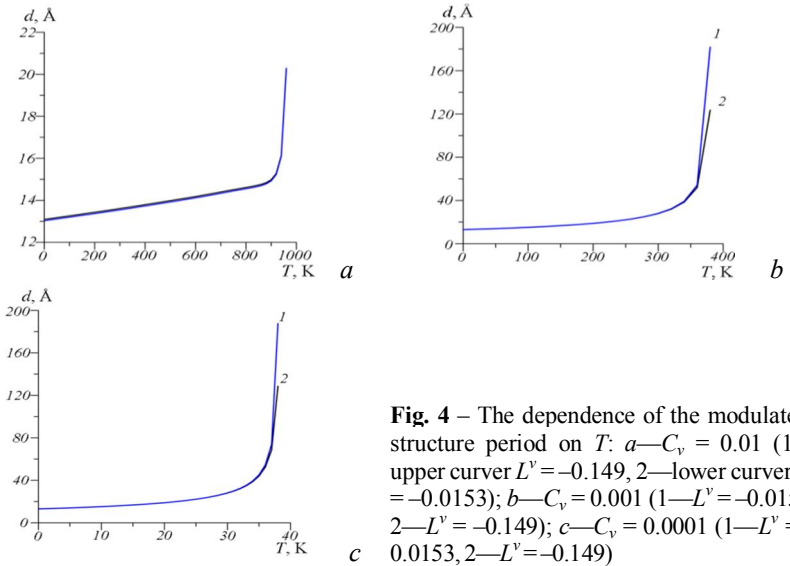
Fig. 4 – The dependence of the modulated-structure period on T: a—$C_v = 0.01$ (1—upper curver $L^v = -0.149$, 2—lower curver $L^v = -0.0153$); b—$C_v = 0.001$ (1—$L^v = -0.0153$, 2—$L^v = -0.149$); c—$C_v = 0.0001$ (1—$L^v = -0.0153$, 2—$L^v = -0.149$)

CONCLUSIONS

The strain-induced vacancy–vacancy interaction energy has the long-range and quasi-oscillating nature. As shown, $B(\mathbf{n})$ is positive along all the high-symmetry [100], [110], [111], [½10] directions in reciprocal space for f.c.c. crystals with negative anisotropy factor ($\xi \equiv (C_{11} - C_{12} - 2C_{44})/C_{44} < 0$) and increases with temperature. As revealed, the two vacancies are attracted at the distance of less than 7 Å. At distances over 7 Å, vacancies do not significantly interact with each other. An elevation of the temperature leads to increase of the period of modulated structure.

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