

Temperature Dependence of a Period of the Modulated Structure in Atom-Vacancy Solid Solution Based on F.C.C. Nickel

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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. A non-analytical behaviour of the \mathbf{k} -dependent Fourier components of the strain-induced vacancy–vacancy-interaction energies near the Brillouin zone centre, $A^{vv}(\mathbf{n}) + B^{vv}(\mathbf{n})|\mathbf{k}|^2$, is analysed. As shown, $A^{vv}(\mathbf{n}) < 0$ and $B^{vv}(\mathbf{n}) > 0$ along all the high-symmetry [100], [110], [111] 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 f.c.c.-Ni–vacancies modulated-structure period on temperature is plotted.

Keywords: Vacancies, Strain-induced interaction, Electrochemical interaction, Modulated structures, Cohesive energy.

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1. INTRODUCTION

Within the crystals under irradiation, modulated structures can form [1]. We consider the case when, due to irradiation, the vacancies were generated in f.c.c. crystal, and then the irradiation was stopped. Another way to fabricate the f.c.c.-crystal-vacancies 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 the governing mechanism of formation of the modulated structures in vacancy-containing crystals.

2. INTERACTION PARAMETERS FOR F.C.C.-CRYSTAL-VACANCIES SOLUTION

With decreasing temperature, T , or increasing concentration of vacancies (v), c , their interaction-caused drift begins dominating in their random motion; the concentration-inhomogeneity damping decrement becomes negative for every values of wave vector, \mathbf{k} , which belongs to the sphere of a radius $q(T, c)$ about $\mathbf{k} = \mathbf{0}$, and the modulated structures appear. For $|\mathbf{k}| > q(T, c)$, the damping decrement is positive, and the modulated structures disappear [2].

A given paper is based on overrunning continuous approximation for the Fourier components of the ‘mixing’ energies [2] for f.c.c.-crystal- v solution, $\tilde{w}(\mathbf{k})$. Within the small finite region near $\mathbf{k} = \mathbf{0}$, $\tilde{w}(\mathbf{k})$ may be represented as follows [2-4]:

$$\tilde{w}(\mathbf{k}) \approx \tilde{V}^{vv}(\mathbf{k}) + \tilde{\varphi}_{\text{el.chem}}(\mathbf{k}) \cong \tilde{V}_{\mathbf{n}}^{vv} + \tilde{\varphi}_{\text{el.chem}}(\mathbf{0}) + \beta(\mathbf{n})|\mathbf{k}|^2; \quad (1)$$

$\tilde{\varphi}_{\text{el.chem}}(\mathbf{k}) \equiv \tilde{\varphi}_{\text{el.chem}}^{\text{Ni-Ni}}(\mathbf{k}) + \tilde{\varphi}_{\text{el.chem}}^{v-v}(\mathbf{k}) - 2\tilde{\varphi}_{\text{el.chem}}^{\text{Ni-v}}(\mathbf{k})$ is the Fourier component of ‘mixing’ energies for direct ‘elec-

trochemical’ interactions in f.c.c.-crystal- v solution; $\tilde{V}^{vv}(\mathbf{k})$ is the Fourier component of strain-induced $v-v$ -interaction energies; $\beta(\mathbf{n})$ is the expansion coefficient ($\mathbf{n} \equiv \mathbf{k}/|\mathbf{k}|$).

3. MODEL

The ‘mixing’ energies, $\varphi_{\text{el.chem}}(r)$, for direct ‘electrochemical’ interactions in f.c.c.-Ni- v solid solution were calculated (Fig. 1) with use of the Machlin potential [5] with exponents selected by means of Machlin recommendations and the Morse potential [6] within the approach developed in Refs. [2, 7-11].

