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# Crystal-geometrical model of grain boundaries structure

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The crystal-geometric model of rigid atomic structure of small-angle and large-angle grain boundaries is considered, which takes into account not only complete but also partial atomic coincidences. The concepts developed allow to determine the grain boundary effective energy depending on misorientation angle, to reveal the primitive cell (containing only one coincidence atom) in the structure of special boundaries, and to show that the maximal misorientation angle $\varphi_{cr}$ for small-angle boundaries depends on the boundary length $l$. So, for the boundary laying plane (111), $\varphi_{cr}$ values vary from 20° (for short boundaries of $l \approx 10^{-7}$ cm) up to $\approx 2°$ (for boundaries with $l \geq 10^{-5}$ cm). The results of special grain boundary modeling show that the low energy of the latter is not determined unequivocally by the density of coincidence sites but, to a greater extent, depends on density of the short-period pattern of partial atoms coincidences within the primitive cell.

Рассматривается кристалло-геометрическая модель жесткой атомной структуры мало- и большеугловых границ зерен, учитывающая не только полные, но и частичные совпадения атомов. Развиваемые представления позволяют определить эффективную энергию границ зерен в зависимости от угла разориентации, выявить в структуре специальных границ примитивную ячейку, содержащую только один совпадающий атом, показать, что максимальный угол разориентации для малоугловых границ $\varphi_{кр}$ зависит от протяженности границы $l$. Так, для плоскости залегания границы (111) значения $\varphi_{кр}$ меняются от 20° (для границ малой протяженности $l \approx 10^{-7}$ см) до $\approx 2°$ (для границ с $l \geq 10^{-5}$ см). Результаты моделирования специальных границ зерен показывают, что низкая энергия последних не определяется однозначно плотностью совпадающих узлов, а в большей степени зависит от плотности короткопериодического узора из частичных совпадений атомов в пределах примитивной ячейки.

It is well known that properties of polycrystalline materials are determined by presence of large amount of interfaces (grain boundaries) therein, which, first of all, differ in crystal-geometric characteristics (the laying plane, the misorientation). Numerous various grain boundary structure models are known. The most perfect one is the model of coincidence site lattice (CSL) [1], the main characteristic thereof being the reciprocal coincidence site density Σ. Depending on the misorientation angle, grain boundaries may be small-angular or large-angular ones. Unfortunately, the critical value of the misorientation angle $\varphi_{cr}$ being the lower limit at which boundaries are considered to be large-angle ones, cannot be determined uniquely for various reasons. First, precise criteria according to which small-angle and large-angle boundaries should be distinguished are not known till now; second, there is no uniform point of view about the maximum Σ value, beyond of which the boundaries are not already special. In other words, there is a question: at what Σ values the conception

of boundary as a special one losses the physical sense. It is to note that $\varphi_{cr}$ values as estimated by various authors differs essentially. For example, in Read and Shockley works [2] value of $\varphi_{cr}$ makes 6 to 9°. In the theory by Li [3] based on coalescence of dislocation cores in boundaries, $\varphi_{cr}$ value can reach ≈40°. According to [4], $\varphi_{cr}$ ~ 11°, on data by Friedel [5] $\varphi_{cr}$ ~ 15° – 20°. In Van Bueren works [6], $\varphi_{cr}$ does not exceed 25°. Unfortunately, as far as we know, the re are neither direct experimental nor reliable theoretical determinations of the misorientation angle critical value $\varphi_{cr}$.

