QUASIPERIODIC AND DISORDERED INTERFACES IN NANOSTRUCTURED MATERIALS

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1. Introduction

This lecture is concerned with quasiperiodic and disordered interfaces in nanostructured materials. The notion of quasiperiodic interfaces is rather new in both solid state physics and materials science. In particular, it is not widespread among experts in the area of nanostructured materials. Therefore, the most attention in this lecture will be paid to the structure and properties of quasiperiodic interfaces as well as to their contribution to macroscopic properties of nanostructured materials. In doing so, for brevity, we will concentrate our theoretical consideration on final results, while intermediate mathematical details will be only outlined.

It should be noted that studies of quasiperiodic interfaces in nanostructured materials are just at the starting point. In these circumstances, the lecture puts more new questions than answers to previously stated questions in this field. The main conclusions of this lecture are as follows: first, quasiperiodic interfaces are inherent elements of the nanostructured materials structure; second, quasiperiodic interfaces represent the special type of interfaces exhibiting the properties which, generally speaking, are different from those of periodic and disordered interfaces; third, quasiperiodic interfaces are capable of significantly contributing to macroscopic (at least, mechanical) properties of nanostructured materials; fourth, quasinanocrystalline materials (consisting of nanocrystallites and quasiperiodic grain boundaries) represent a new class of nanostructured materials.

In addition, here we will discuss the features of disordered interfaces in nanostructured materials. In doing so, the special attention will be paid to transformations of disordered interfaces into ordered (periodic and quasiperiodic) ones in nanocrystalline materials as well as to spreading of disordered interfaces in nanoamorphous materials (nanoglasses).

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The lecture is organized as follows. In section 2 definitions of periodic, quasiperiodic and disordered solid state structures are considered. Section 3 deals with description of quasiperiodic interfaces in film–substrate systems. In section 4 we examine quasiperiodic tilt boundaries in nanostructured polycrystals and discuss the notion of quasinanocrystalline materials. Section 5 is concerned with disordered interfaces in nanostructured materials. Section 6 contains concluding remarks.

2. Periodic, Quasiperiodic and Disordered Structures

Solid state structures are specified by their mass distributions in space. In this context, $\rho(\mathbf{r})$, a mass density at position $\mathbf{r}$ in a d–dimensional space, serves as the main characteristic of a d–dimensional solid. In general, there are the three basic categories of solid state structures: periodic, quasiperiodic, and disordered ones. Periodic and quasiperiodic structures exhibit a long–range translational ordering, in which case their diffraction patterns consist of sharp peaks. Disordered structures do not have any long–range translational order.

A periodic solid is by definition specified by mass density $\rho(\mathbf{r})$ that is periodic:

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R}) \tag{1}$$

for every vector $\mathbf{R}$ in some periodic lattice L. Due to periodicity in d–dimensional coordinate space, $\rho(\mathbf{r})$ can be expressed as a discrete Fourier series:

$$\rho(\mathbf{r}) = \sum_{\mathbf{q} \in Q} \rho_{\mathbf{q}}(\mathbf{r}) exp\{i\mathbf{qr}\} \tag{2}$$

with $\mathbf{q}$ being vectors in a d–dimensional periodic lattice Q reciprocal to the d–dimensional periodic lattice L of vectors $\mathbf{R}$. The reciprocal lattice Q is generated by d basis vectors. Crystalline materials are examples of periodic solids.

A d–dimensional quasiperiodic solid is by definition specified by mass density $\rho(\mathbf{r})$ which can be expressed as a discrete Fourier series:

$$\rho(\mathbf{r}) = \sum_{\mathbf{q} \in \tilde{Q}} \rho_{\mathbf{q}}(\mathbf{r}) exp\{i\mathbf{qr}\}, \tag{3}$$

with $\mathbf{q}$ being vectors in a reciprocal lattice $\tilde{Q}$ generated by $\tilde{d}$ basis vectors, where $\tilde{d} > d$, e.g. [1,2]. That is the number $\tilde{d}$ of basis vectors of the reciprocal lattice $\tilde{Q}$ is larger than dimension d of quasiperiodic solid. Quasicrystals serve as the most known example of quasiperiodic solids, e.g. [1-3].