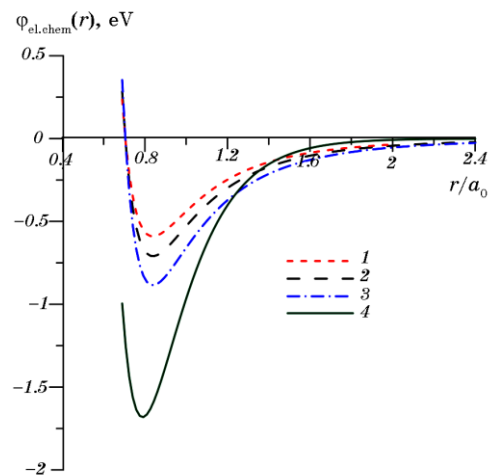


Fig. 1 – The ‘mixing’ energies for direct ‘electrochemical’ interactions in atom- v solid solution based on an f.c.c. crystal characterized with various cohesive energies, ε : 1 $\varepsilon = -3.7$ eV/atom [12], 2 $\varepsilon = -4.45$ eV/atom [13, 14], 3 $\varepsilon = -5.55$ eV/atom [15]; 4 Morse potential for Ni–Ni interatomic interaction; $a_0 = 3.5243$ Å at $T = 300$ K

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As revealed, the two vacancies are attractive at the distances less than 7 Å, but over $r \cong 2.46$ Å. At the distances over 7 Å, vacancies do not interact with each other significantly.

Within the long wavelength approximation, the Fourier components of ‘mixing’ energies for direct ‘electrochemical’ interactions in f.c.c.-crystal- v solution are defined as follows:

$$\tilde{\varphi}_{\text{el.chem}}(\mathbf{k}) \cong \tilde{\varphi}_{\text{el.chem}}(\mathbf{0}) + \gamma |\mathbf{k}|^2, \quad (2a)$$

where

$$\tilde{\varphi}_{\text{el.chem}}(\mathbf{0}) = 12\varphi(r_I) + 6\varphi(r_{II}) + 24\varphi(r_{III}) + 12\varphi(r_{IV}) + 24\varphi(r_V) + 8\varphi(r_{VI}) + \dots; \quad (2b)$$

$$\gamma = -\alpha_0^2(\varphi(r_I) + \varphi(r_{II}) + 6\varphi(r_{III}) + 4\varphi(r_{IV}) + 10\varphi(r_V) + 4\varphi(r_{VI})) + \dots; \quad (2c)$$

$\varphi(r_I)$, $\varphi(r_{II})$, ..., $\varphi(r_{VI})$ are ‘electrochemical’-interaction energies at the first, second, ..., sixth coordination spheres; α_0 —an f.c.c. lattice parameter.

Within the small finite region near $\mathbf{k} = \mathbf{0}$, $\tilde{V}^{vv}(\mathbf{k})$ may be represented as follows [2, 3]:

$$\tilde{V}^{vv}(\mathbf{k}) \cong A^{vv}(\mathbf{n}) + B^{vv}(\mathbf{n})|\mathbf{k}|^2 + Q^{vv}. \quad (3)$$

Here, the well-known first term is based on the long-wave-limit approximation [2, 3]; the second term is a correction to this approximation [3, 16], and the third term is a gauge, which eliminates strain-induced self-action of vacancies [2, 4, 11, 16-18].

$$A^{vv}(\mathbf{n}) = -9K^2\alpha_0^3(L^v)^2(1 + 2\xi\tilde{X}(\mathbf{n}) + 3\xi^2\tilde{Y}(\mathbf{n})) / (4D(\mathbf{n})), \quad (4)$$

where L^v is a concentration coefficient of f.c.c.-lattice dilatation. $K = (C_{11} + 2C_{12})/3$ is a compressibility modulus, $\xi = (C_{11} - C_{12} - 2C_{44})/C_{44}$ is an elastic-anisotropy factor, C_{11} , C_{12} , C_{44} are the elasticity modules [19], $D(\mathbf{n}) = C_{11} + \xi(C_{11} + C_{12})\tilde{X}(\mathbf{n}) + \xi^2(C_{11} + 2C_{12} + C_{44})\tilde{Y}(\mathbf{n})$, $\tilde{X}(\mathbf{n}) = n_x^2n_y^2 + n_x^2n_z^2 + n_y^2n_z^2$, $\tilde{Y}(\mathbf{n}) = n_x^2n_y^2n_z^2$ [2, 3].

