
<https://doi.org/10.15407/ujpe68.6.369>

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MECHANISM OF NON-FLUCTUATIONAL FORMATION OF INTERSTITIAL ATOMS IN DEFORMED CRYSTALS

We have proposed a mechanism according to which interstitial atoms appear in the crystal lattice as a result of compressive strains. This occurs, when the relative volume strain exceeds a certain critical value. The equilibrium concentration of interstitial atoms appearing due to the proposed mechanism is calculated. A characteristic feature of this effect is the rapid, at the sound velocity, establishment of the indicated concentration over the crystal volume.

Keywords: thermal fluctuations, vacancy, interstitial atoms, non-fluctuation mechanism.

1. Introduction

It is known (see, e.g., works [1–3]) that there are point defects of two main types in crystals: vacancies and interstitial atoms. They are considered to appear as a result of thermal fluctuations. This approach was applied till now in most of the works devoted to the study of point defects (see, e.g., work [4]).

In works [5–7], it was found that, besides the mentioned fluctuational mechanism of vacancy formation, another one, non-fluctuational, is also possible. According to it, vacancies appear in a crystal subjected to the uniform stretching, when the relative volume strain exceeds a certain critical value.

The aim of this work is to elucidate the non-fluctuational mechanism giving rise to the appearance

of interstitial atoms in crystals subjected to a uniform compression.

2. Equilibrium State of a Deformed Crystal with Interstitial Atoms

The issue concerning the possibility of the non-fluctuational formation of interstitial atoms as a result of the crystal deformation is actually reduced to the issue concerning the possibility of the existence of interstitial atoms in a deformed crystal that is in a stable equilibrium state. An important problem, in this case, is a determination of the concentration of interstitial atoms. An answer to this question will be sought using standard thermodynamic approaches (see, e.g., work [8]).

Let a crystal be subjected to a uniform compression, and let us choose the crystal volume V as an external parameter. Due to this choice, the free energy has to be the characteristic thermodynamic function.

The free energy F'_E of a crystal in a stable equilibrium state is a function of two variables: the crystal volume V and the temperature T ,

$$F_E = F'_E(V, T). \quad (1)$$

Citation: Bulavin L.A., Zabashta Yu.F., Lazarenko M.M., Vergun L.Yu., Hnatiuk K.I., Alekseev O.M., Kovalchuk V.I. Mechanism of non-fluctuational formation of interstitial atoms in deformed crystals. *Ukr. J. Phys.* **68**, No. 6, 369 (2023). <https://doi.org/10.15407/ujpe68.6.369>.

Цитування: Булавін Л.А., Забашта Ю.Ф., Лазаренко М.М., Вергун Л.Ю., Гнатюк К.І., Алексєєв О.М., Ковальчук В.І. Нефлуктуаційний механізм появи міжвузлових атомів у деформованому кристалі. *Укр. фіз. журн.* **68**, № 6, 369 (2023).

ISSN 2071-0194. Ukr. J. Phys. 2023. Vol. 68, No. 6

Let V_0 denote the volume of the undeformed crystal. Then, by introducing the relative volume variation

$$\theta = -\frac{V - V_0}{V_0} \quad (2)$$

into consideration, let us change the variable V in expression (1),

$$F_E = F_E(\theta, T). \quad (3)$$

Let N denote the total number of atoms in the crystal, and n the number of interstitial atoms. Then the concentration of interstitial atoms in the crystal equals

$$c = \frac{n}{N}. \quad (4)$$

If the crystal contains a certain number of interstitial atoms, its free energy F is a function of three variables: θ, T , and c , i.e.,

$$F = F(\theta, T, c). \quad (5)$$

This state of the crystal is not a stable equilibrium one. Instead, we have a relatively stable equilibrium state. By definition, the crystal in such a state must relax tending to the equilibrium state of the system, which is characterized by the minimum of the free energy F_E . However, this energy, as was already mentioned, is a function of only two variables. Therefore, if the interstitial atoms remain to stay in the crystal, and if the latter is in the stable equilibrium state, their concentration c_E has to depend on θ and T . Hence, the following formula is valid:

$$F_E = F(\theta, T, c_E(\theta, T)), \quad (6)$$

where the function $c_E(\theta, T)$ is determined from the equation

$$\left. \frac{\partial F}{\partial c} \right|_{\theta = \text{const}, T = \text{const}} = 0. \quad (7)$$