Disordered solids do not exhibit any long–range translational order, in which case their diffraction patterns do not contain sharp peaks; such patterns consist of continuous extended regions. A disordered solid is specified by mass density $\rho(\mathbf{r})$ which can be expressed as a Fourier integral:

$$\rho(\mathbf{r}) = \int_{Q'} \rho_{\mathbf{q}}(\mathbf{r}) exp\{i\mathbf{q}\mathbf{r}\} d\mathbf{q}, \tag{4}$$

where $\rho_{\mathbf{q}}$ is a non–zero function in the continuous extended regions Q' of reciprocal space. Amorphous solids serve as well–known examples of disordered solid state structures.

3. Quasiperiodic Interfaces in Film–Substrate Systems

This lecture is concerned mostly with quasiperiodic interfaces. Let us start our discussion of quasiperiodic interfaces with description of such interfaces in film–substrate systems (in particular, in nanostructured–film–substrate systems). Such interfaces serve as the simplest example of quasiperiodic interfaces and, on the other hand, have the same basic features as more complicately structured, quasiperiodic grain boundaries in polycrystalline and nanocrystalline materials.

3.1. STRUCTURAL FEATURES OF QUASIPERIODIC INTERFACES

Let us consider a one–dimensional infinite interface between a two–dimensional film and substrate both having square lattices with different parameters. Such interfaces can be used as effective models of real interfaces in film–substrate systems, in which case analysis of model interfaces allows one to reveal the basic peculiarities of real interfaces, e.g. [4-7]. Let a and c be the square lattice parameters of film and substrate, respectively. For definiteness, we assume that $c > a$. Misfit parameter $f = 1 - a/c$ characterizes misfit between lattices of film and substrate.

Formation of ensemble of misfit dislocations at interface (Fig.1) is the effective way for relaxation of misfit stresses which is most often realized in real film–substrate systems [4-7]. Usually models of interfaces containing misfit dislocations deal with infinite interfaces between lattices with relatively rational parameters a and c, that is, $c/a = n/m$, where n and m are co–prime integers. In this situation, equilibrium spatial organization of misfit dislocation ensemble is periodic at an infinite interface with period $na = mc$ (Fig.1a).

However, in general, ratio c/a which characterizes infinite interface is either rational or irrational. In the second situation, interface with its misfit dislocations is quasiperiodically ordered (Fig.1b). As to details, let us determine and examine the quasiperiodic ordering of an interface with irrational a/c (and irrational $f = 1 - a/c$) by means of the geometric model.

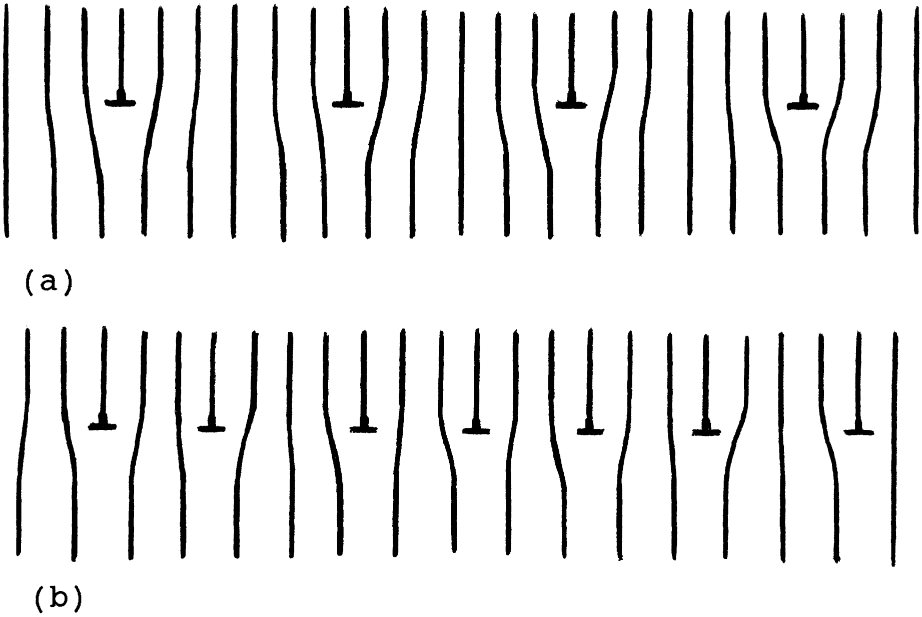

Fig.1. Misfit dislocations at interface. (a) Periodically and (b) quasiperiodically ordered ensembles of misfit dislocations.