The coefficient $B^{vv}(\mathbf{n})$ was derived in revised form in [16].

Within the long wavelength approximation, values of the Fourier components of strain-induced v - v -interaction energies, $\tilde{V}^{vv}(\mathbf{k})$, for \mathbf{k} -directions from high-symmetry points to centre $\mathbf{0}$ of the 1st Brillouin zone (BZ) of reciprocal space of f.c.c. lattice are as follows:

$$\tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_X} \rightarrow \mathbf{0}) \cong -\frac{9K^2\alpha_0^3(L^v)^2}{4C_{11}} + B^{vv}(\mathbf{n}_{\Gamma\rightarrow X})|\mathbf{k}|^2 + Q^{vv}; \quad (5)$$

$$\tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_K} \rightarrow \mathbf{0}) \cong -18K^2\alpha_0^3(L^v)^2 \times \frac{(2 + \xi)}{4(4C_{11} + \xi(C_{11} + C_{12}))} + B^{vv}(\mathbf{n}_{\Gamma\rightarrow K})|\mathbf{k}|^2 + Q^{vv}; \quad (6)$$

$$\tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_L} \rightarrow \mathbf{0}) \cong -27K^2\alpha_0^3(L^v)^2 \times$$

$$\times \frac{(3 + \xi)^2}{4(27C_{11} + 9\xi(C_{11} + C_{12}) + (C_{11} + 2C_{12} + C_{44})\xi^2)} + B^{vv}(\mathbf{n}_{\Gamma\rightarrow L})|\mathbf{k}|^2 + Q^{vv}. \quad (7)$$

The dispersion curves for $\tilde{V}^{vv}(\mathbf{k})$ along all the high-symmetry directions within the 1st BZ [16] are presented on Fig. 2.

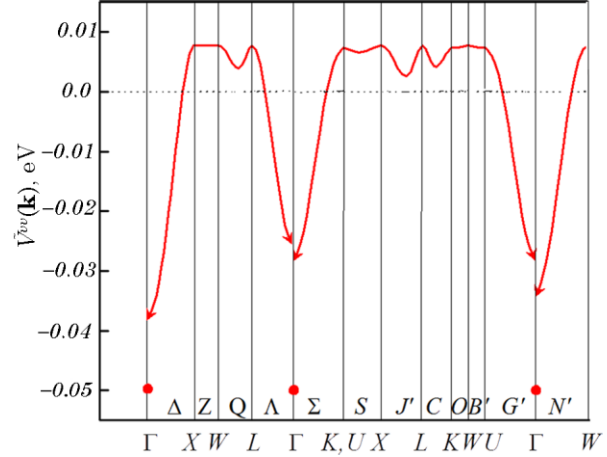


Fig. 2 – Dispersion curves for the Fourier components of the strain-induced v - v -interaction energies along all the high-symmetry directions in reciprocal space (with $L^v = -0.025$ estimated from data [13, 14], using the Machlin potential [5])

If $\xi < 0$, $\tilde{V}^{vv}(\mathbf{k})$ has a one-sided minimum along the [100] direction, but it is greater than $\tilde{V}^{vv}(\mathbf{0})$ because of the long-range nature of strain-induced interaction. Besides, there are inequalities as follow [4, 16]:

$$\begin{aligned} \tilde{V}^{vv}(\mathbf{0}) &< \tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_X} \rightarrow \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_W} \rightarrow \mathbf{0}) < \\ &< \tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_K} \rightarrow \mathbf{0}) < \tilde{V}^{vv}(\mathbf{k}_{\downarrow\uparrow\mathbf{k}_L} \rightarrow \mathbf{0}) < 0 < \\ &< \tilde{V}^{vv}(\mathbf{k}_X) = \tilde{V}^{vv}(\mathbf{k}_W) = \tilde{V}^{vv}(\mathbf{k}_{K(U)}) = \tilde{V}^{vv}(\mathbf{k}_L) \end{aligned} \quad (8)$$

that confirms *non-analytical* behaviour, long-range character, and anisotropy of ‘elastic’ interaction between vacancies in f.c.c.-crystal- v solution.