In this work, a crystal-geometric rigid grain boundary structure modeling is proposed taking into account not only the complete atomic coincidences in the boundary but also partial ones, allowing to simulate the grain boundary structure and to obtain the boundary effective energy value (the coincidence degree of lattices in the boundary) at any misorientation angle. The essence of the modeling method is reduced to construction of two identical schemes of lattice atomic arrangement in a certain crystallographic plane [7, 8]. Then, one of the schemes is turned about an axis passing through the common site perpendicularly of this plane with respect to another one. To take into account the partial coincidences, the atomic arrangement scheme (interatomic distances) and the atomic sizes are submitted in the same scale. As will be shown below, such modeling technique allows, firstly, to derive the dependence of boundary effective energy (both full and partial coincidence degree of atoms in the boundary) from the misorientation angle, secondly, to determine the $\varphi_{cr}$ value and to show that it depends on the boundary length and its laying plane, and, thirdly, to reveal the structural element representing a primitive structural cell with a short-period pattern consisting of partially coincident atoms and one completely coincident center atom.

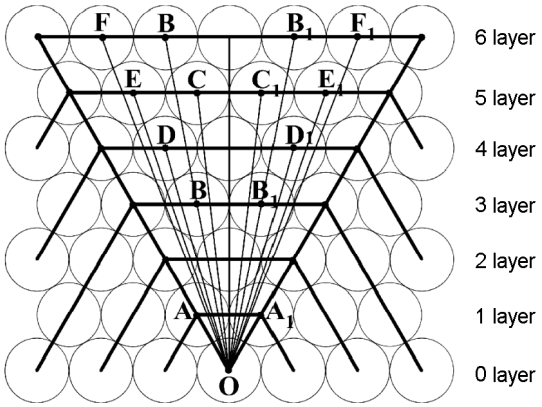


Fig. 1. Determination scheme of φ angles corresponding to CSL for boundary laying plane (111).

The modeling results obtained for two boundary laying planes (100) and (111) of f.c.c. structure are presented below. Fig. 1 shows the determination scheme of angles φ corresponding to coincidence site lattices for boundary laying plane (111). Since the atomic arrangement scheme in this plane is

Table. Misorientation angles $\varphi_{n,k}$, corresponding to CSL for boundary laying plane (111) (Σ is surface density of coincidence sites; $\Sigma^*$, volume density of coincidence sites).

| $\varphi_{n,k}$ (deg.) | | | | |
|---|---|---|---|---|
| | *k* | | | |
| *n* | 1 | 2 | 3 | 4 |
| 3 | 21.79 (Σ7; $\Sigma^*$21) | | | |
| 4 | 32.20 (Σ13; $\Sigma^*$39) | | | |
| 5 | 38.21 (Σ7; $\Sigma^*$7) | 13.17 (Σ19; $\Sigma^*$57) | | |
| 6 | 42.10 (Σ31; $\Sigma^*$93) | 21.79 (Σ7; $\Sigma^*$21)[1] | | |
| 7 | 44.82 (Σ43; $\Sigma^*$129) | 27.80 (Σ13; $\Sigma^*$13) | 9.43 (Σ37; $\Sigma^*$111) | |
| 8 | 46.83 (Σ19; $\Sigma^*$19) | 32.20 (Σ19; $\Sigma^*$39)[1] | 16.43 (Σ49; $\Sigma^*$147) | |
| 9 | 48.37 (Σ73; $\Sigma^*$219) | 35.57 (Σ67; $\Sigma^*$201) | 21.79 (Σ7; $\Sigma^*$21)[1] | 7.34 (Σ61; $\Sigma^*$183) |
| 10 | 49.58 (Σ91; $\Sigma^*$273) | 38.21 (Σ7; $\Sigma^*$7)[1] | 26.01 (Σ79; $\Sigma^*$237) | 13.17 (Σ19; $\Sigma^*$57)[1] |

In the Table, it is possible to find the same angles corresponding to CSL for different pairs (*n*, *k*). From the scheme of angle determination, Fig. 1, it is seen that this recurrence can be avoided considering only *n* and *k* having no common multipliers.