Within the framework of the geometric model, an interface is treated as the two non–interacting atomic layers of film and substrate (Fig.2). This model directly deals with the symmetry properties of the interface, related to long–range ordering in adjacent film and substrate. In this model, atoms belonging to different layers do not interact, that is, each atom of the film (substrate) layer "feels" only the atoms of the film (substrate) layer.

When atoms of film and substrate are modeled as point balls with masses m_f and m_s, respectively, the atomic (mass) density function of the interface is

$$\rho(x) = \sum_{\alpha,\beta} [m_f \delta(x - U_f - \alpha a) + m_s \delta(x - U_s - \beta c)], \qquad (5)$$

where α and β are integers, U_f and U_s define the origins of the atomic chains of film and substrate, respectively, x denotes the coordinate along the interface line.

Since c/a is irrational, the basis one–dimensional vectors c and a of the model interface are relatively irrational. As a corollary, Fourier image of the interface (Fig.2) is a reciprocal lattice (determined by convolution of reciprocal lattices of film and substrate) having the two relatively irrational basic vectors, $2\pi/a$ and

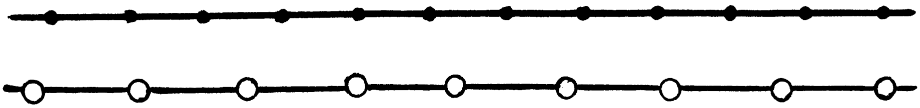

Fig.2. Quasiperiodic interface as a line with superimposed atomic layers of film and substrate. Atoms of film and substrate are shown as full and open circles, respectively.

$2\pi/c$. Then the atomic density function of the interface can be represented as:

$$\rho(x) = \sum_{p_1,p_2} \rho_{p_1p_2} exp(\frac{i2\pi p_1 x}{a} + \frac{i2\pi p_2 x}{c} + i\varphi_1 + i\varphi_2) \tag{6}$$

where p_1 and p_2 are integers, $\varphi_1(= 2\pi U_f/a)$ and $\varphi_2(= 2\pi U_s/c)$ are the phases such that a displacement (along the interface line) of the atomic layer of the film (substrate, respectively) as a whole corresponds to a shift in the phase φ_1 (φ_2, respectively). The atomic density function (6) of the one-dimensional interface is quasiperiodic having the two relatively irrational basis vectors of its Fourier transform.

As to beyond the geometric model, analysis which takes into account both the symmetry properties of the interface and a short-range interaction between atoms belonging to film and substrate leads to the same conclusion: the interface is quasiperiodic having the reciprocal lattice generated by the two relatively irrational basic vectors (for details, see [1]).

The spatial positions of misfit dislocations are determined as follows. First, one connects each atom of the substrate with the nearest atom of the film (Fig.1). After this procedure, some atoms of the film are extracted which are not in the connection with atoms of the substrate. Such atoms of the film are treated to be associated with cores of misfit dislocations. As a result, we have a quasiperiodic interface as an interface with the smoothest (but non-periodic) arrangement of misfit dislocations separated by either distance $n'a$ or distance $(n' + 1)a$, where n' is the positive integer such that $n'af < a < (n' + 1)af$ (Fig.1b). It is related to the fact that misfits $-n'af$ and $-(n' + 1)af$ accumulated at respective distances $n'a$ and $(n' + 1)a$ can not be completely compensated by a misfit dislocation with Burgers vector a. Though n' is by definition the positive integer such that (irrational) quantities $n'f$ and $(n'+1)f$ are closest to 1, $n'af \neq a$ and $(n'+1)af \neq a$, because f is irrational. In this situation, the maximum that is possible in compensating misfit between film and substrate lattices with relatively irrational expansion contains products of the form:

$$|\rho_1|^{s_1}|\rho_2|^{s_2}exp\{i(z_1\frac{2\pi x}{a}+z_2\frac{2\pi x}{c})\}exp\{i(z_1\varphi_1+z_2\varphi_2)\}-(c.c.), \tag{7}$$

where z_1 and z_2 are integers, $s_{1,2}=0,...,k$, $|z_{1,2}|\le s_{1,2}$, and $s_1+s_2=k$.