The transition to the direct-lattice \mathbf{r} -space description is defined according to the formula:

$$V^{vv}(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k} \in 1^{\text{st}} \text{BZ}} \tilde{V}^{vv}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (9)$$

where summation is carried out over all N \mathbf{k} -points of quasi-continuum within the 1st BZ of f.c.c. lattice.

In the direct-lattice space, the dependence of the strain-induced v - v -interaction energy on the normalized radius of coordination sphere, r/a_0 , is shown in Fig. 3. One should pay attention to the quasi-oscillating and long-range character of the strain-induced v - v -interaction energies.

$B^{vv}(\mathbf{n})$ is positive along all the high-symmetry [100], [110], [111] directions in reciprocal space for f.c.c. crystals with a negative anisotropy factor ($\xi < 0$) [16]:

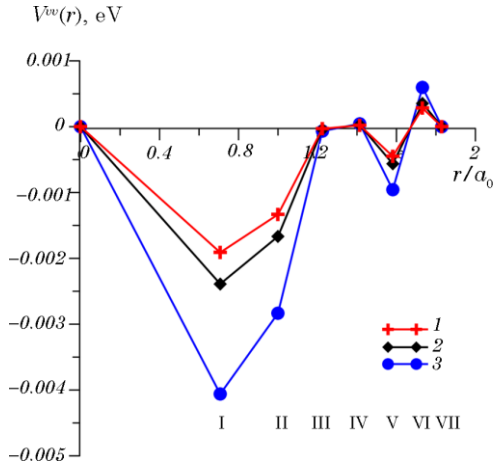


Fig. 3 – Dependence of the strain-induced v - v -interaction energies on the normalized radius of coordination sphere in f.c.c. crystal characterized with various cohesive energies, ε : 1 $\varepsilon = -3.7$ eV/atom [12], 2 $\varepsilon = -4.45$ eV/atom [13, 14], and 3 $\varepsilon = -5.55$ eV/atom [15], which are used to estimate the concentration-dependent-dilatation coefficient, L^v

$$B^{vv}(\mathbf{n}_{X \rightarrow \Gamma}) \cong 9K^2 a_0^4 (L^v)^2 M \omega_{LX}^2 / (256C_{11}^2); \quad (10)$$

$$B^{vv}(\mathbf{n}_{K \rightarrow \Gamma}) \cong 9K^2 a_0^4 (L^v)^2 (8a_0(C_{11} + C_{12} + 2C_{44}) + M \omega_{TX}^2) \times (256(C_{11} + C_{12} + 2C_{44})^2)^{-1}; \quad (11)$$

$$B^{vv}(\mathbf{n}_{L \rightarrow \Gamma}) \cong 9K^2 a_0^5 (L^v)^2 (16(C_{11} + 2C_{12} + 4C_{44}))^{-1}; \quad (12)$$

here, M is a Ni atom mass.

The temperature dependences of transversal (ω_{TX}) and longitudinal (ω_{LX}) phonon frequencies at the high-symmetry point $X(100)$ on the 1st BZ surface are approximated, following [20]:

$$\omega_{TX} \cong \omega_{0TX}(1 - \alpha_{TX}T), \quad \omega_{LX} \cong \omega_{0LX}(1 - \alpha_{LX}T); \quad (13)$$

$\omega_{0TX} \approx 40.23761$ THz and $\omega_{0LX} \approx 54.21649$ THz are transversal and longitudinal phonon frequencies, respectively, estimated by extrapolation of data [21] to $T = 0$ K ($\alpha_{TX} \approx 7.02270 \cdot 10^{-5}$ K⁻¹, $\alpha_{LX} \approx 3.06588 \cdot 10^{-5}$ K⁻¹ – the temperature coefficients of frequencies).