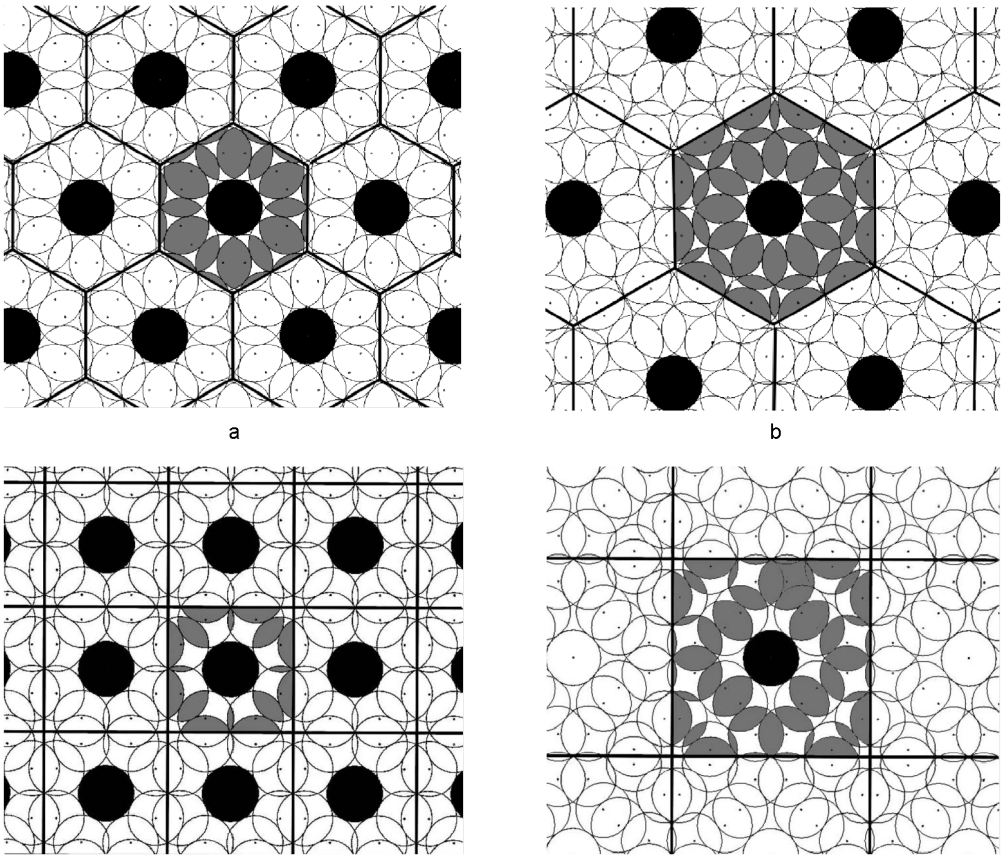


Fig. 2. Grain-boundary structures arising at turning of one atomic arrangement scheme with respect to another one by various angles φ corresponding to special misorientations: a) boundary laying plane (111), φ = 38.21°, Σ7; b) boundary laying plane (111), φ = 27.79°, Σ13; c) boundary laying plane (100), φ = 36.87°, Σ5; d) boundary laying plane (100), φ = 22.62°, Σ13.

characterized by a 6-th order symmetry axis perpendicular to this plane, to determine all turn angles φ resulting in coincidence of the lattice sites, it is possible to restrict ourselves to only part of this scheme, namely, to a 60-degrees sector as it is shown in Fig. 1. Let the point O be the center through which passes the misorientation axis, and $n$ be a number of layers in the structure being considered. The sequential consideration of coincidence opportunity of lattice sites in each layer and determination of the angles resulting in such coincidence, allows to determine all necessary values of φ. The determination scheme is simple enough. For example, in the first layer, sites $A$ and $A_1$ can coincide only, the necessary value of $\varphi_1$ angle makes 60°. From Fig. 1, it is seen that in the second layer, coincidence of sites occurs at turning through 60° as well as in the first layer. Only in the third layer, the coincidence of sites $B$ and $B_1$ is possible at turning throughn angle $\varphi_2$ different from 60°, which can be determined easily from geometrical consideration:

$$\varphi_2 = 2\mathrm{arctg}\left(\frac{1}{3\sqrt{3}}\right). \qquad (1)$$

Consecutive consideration of atomic coincidence opportunity in subsequent layers allows to derive an expression for determination of all angles resulting in occurrence CSL:

$$\mathrm{tg}\frac{\varphi_{n,k}}{2} = \frac{n-2k}{n\sqrt{3}}, \qquad (2)$$

where $n = 3, 4, 5\ldots$, $k = 1, 2, 3\ldots$, $k < n/2$. The f.c.c.lattice misorientation angles ($\varphi_{n,k}$), creating CSL for the boundary laying plane (111) calculated using formula (2) are summarized in Table.