To obtain an expression for the free energy, it is necessary to integrate the products of the form (7) with respect to the space coordinate x. For the case $z_1 2\pi/a+z_2 2\pi/c\neq 0$, all integrals of products of the form (7) with respect to x are equal to zero. The integrals of expressions (7) with $z_1 2\pi/a+z_2 2\pi/c=0$, on the other hand, have non–zero values. However, since (one–dimensional) vectors $2\pi/a$ and $2\pi/c$ are relatively irrational, the linear combination of such vectors with the coefficients z_l is equal to zero only if $z_1=z_2=0$. As a result, we find that only a product of the form (7) with parameters $z_1=0$ and $z_2=0$ are not transformed into zero by integration with respect to x. For such products, the factor $exp\ i(z_1\varphi_1+z_2\varphi_2)=1$ for any values of the phases φ_1 and φ_2. In this way, the free energy L is invariant with respect to changes in the two phases φ_1 and φ_2, which correspond to displacements of film and substrate, respectively. The phases φ_1 and φ_2 are hydrodynamic (Goldstone) modes or, in other words, the degrees of freedom of a quasiperiodic interface.

As noted above, hydrodynamic modes φ_1 and φ_2 parametrize respectively displacement of film $U_s=a\varphi_1/2\pi$ and displacement of substrate $U_f=c\varphi_2/2\pi$. Since the free energy of the quasiperiodic interface is invariant at any variations of the phases φ_1 and φ_2, it also is invariant for any changes of the joint displacement $U=\frac{1}{2}(U_f+U_s)$ and relative displacement $\Delta U=\frac{1}{2}(U_f-U_s)$ of film and substrate. So, the free energy is the same for any relative displacement ΔU of film and substrate. It is a very interesting feature that emphasizes the difference between quasiperiodic and periodic interfaces. In geometric terms, this feature is equivalent to the statement that the displacement–shift–complete (DSC) lattice of the one–dimensional quasiperiodic interface is the interface line. (One–dimensional periodic interfaces have rows of isolated points as their DSC lattices.)

Displacements of film relative to substrate. In spite of the fact that the free energy of a quasiperiodic interface is the same for any value of $\Delta U=U_f-U_s$, any displacement of the film relative to the substrate is related to overcoming an energetic barrier. As to details, let us consider the layer of film atoms placed in a periodic potential of substrate atoms, when the film and the substrate have relatively irrational periods (Fig.3a).

For a moment, let atoms of the film be assumed to do not interact with atoms of the substrate, that is, atoms of the film do not "feel" the periodic potential. In this situation (which corresponds to geometric model), as shown in the theory of incommensurate systems (e.g., [1,2]), the set of distances $\Delta_{\alpha\beta}=x_{f\alpha}-x_{s\beta}$ between film atoms (with coordinates $x_{f\alpha}$) and periodic potential maxima (with