$B^{vv}(\mathbf{n})$ along the [100], [110], [111] directions increases with temperature (for Fig. 4, $L^v = -0.021$, $L^v = -0.025$, $L^v = -0.031$ were estimated, using the Machlin potential [5] with various ε , and $L^v = -0.0153$ corresponds to the Morse potential [6]).

4. RESULTS

The modulated structure is formed along crystallographic direction, which is parallel to corresponding direction \mathbf{n}_c of the highest growth rate of inhomogeneity-wave amplitude [2, 3] characterized by the wave vector of a magnitude [2]

$$|\mathbf{k}_c| \cong -(A^{vv}(\mathbf{n}_c) + Q^{vv} + \tilde{\varphi}_{\text{el.chem}}(\mathbf{0}) + k_B T / [c(1-c)])^{1/2} \times (2(B^{vv}(\mathbf{n}_c) + \gamma))^{-1/2}, \quad (14)$$

where k_B is the Boltzmann constant.

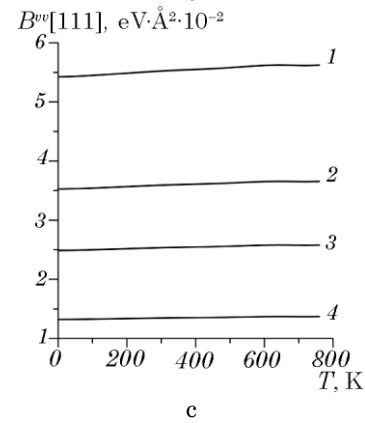
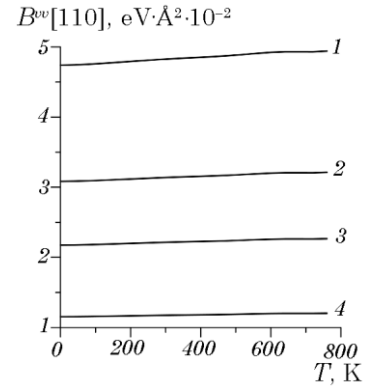
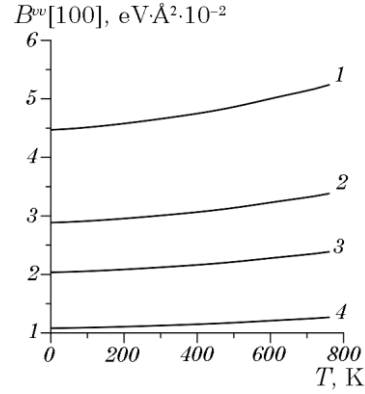


Fig. 4 – The temperature dependence of $B^{vv}(\mathbf{n})$: $B^{vv}[100]$ (a), $B^{vv}[110]$ (b), $B^{vv}[111]$ (c) for 1 $L^v = -0.031$, 2 $L^v = -0.025$, 3 $L^v = -0.021$, 4 $L^v = -0.0153$

The expansion coefficients for Fourier components of the strain-induced v - v -interaction energies are dependent on all the elasticity moduli and transversal and longitudinal phonon frequencies at the point $X(100)$ for an f.c.c. crystal. For instance,

$$A^{vv}[100] = -9K^2 a_0^3 (L^v)^2 / (4C_{11}) \quad [2, 3], \quad (15)$$

$$B^{vv}[100] \cong 9K^2 a_0^5 (L^v)^2 / (64C_{11}), \quad (16)$$

within the assumption $M \omega_{LX}^2 \cong 4\alpha_0 C_{11}$ [3, 4, 18].