Fig. 2 (a, b) presents as an example the grain-boundary structures arising as a turning result of one atomic arrangement scheme with respect to another one by an-

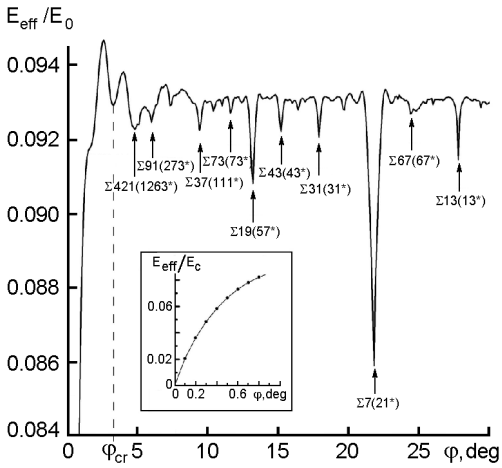


Fig. 3. Dependence of $E_{eff}/E_0$ on misorientation angle φ, boundary laying plane (111), array of 1027 atoms.

gles φ (38.21°; 27.79°), corresponding to the special misorientations (Σ7, 13) for boundary laying plane (111). From Fig. 2, it is seen that the grain-boundary structure includes completely coincident lattice sites as well as partially coincident ones. A distinctive and important feature of all these structures is that everyone thereof can be described with the help of the identical cells representing primitive structures containing in the center only one completely coincident site (atom). The shape of such a cell reflects atomic arrangement symmetry in the plane being considered. So, for plane (111), the cell has the shape of a regular hexagon.

The modeling scheme proposed permits to determine easily parameter of the primitive cell mentioned above ($a_{cell}$):

$$a_{cell}^{n,k} = \frac{nr}{\cos\left(\frac{\varphi_{n,k}}{2}\right)}, \qquad (3)$$

where $r$ is the atomic radius.

For laying plane (100), the primitive cell making it possible to describe the whole structure also contains only one coincident atom (Fig. 2 c, d). The cell is square-shaped. The formulas to determine the φ angles and the primitive cell parameter acell are as follows:

$$\mathrm{tg}\frac{\varphi_{n,k}}{2} = \frac{n-k}{n}, \qquad (4)$$

$$a_{cell}^{n,k} = \frac{2nr}{\cos\left(\frac{\varphi_{n,k}}{2}\right)}, \qquad (5)$$

where $r$ is the atomic radius, $n = 2, 3, 4...$, $k = 1, 2, 3...(n-1)$.

It is easy to show that the ratio between the value of coincident sites reciprocal density Σ and the primitive cell parameter is given by:

$$\Sigma = k \cdot \left(\frac{a_{cell}}{r}\right)^2. \qquad (6)$$

The coefficient $k$ is different and depends on the boundary laying plane. So, the $k$ value makes 3/4 for laying plane (111), and 1/4 for plane (100).