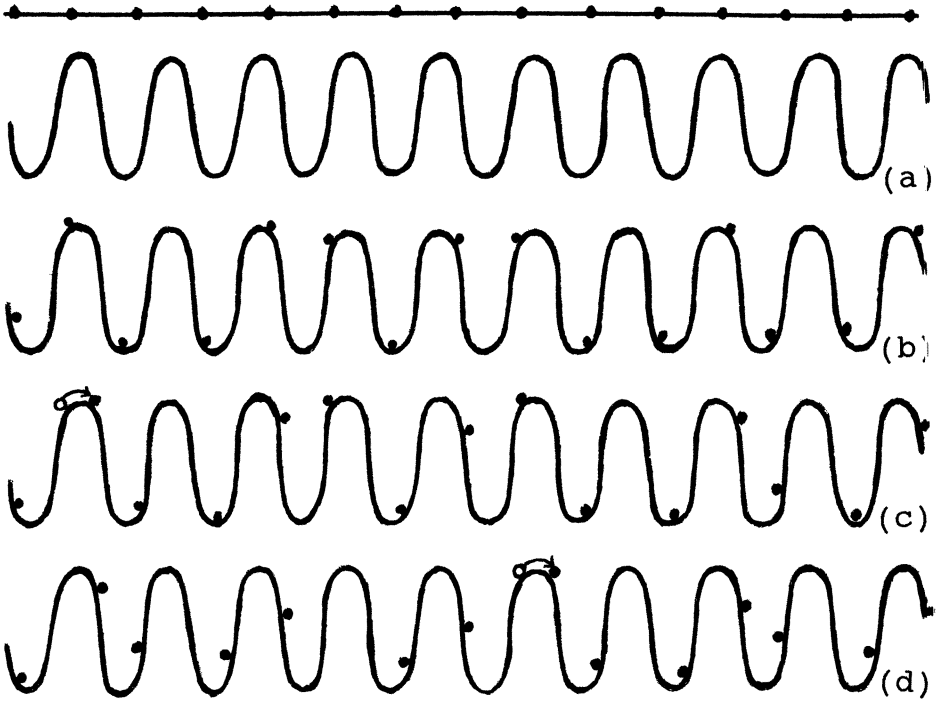

Fig.3. Atoms of film in potential created by atoms of substrate: (a) atoms of film do not "feel" the potential; (b) atoms of film "feel" the potential; (c) and (d) displacement of film occurs via jumps of film atoms.

coordinates $x_{s\beta}$) forms a DSC lattice being simply a line. As a corollary, for every distance $\Delta_{\alpha\beta}$ in the range from 0 to $c/2$, one can find a pair of atom α and its neighbouring maximum β of the periodic potential, which are separeted by distance $\Delta_{\alpha\beta}$.

Now let us return to the situation with the interaction between the atomic layers of the film and the substrate taken into account. This interaction causes atoms of the film and the substrate to be shifted to new positions, in which case the coordinates $x_{f\alpha}$ and $x_{s\beta}$ transform into $x'_{f\alpha}$ and $x'_{s\beta}$, respectively (Fig.3b). New coordinates $x'_{f\alpha}$ ($x'_{s\beta}$, resp.) depend on parameters of interaction between film (substrate, resp.) atoms, film–substrate interaction, and the coordinate $x_{f\alpha}$ ($x_{s\beta}$, resp.). For any realistic values of the above parameters, there is the following obvious tendency: the larger/smaller values of $\Delta_{\alpha\beta} = x_{f\alpha} - x_{s\beta}$ correspond to larger/smaller values of $\Delta'_{\alpha\beta} = x'_{f\alpha} - x'_{s\beta}$. In turn, a film atom characterized by a larger/smaller value of $\Delta'_{\alpha\beta}$ are placed at a lower/higher level of the potential (Fig.3b).

Let us consider a microscopic picture of a film displacement. Any such a displacement is realized via consequent-in-time jumps of film atoms associated with misfit dislocations (or, in other words, via consequent-in-time displacements of misfit dislocations) plus displacements of other atoms within "their" hollows of the potential (Fig.3c and d). In these circumstances, first, the atom jumps which is placed at the highest level of the potential, that is, the atom with the lowest value of $\Delta'_{\alpha\beta}$ (corresponding to $\Delta_{\alpha\beta} = 0$). This atom overcomes the lowest energetic barrier ΔU_{min}, when it jumps (Fig.3c). The jump of the atom and corresponding infinitesimal displacements of all other atoms within "their" potential hollows provide infinitesimal displacement of the film, resulting in a new (also quasiperiodic) configuration of the interface (Fig.3c). In this configuration a new atom of the film has the lowest value of $\Delta'_{\alpha\beta}$ (corresponding to $\Delta_{\alpha\beta} = 0$). When the film moves (by infinitesimal distance), this atom jumps and all other atoms displace within "their" potential hollows (Fig.3d). As a result, a new configuration of the atomic layers is formed with a new atom characterized by the lowest value of $\Delta x'_{\alpha\beta}$ (corresponding to $\Delta_{\alpha\beta} = 0$). Such a process repeatedly occurs providing a displacement of the film by any distance.