If

$$(A^{vv}(\mathbf{n}_c) + Q^{vv} + \tilde{\varphi}_{\text{el.chem}}(\mathbf{0}) + k_B T / [c(1-c)]) \times$$

$$\times(2(B^{vv}(\mathbf{n}_c) + \gamma))^{-1} < 0, \quad (17)$$

modulated structure can appear along the [100] direction. Note that, *e.g.*, within the scope of the Debye approximation [2, 17],

$$Q^{vv} \cong 9K^2 \frac{\alpha_0^3}{4} (L^v)^2 \left\langle (1 + 2\xi \tilde{X}(\mathbf{n}) + 3\xi^2 \tilde{Y}(\mathbf{n})) / D(\mathbf{n}) \right\rangle_{\mathbf{n}}. \quad (18)$$

In particular [17],

$$Q^{vv} \cong \frac{\alpha_0^3 (L^v)^2 (C_{11} + 2C_{12})^2 (\zeta_1 + \zeta_2/5 + \zeta_3/105)}{4}, \quad (19)$$

where

$$\zeta_1 = \frac{1}{C_{11}}, \quad \zeta_2 = \frac{C_{44}\xi}{(C_{11} - C_{12})(C_{11} + C_{12} + 2C_{44})},$$

$$\zeta_3 = \frac{18C_{44}^2 \xi^2}{C_{11}(C_{11} + C_{12} + 2C_{44})(C_{11} + 2C_{12} + 4C_{44})},$$

or

$$Q^{vv} \cong \frac{\alpha_0^3 (L^v)^2 (C_{11} + 2C_{12})^2 (1 + 2\xi \tilde{X}(\mathbf{n}_B) + 3\xi^2 \tilde{Y}(\mathbf{n}_B))}{4D(\mathbf{n}_B)}, \quad (20)$$

where $\mathbf{n}_B \equiv \mathbf{k}_B / |\mathbf{k}_B|$ corresponds to so-called Baldeschi mean-value point \mathbf{k}_B (see references in [17, 18]).

Dependence of the modulated-structure period, $d = 2\pi / |\mathbf{k}_c|$, on T is calculated on the basis of Eqs. (2b), (2c), (10), (15), (19) (or (20)) and plotted in Fig. 5. (Note that results of calculation with Eq. (19) or Eq. (20) are, in fact, coincident because of dominant contribution of ‘electrochemical’ interaction into numerator of fraction in right side of Eq. (14).) So, with increasing temperature, the period of modulated structures increases.

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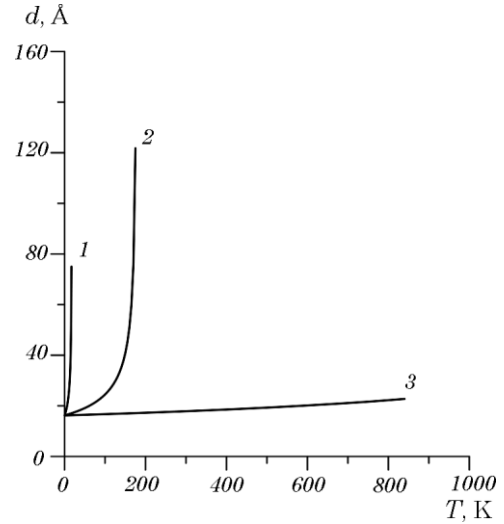


Fig. 5 – The dependence of the modulated-structure period on T for: 1 $c = 0.0001$, 2 $c = 0.001$, 3 $c = 0.01$ ($L^v = -0.025$)

5. CONCLUSIONS

The strain-induced v - v -interaction energy has the long-range and quasi-oscillating nature.

As revealed, the two vacancies are attractive ‘electrochemically’ mostly at the distances of less than 7 Å, but over 2.46 Å. At distances over 7 Å, vacancies do not interact with each other significantly.

As shown in Fig. 5 (see also Eq. (14)), at $T \rightarrow 0$ K, $d(T) \rightarrow d(0) \cong 16$ Å independently on the content of vacancies. This period of corresponding modulated structure, $d(0)$, is determined by both the ‘electrochemical’ interaction of Ni atoms and the elastic properties of f.c.c. nickel only.

An elevation of the temperature leads to increase of the modulated-structure period.