A distinctive feature of grain boundary structure crystal-geometric model proposed is the determination possibility of effective energy $E_{eff}$ not only for the special boundaries, but also for the general type ones at any misorientation angles:

$$E_{eff} = \frac{S_0 - S}{S_0} \cdot E_0, \qquad (7)$$

where $S_0$ is the overlapped area of atom projections on the boundary laying plane at $\varphi = 0$, $S$, the overlapped area at an arbitrary φ (both complete and partial coincidences being taken into account), $E_0$, the coefficient depending on the boundary laying plane only (the energy of general type boundary with the minimal $S/S_0$ value). This purpose is reached by constructing the dependence of the atomic coincidence relative degree $(S_0 - S)/S_0 = E_{eff}/E_0$ on the misorientation angle φ. A computer program developed specially permit to determine the overlapped area of atomic projections on this plane for various boundary length (atomic array) at any turning angle of the above-mentioned atomic arrangement schemes in a certain crystallographic plane (the boundary laying plane). Calculation results for array of about 1000 atoms are presented below. The increase of atomic array up to 10000 and more does not change essentially the results obtained. As an example, Fig. 3 shows such dependence in $E_{eff}/E_0 - \varphi$ coordinates for the laying plane (111) in φ angle range from 0 up to 30°. The dependence $E_{eff}/E_0 = f(\varphi)$ is presented in the specified angular range as the

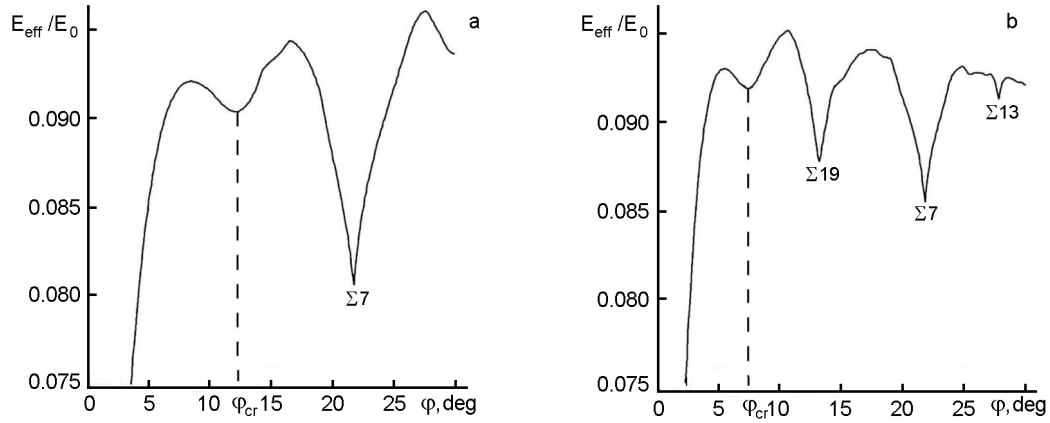


Fig. 4. Dependence of $E_{eff}/E_0$ on misorientation angle φ for various arrays. Boundary laying plane (111): a) 3 layers (37 atoms); b) 5 layers (91 atoms).

curve appears symmetric to that corresponding to the φ = 30° one in the 30 to 60° range for laying plane (111). It is seen from the Figure that the complete coincidence of sites ($S = S_0$) takes place at φ = 0. This means that there is no boundary ($E_{eff} = 0$). As the misorientation angle increases, the $E_{eff}$ rises sharply, reaching the maximal value at misorientation angle φ = 2.6°. The further φ increasing results in minima appearing in curve $E_{eff} = E_{eff}(\varphi)$. Determination of φ angles corresponding to these minima shows that all of them answer to special boundaries, except only for the first minimum corresponding to φ = 3.3°. To clarify the nature of this minimum, additional determinations of atoms (sites) coincidence degree in short boundaries have been carried out depending on atoms array.

A consecutive consideration of various atomic arrays, admitting appearance, according to the scheme presented in Fig. 1 and Table, one, two, three, etc. minima on the $E_{eff} = E_{eff}(\varphi)$ curve corresponding to coincidence site lattices, has allowed to show unequivocally that the first minimum found out in then curve (Fig. 3) does not correspond to any special boundary. This is confirmed by $E_{eff} = E_{eff}(\varphi)$ dependences given for various arrays in Fig. 4 (a, b). In Fig. 4a, results for array that makes three layers are shown. According to Table and the scheme shown in Fig. 1, in the three-layer array only one minimum at angle φ = 21.79° corresponding to Σ7 appears. In experiment, one more minimum in the curve is found which cannot be explained of course by the CSL presence. As the array increases up to 5 layers (Fig. 4b), besides the minima corresponding to Σ 7, 13, 19, as it is shown in Table, too, an additional minimum is found, but at φ ≈ 7.5°. Thus, independently of the atomic array considered and, hence, of the boundary length, the additional minimum is always found out which does not answer to CSL. As the boundary length increases, the minimum position is shifted towards small φ angles.