In the discussed scenario, consequent-in-time displacements of misfit dislocations (Fig.3c and d) occur in different places of the film-substrate interface, namely the places where the energetic barrier ΔU_q for a dislocation displacement is lowest: $\Delta U_q = \Delta U_{min}$. In this event, for any quasiperiodic configuration of the interface (or, in other terms, for any relative displacement $U_f - U_s$ of the film and the substrate), there is only one misfit dislocation characterized by the lowest barrier U_{min} for its displacement. Other misfit dislocations are characterized by values of $\Delta U_q > \Delta U_{min}$, where

$$\Delta U_q = \Delta U_{min} h(\Delta_{\alpha\beta}) \tag{8}$$

and function $h(\Delta_{\alpha\beta})$ monotonically increases as $\Delta_{\alpha\beta}$ increases. In the first approximation, we can write

$$h(\Delta_{\alpha\beta}) \approx 1 + \frac{\Delta U_{max}}{\Delta U_{min}} \frac{2\Delta_{\alpha\beta}}{(c-a)} \tag{9}$$

where ΔU_{max} is the maximum barrier for a misfit dislocation displacement, and $\Delta_{\alpha\beta}$ ranges from 0 to $(c-a)/2$.

When a film–substrate interface is periodic, displacements of a film are effectively realized via elementary displacements of misfit dislocations [8], which (locally) break the periodic translational order (Fig.4). Such breaks lead to an increase ΔU_{el} in the elastic energy of the initially periodic ensemble of misfit dislocations. In these circumstances, there is the following energetic barrier for a misfit dislocation displacement:

$$\Delta U_p \approx \Delta U_{min} h(a/2) + \Delta U_{el} \tag{10}$$

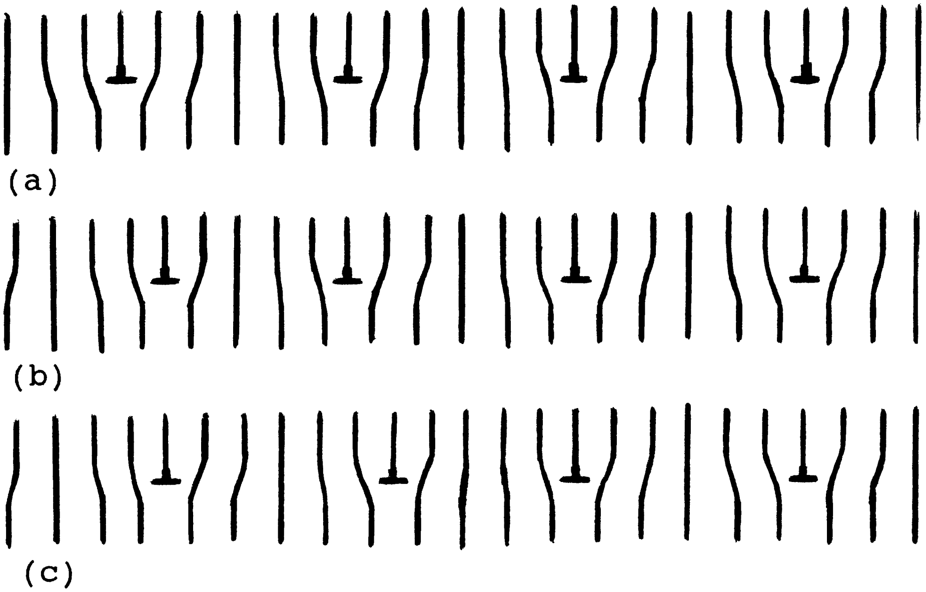

Fig.4. Displacement of film via transformations of initially periodic interface. (a) Periodically ordered ensemble of misfit dislocations (initial state). (b) and (c) Displacements of misfit dislocations, which locally break the initial periodicity.

where $\Delta_{\alpha\beta} = a/2$ corresponds to position of a film atom associated with a misfi dislocation core in the geometric model.

From (8)–(10) we find that $\Delta U_p > (or >>)\Delta U_q$. Hence film migration occuring via transformations of a quasiperiodic interface (Fig.3c and d) is more easier than that occuring via transformations of a periodic interface (Fig.4).