As was already mentioned, the matter concerns the possibility for interstitial atoms to appear only due to a deformation. Therefore, let us exclude the temperature T from consideration by assuming that the crystal deformation occurs at $T = 0$. Then the well-known expression $F = U - TS$, where U is the internal energy, and S is the entropy, transforms into the equality $F = U$. In other words, now the role of the characteristic thermodynamic function is played by

the internal energy, and expressions (3) and (5)–(7) should be replaced by the formulas

$$U_E = U_E(\theta), \quad (8)$$

$$U = U(\theta, c), \quad (9)$$

$$U_E = U(\theta, c_E(\theta)), \quad (10)$$

$$\left. \frac{\partial U}{\partial c} \right|_{\theta = \text{const}} = 0, \quad (11)$$

respectively, where U and U_E are the energies of the relatively stable and stable equilibrium states, respectively, of the crystal with interstitial atoms. As was mentioned above, the feasibility of the formation of interstitial atoms only due to a crystal deformation will be confirmed, if the deformed crystal in the stable equilibrium state contains a certain number of interstitial atoms. Such a confirmation can be obtained by solving Eq. (11) to determine the function $c_E(\theta)$. However, for this purpose, it is necessary to know the analytic expression for function (9).

3. Volume of a Deformed Crystal with Interstitial Atoms

By definition, an undeformed crystal is characterized by the parameter values $\theta = 0$ and $c = 0$. Its volume equals

$$V_0 = Nv_0, \quad (12)$$

where v_0 is the volume per atom in the undeformed crystal.

Let us present the volume of the deformed crystal in the form

$$V = V_1 + V_2, \quad (13)$$

where V_1 is the volume occupied by the lattice, and V_2 is the volume occupied by interstitial atoms. The terms in this sum are determined by the formulas

$$V_1 = (N - n)v, \quad (14)$$

$$V_2 = nv', \quad (15)$$

where v is the volume occupied by an atom located at a lattice site, and v' is the volume occupied by an interstitial atom. Assume that the equality

$$v' = \alpha v \quad (16)$$

holds, where $\alpha < 1$ is a constant.

Substituting Eqs. (14), (15), and (16) into formula (13), taking equality (4), into account and introducing the notation

$$\beta = 1 - \alpha, \quad (17)$$

we obtain

$$V = Nv(1 - \beta c). \quad (18)$$

Taking Eqs. (2) and (12) into account, we can rewrite the last formula in the form

$$1 - \theta = \frac{v}{v_0}(1 - \beta c). \quad (19)$$

4. Energy of a Deformed Crystal with Interstitial Atoms

Let us write down the energy U of the deformed crystal as the sum

$$U = U_1 + U_2, \quad (20)$$

where U_1 is the energy of the atoms located at the lattice sites, and U_2 is the energy of interstitial atoms. The terms in this sum equal

$$U_1 = (N - n)w, \quad (21)$$

$$U_2 = nw', \quad (22)$$

where w and w' are the energies of the atom located at the lattice site and interstice, respectively. We will also assume the equality

$$w' = \gamma w, \quad (23)$$

where $\gamma > 1$ is a constant. Taking Eqs. (4) and (21)–(23) into account and introducing the notation

$$\phi = \gamma - 1, \quad (24)$$

let us rewrite formula (20) as

$$U = Nw(1 + \phi c). \quad (25)$$

Let the interaction between the lattice atoms be central. The formula for the lattice energy looks like

$$U_1 = \sum_{i=1}^{\mu} E_i, \quad (26)$$

where E_i is the energy of the i -th bond, and μ is the number of the bonds connecting the lattice atoms

interacting with one another. Let us approximately assume that the lattice subjected to a uniform compression undergoes a similarity transformation, i.e., all linear dimensions are reduced identically by the factor λ .

Assuming that the dependences $E_i(\lambda)$ have the same power-law character for all bonds, we can write down the following expression for the energy of the i -th bond:

$$E_i = \frac{\varepsilon_i}{m - q} (-q\lambda^{-m} + m\lambda^{-q}), \quad (27)$$

where q and m are constants, and ε_i is the corresponding bond-breaking energy. Substituting expression (27) into formula (26), we obtain the equality

$$U_1 = \frac{1}{m - q} (-q\lambda^{-m} + m\lambda^{-q}) \sum_{i=1}^{\mu} \varepsilon_i, \quad (28)$$

whence it follows that

$$w = \frac{1}{m - q} (-q\lambda^{-m} + m\lambda^{-q}) \frac{\sum_{i=1}^{\mu} \varepsilon_i}{N - n}. \quad (29)$$