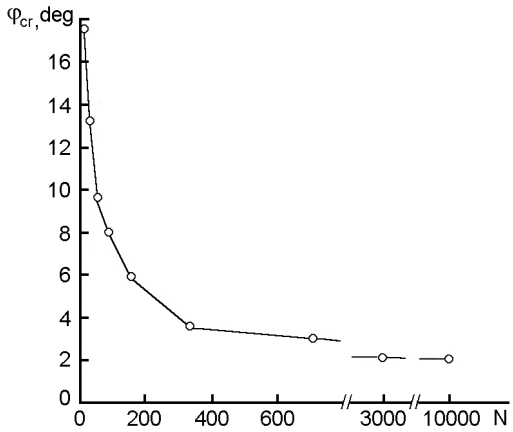


Fig. 5. Dependence $\varphi_{cr}$ on boundary length (array of $N$ atoms) for boundary laying plane (111).

The $\varphi_{cr}$ dependence on the boundary length (atomic array) is shown in Fig. 5. From the Figure it is seen that at small length ($l$) of boundary with laying plane (111), less than 50 atomic sizes ($l \geq 10^{-6}$ cm), the $\varphi_{cr}$ value depends heavily on the number of atoms $N$ and can attain 18°. In other words, for small-angle boundaries of insignificant length, the misorientation angle value can amount to about 20°. For longer boundaries ($l \leq 10^{-5}$ cm), the $\varphi_{cr}$ does not depend practically on the boundary length

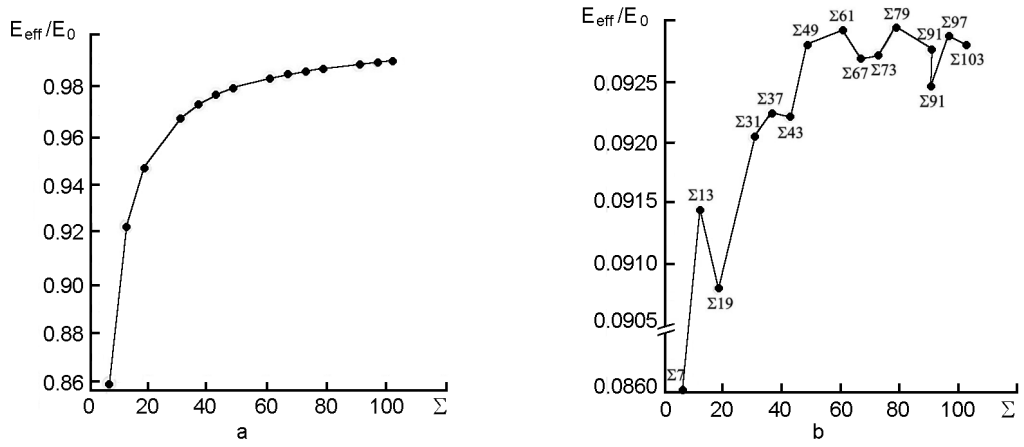


Fig. 6. Dependence of $E_{eff}/E_0$ on Σ value for plane (111): a) by results of [9], b) by results of this work.