In paper [8] a simplified model of island film migration via displacements of misfit dislocations has been proposed. This model is simplified in the sense that it does not take into account any changes in the elastic energy of misfit dislocations, though it operates with displacements of either isolated misfit dislocations or their periodically ordered ensemble, which are undoubtedly related to changes in the elastic energy. At the same time, predictions of the model [8] are in a good agreement with experimental data (e.g., [9, 10]) on island film migration. This contradiction can be explained, if we accept that the model [8], in reality, describes island film migration occuring via transformations of quasiperiodic interfaces, in which case the contribution of ΔU_{el} to the energetic barrier for a dislocation displacement actually should be neglected. In this context, the agreement between theoretical estimates [8] and experimental data [9, 10] on island film migration can be treated as an indication of the specific properties of quasiperiodic interfaces.

3.3. QUASIPERIODIC INTERFACES OF FINITE EXTENT. FORMATION OF QUASIPERIODIC INTERFACES

Up to now, we have examined infinite interfaces with infinite rows of misfit dislocations. Real film–substrate interfaces have finite lengths. In this subsection, we will demonstrate that interfaces of finite extent can exhibit quasiperiodic translational order even when the initial ratio a/c is rational. Let us consider an one–dimensional interface (consisting of the two atomic chains of a film and a substrate) with a finite length and a rational misfit parameter $f = 1 - a/c = 1 - m/n$. Let k_f and k_s be respectively the numbers of atoms in the chain of the film and the chain of the substrate, which belong to the interface. For given k_f, n and m (or, in other terms, k_f, a and c), the two following situations are possible: (i) ratio k_f/n is integer, and (ii) ratio k_s/n is non–integer. In the former situation, the interface is periodic, that is, misfit dislocations in the relaxed interface are periodically arranged with spacing $na (= mc)$ (Fig.1a). $k_f/n (= k_s/m)$ indicates the number of periods within the interface. In situation (ii), the smoothest arrangement of misfit dislocations is provided by quasiperiodic ordering of such dislocations. It minimizes the elastic energy density of the system [1] and, therefore, is realized when the film–substrate system reaches its equilibrium state.

In real processes of film deposition on substrates, film sizes (and, therefore, parameters k_f and k_s), in general, are arbitrary. In these circumstances, situation (i) with strict restrictions on values of n and m occurs very seldom as compared with situation (ii). In the first approximation, frequencies of appearance of situations (i) and (ii) are f and $1 - f$, respectively, where f denotes the misfit parameter. Usually, $f << 1$. As a corollary, within the framework of widely used model of film–substrate interfaces as one–dimensional interfaces with misfit dislocations [2], we come to conclusion that quasiperiodic interfaces are inherent elements of real film–substrate systems (at equilibrium).

3.4. CONCLUDING REMARKS

Thus quasiperiodic interfaces are theoretically revealed here to be inherent structural elements of film–substrate systems. In order to verify definitely this conclusion, the corresponding experimental investigations in future are of utmost interest, namely investigations which use the concept of quasiperiodic interfaces. (At

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[1] In general, film edges influence on spatial positions of misfit dislocations, in which case this effect can violate the quasiperiodic arrangement of dislocations near the edges. Since the effect in question manifests itself near film edges only, hereafter, for simplicity, we will not take it into account.

[2] This model, being convenient for analysis, takes into account the basic features of real interfaces in film–substrate systems [4, 5].

present, in fact, most experimental studies of interfaces are based on the concept of periodic interfaces.) In addition, interpretation of available experimental data, which uses the notion of quasiperiodic interfaces in film–substrate systems, is also important.

4. Quasiperiodic Interfaces in Nanostructured Polycrystals. Quasinanocrystalline Materials

In this section we consider quasiperiodic grain boundaries in nanostructured polycrystals and determine quasinanocrystalline solids (consisting of nanocrystallites and quasiperiodic grain boundaries) as a new type of nanostructured materials. In description of quasiperiodic grain boundaries, we will focus our attention to quasiperiodic tilt boundaries being a widespread type of interfaces.

4.1. STRUCTURAL-UNIT MODEL OF TILT BOUNDARIES. QUASIPERIODIC TILT BOUNDARIES

In terms of widely used model of structural units [11], a tilt boundary in a crystal is viewed as a packing of structural units of either one or (usually) two types, say, A and B. In general, two types, A and B, of structural units alternate with each other (in a certain consequence depending on misorientation of boundary) in boundary plane in direction perpendicular to tilt axis. Each row of structural units which is parallel with tilt axis consists of units of one type (either A or B). In these circumstances, only ordering of structural–units consequence in one direction (perpendicular to tilt axis) is significant for identification of a tilt boundary. Therefore, in context of structural–unit representation [11], hereafter we will treat tilt boundaries as one–dimensional consequences of structural units.