For the energy w_0 of an atom in the undeformed crystal ($\lambda = 1$), we obtain

$$w_0 = \frac{1}{N} \sum_{i=1}^{\mu_0} \varepsilon_i, \quad (30)$$

where μ_0 is the number of bonds in the undeformed crystal. Since

$$c \ll 1, \quad (31)$$

we assume that, in the zeroth approximation in the small parameter c , the equality

$$\frac{1}{N - n} \sum_{i=1}^{\mu} \varepsilon_i \approx w_0 \quad (32)$$

holds, so that formula (29) takes the form

$$w = \frac{w_0}{m - q} (-q\lambda^{-m} + m\lambda^{-q}). \quad (33)$$

If the lattice undergoes the similarity transformation and if all of its linear dimensions are reduced by the factor λ , the lattice volume is reduced by λ^3 times, i.e.,

$$\frac{V_1}{V_{10}} = \lambda^3, \quad (34)$$

where V_{10} is the volume occupied by $(N - n)$ atoms in the undeformed crystal. The both volumes in equality (34) are proportional to $N - n$, so this equality can be rewritten in the form

$$\frac{\nu}{\nu_0} = \lambda^3. \quad (35)$$

Accordingly, formula (33) reads

$$w = \frac{w_0}{m - q} \left(-q \left(\frac{\nu}{\nu_0} \right)^{-\frac{m}{3}} + m \left(\frac{\nu}{\nu_0} \right)^{-\frac{q}{3}} \right). \quad (36)$$

Substituting relation (36) into formula (25) and taking equality (19) into account, we obtain the following expression for the energy of the deformed crystal with interstitial atoms:

$$U = \frac{Nw_0}{m - q} \left[-q \left(\frac{1 - \beta c}{1 - \theta} \right)^{\frac{m}{3}} + m \left(\frac{1 - \beta c}{1 - \theta} \right)^{\frac{q}{3}} \right] (1 + \phi c). \quad (37)$$

5. Equilibrium Concentration of Interstitial Atoms in a Deformed Crystal

Since condition (31) holds, we may approximately write

$$(1 + \phi) \approx (1 - \beta)^{-\xi}, \quad (38)$$

where the notation

$$\xi = \frac{\phi}{\beta} \quad (39)$$

is introduced. In this case, expression (37) takes the form

$$U = \frac{Nw_0}{m - q} \left[-q \left(\frac{1 - \beta c}{1 - \theta} \right)^{\frac{m}{3} - \xi} + m \left(\frac{1 - \beta c}{1 - \theta} \right)^{\frac{q}{3} - \xi} \right]. \quad (40)$$

Differentiating this expression with respect to c and in accordance with condition (11), we obtain the following formula for the equilibrium concentration of interstitial atoms:

$$c_E = \frac{\theta - \theta_C}{\beta(\lambda - \theta_C)} H(\theta - \theta_C), \quad (41)$$

where $H(\theta - \theta_C)$ is the Heaviside unit function, and the notation

$$\theta_C = 1 - \left[\frac{m \left(\frac{q}{3} - \xi \right)}{q \left(\frac{m}{3} - \xi \right)} \right]^{-\frac{3}{m - q}} \quad (42)$$

is introduced.

6. Peculiarities of the Formation of Interstitial Atoms in a Deformed Crystal

The considerations that brought us to formula (41) allow the conclusion to be drawn that, under the action of external pressure, an equilibrium crystalline state, in which the crystal must contain a certain number of interstitial atoms, can arise. In principle, this process can run at a constant temperature. In other words, the formation of interstitial atoms in this case is not related to thermal fluctuations. The crystal deformation induced by external pressure is the reason for such atoms to appear in the crystal. Therefore, in our opinion, it is reasonable to call the proposed formation mechanism for interstitial atoms non-fluctuational.

As follows from formula (41), the formation of interstitial atoms in a deformed crystal has a threshold character: they begin to appear, when the relative volume deformation θ reaches a certain critical value θ_c . A further increase of θ is accompanied by a growth of the concentration of interstitial atoms.

Let us evaluate the critical deformation θ_c . According to work [9], we choose the parameter values $m = 24$ and $q = 6$. In view of formulas (16), (17), and (23), we put $\gamma = 1.5$ and $\beta = 0.5$, which leads to the equality $\xi \approx 1$. Substituting the obtained numerical value into formula (29), we get the estimate $\theta_c \approx 0.1$.

The appearance of interstitial atoms in a deformed crystal is governed by the behavior of the energy U . If $\theta < \theta_c$, the minimum of the energy U corresponds to the situation, where all atoms in the deformed crystal remain to stay at the lattice sites. However, if $\theta > \theta_c$, the situation changes. Now, the minimum of the energy U is attained, if there are interstitial atoms in the crystal. Such a behavior is explained by the fact that the appearance of an interstitial atom decreases the energy of the lattice environment around it. At $\theta > \theta_c$, this process prevails. Therefore, despite that the formation of interstitial atoms is accompanied an energy growth, it is energetically advantageous for the crystal in the equilibrium state to contain a certain number of interstitial atoms in its composition.

The reason that makes the crystal transit from the initial equilibrium state characterized by the equality $\theta = 0$ to a new equilibrium state, in which $\theta > 0$, is the external pressure. The deformation created by the external pressure at the crystal boundary propagates into the crystal volume at the sound velocity. Accord-

dingly, the time τ required for the deformation θ to be established over the whole crystal volume can be estimated as

$$\tau \approx \frac{L}{c_s}, \quad (43)$$

where L is the crystal size, and c_s is the sound velocity in the crystal. Adopting the value $c_s \approx 10^3$ m/s, we obtain $\tau \approx 10^{-5}$ s for a crystal with the size $L \approx 10^{-2}$ m.