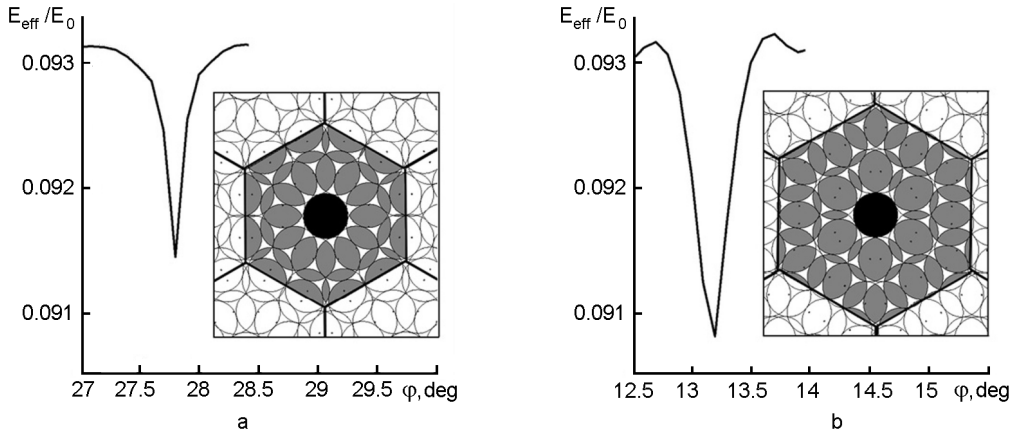


Fig. 7. Profiles of minima in the dependence of $E_{eff}/E_0$ on misorientation angle for Σ13 (a) and Σ19 (b) and corresponding primitive cells with short-period patterns. The plane is (111).

and makes ≈2°. Thus, depending on the boundary extension, $\varphi_{cr}$ may vary by one decimal order even for and the same boundary laying plane, and this allows to explain the ambiguous estimations of $\varphi_{cr}$ given by various authors. In our opinion, a significant result provided by the considered model consists in the explanation of the special boundary low energy. Traditionally, the special boundary energy is connected only with the Σ value (the density of complete coincidence sites). For example, in [9], the relation $E = E_{GT}(1 - \Sigma^{-1})$ is given where $E_{GT}$ is the energy of general type boundary; this expression, however, does not correspond always to experimental Σ estimations. Fig. 6 presents the $E_{eff}/E_0$ dependence on Σ for laying plane (111) obtained in this work. The dependence presented is not monotonous. It is not necessarily that smaller Σ values correspond to low $E_{eff}$ value. So, for example, value of $E_{eff}$ for Σ19 appears lower than for Σ13; for Σ73, $E_{eff}$ is lower than for Σ49, etc. Explanation of this effect can be seen in Fig. 7 where minima profiles in the curve $E_{eff} = E_0$ for Σ13 and Σ19 and the primitive cells with short-period pattern forming structure of such grain boundaries are shown. Since on the ordinate axis, coincidence density values are laid, i.e. the density of primitive cells pattern, the latter determine the energy of special grain boundaries. In other words, low energy of the special grain boundaries is determined by high density of short-period patterns of the primitive cell structure. The increase of the pattern density results in the boundary energy decrease.

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## Кристало-геометрична модель структури меж зерен

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Розглядається кристало-геометрична модель жорсткої атомної структури мало - та великокутових меж зерен, яка ураховує не тільки повні, але й часткові збіжності атомів. Уявлення, які розвиваються, дозволяють визначити ефективну енергію меж зерен у залежності від кута дезорієнтації, виявити у структурі спеціальних меж примітивну комірку, яка вміщує тільки один збіжний атом, показати, що максимальний кут дезорієнтації для малокутових меж $\varphi_{кр}$ залежить від протяжності межі $l$. Так, для площини залягання межі (111) значення $\varphi_{кр}$ змінюються від $20^{\circ}$ (для меж невеликої протяжності $l \approx 10^{-7}$ см) до $\approx 2^{\circ}$ (для меж з $l \geq 10^{-5}$ см). Результати моделювання спеціальних меж зерен показують, що низька енергія останніх не визначається однозначно густиною збіжних вузлів, а більше залежить від густини короткоперіодичного узору із часткових збіжностей атомів у межах примітивної комірки.