According to formula (41), there is no lag of the concentration c_E with respect to the deformation θ . As a result, the time τ determined by the approximate equality (43) is also the time during which the equilibrium concentration c_E is established over the crystal.

As is known [1–3], the equilibrium concentration c_f of interstitial atoms that are formed via the fluctuational mechanism is determined by the formula

$$c_f = \exp\left(-\frac{U_f + pv'}{k_B T}\right), \quad (44)$$

where $p = p(\theta)$ is the pressure, U_f the energy of formation of an interstitial atom, and k_B the Boltzmann constant. As one can see from this formula, the crystal deformation affects the concentration of interstitial atoms formed via the fluctuational mechanism, with the growth of pressure, and, hence, θ , resulting in a reduction of c_f . In this case, the deformation puts the crystal lattice atoms in some order, which is in contrast to the non-fluctuational mechanism, when, at $\theta > \theta_c$, the concentration c increases with the growth of θ , and, accordingly, the crystalline ordering becomes lower. At $T > 0$, both of the above-mentioned mechanisms, fluctuational and non-fluctuational, can be realized. The time interval τ_f required for the equilibrium concentration of interstitial atoms arising due to the fluctuational mechanism to be established over the crystal is determined by the formula [1–3]

$$\tau_f \approx \frac{L^2}{D}, \quad (45)$$

where D is the diffusion coefficient of interstitial atoms. The inequality

$$\frac{D}{L} \ll c_s \quad (46)$$

is obvious. From whence, the inequality

$$\tau \ll \tau_f \quad (47)$$

follows.

Let the crystal deformation rate $\frac{d\theta}{dt}$, where t is the time, satisfy the inequality

$$\frac{1}{\tau_f} \ll \frac{d\theta}{dt} \ll \frac{1}{\tau}. \quad (48)$$

It is obvious that, in this case, the crystal deformation practically does not change the concentration of interstitial atoms formed according to the fluctuational mechanism. In other words, the mechanism of non-fluctuational formation of interstitial atoms is pertinent to rapid deformation processes. By order of magnitude, the bulk elastic modulus of solid bodies equals $K = (10^{10} \div 10^{11})$ Pa. Accordingly, the pressure that creates the critical deformation $\theta_c = 0.1$ equals $(10^9 \div 10^{10})$ Pa. In work [10], it was shown that such pressures bring about a strong interaction between the electron and lattice subsystems, and the crystal transits into a “highly excited” “liquid-like” state. There emerges a structure in which a convective flow can arise. In the cited work, some examples of crystal systems, where the appearance of the mentioned states was observed, were given. In our opinion, the mechanism of non-fluctuational formation of interstitial atoms, which was proposed in the presented work, can make a significant contribution to the theory of the formation of indicated “highly excited” states.

7. Conclusions

Along with the mechanism of fluctuational formation of interstitial atoms in crystals, i.e., according to thermal fluctuations, there is also a non-fluctuational mechanism. According to the latter, interstitial atoms are formed as a result of the uniform compression deformation created by an external pressure, when the relative volume deformation θ exceeds a certain critical value θ_c . In this case, the crystal in the stable equilibrium state contains a certain number of interstitial atoms, and this number increases with the growth of θ . By order of magnitude, the critical deformation θ_c equals 0.1. The establishment of the equilibrium concentration of interstitial atoms propagates over the crystal volume at the sound velocity.

Owing to those features, the mechanism of non-fluctuational formation of interstitial atoms can make a substantial contribution to the disordering in the crystals subjected to the action of considerable rapid compressive deformations, which are characteristic, for example, of explosive processes, as well as to the formation of the so-called “highly excited” states in them.

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Received 02.04.23.

Translated from Ukrainian by O.I. Voitenko

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НЕФЛУКТУАЦІЙНИЙ МЕХАНІЗМ ПОЯВИ МІЖВУЗЛОВИХ АТОМІВ У ДЕФОРМОВАНОМУ КРИСТАЛІ

Пропонується механізм появи міжвузлових атомів, відповідно до якого згадані атоми з'являються в результаті дії стискаючих деформацій. Показано, що поява міжвузлових атомів відбувається, коли відносна об'ємна деформація перевищує деяке критичне значення. Розрахована рівноважна концентрація міжвузлових атомів, які з'являються внаслідок запропонованого механізму. Характерною особливістю останнього є швидке, протікаюче зі швидкістю звуку, встановлення вказаної концентрації.

Ключові слова: термічні флуктуації, вакансія, міжвузлові атоми, нефлуктуаційний механізм.