There are so-called favoured tilt boundaries each consisting of one type of structural units [11]. Say, boundaries described as consequences ...$AAAAA$... (Fig.5a) and ...$BBBBB$... (Fig.5b) are favoured. A tilt boundary in the misorientation range between two favoured boundaries is described as a consequence of deformed structural units of the favoured boundaries [11]. For example, tilt boundaries in the misorientation range between the favoured boundaries of ...$AAAAA$... and ...$BBBBB$... types can be represented as consequences of both A and B units (Fig.5c and d).

First, let us consider a periodic tilt boundary consisting of A and B units. It is effectively modeled as a periodic consequence of deformed units A and B, with r units A and s units B composing each one–period fragment of this boundary (Fig.5c). As with any periodic tilt boundary, value of r/s is rational, and period

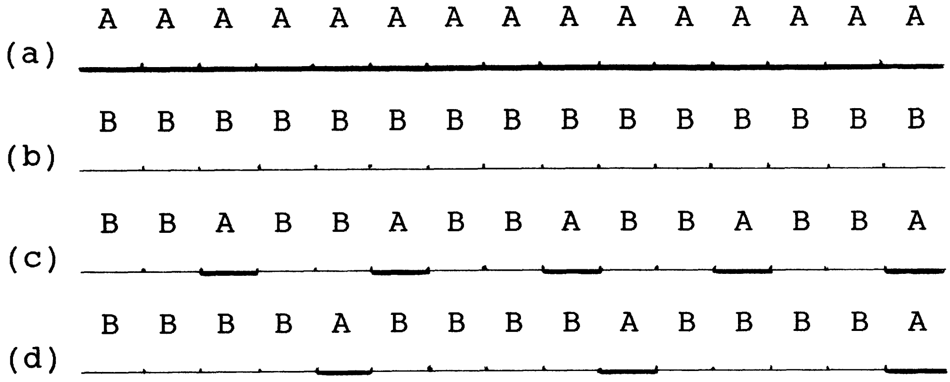

Fig.5. Structural-unit-representation of tilt boundaries. (a) and (b) Favoured tilt boundaries. (c) and (d) General tilt boundaries.

is finite.

Structural units (A or B) whose number is lower in a tilt boundary are called minority units. Hereafter, for definiteness, we will assume A units as the minority ones. With each minority unit a secondary grain boundary dislocation is associated [11]. Elastic fields of such dislocations determine the elastic energy of a tilt boundary.

Misorientation θ of a tilt boundary with the periodic structure is related to the characteristics of structural units and favoured boundaries as follows [12]:

$$\sin(\theta/2) = \frac{rd_A \sin(\theta_A/2) + sd_B \sin(\theta_B/2)}{H} \tag{11}$$

where d_A and d_B are the lengths of non-deformed A and B units , respectively; θ_A and θ_B are misorientations of the favoured boundaries consisting of only A units and only B units, respectively; H is the period of the tilt boundary. Since there are r deformed units A (each having length d'_A) and s deformed units B (each having the length d'_B) within one period of the tilt boundary, we find

$$H = rd'_A + sd'_B \tag{12}$$

The lengths d'_A and d'_B are the projections of respectively d_A and d_B on the boundary plane:

$$d'_A = d_A \cos(\theta + \kappa - \theta_A) \tag{13}$$

$$d'_B = d_B \cos(\theta + \kappa - \theta_B) \tag{14}$$

Here κ denotes the inclination angle characterizing assymetry of the boundary, in which case $\theta + \kappa - \theta_A$ $(\theta + \kappa - \theta_B)$ is the tilt angle of the boundary plane relative

Fig.6. Quasiperiodic tilt boundary as a quasiperiodic consequence of structural units A and B.

to the plane of the symmetric tilt boundary consisting of only non–deformed A units (B units, respectively).

For periodic boundaries, the characteristic angle $\theta + \kappa$ is rational. When it is irrational, d'_A and d''_B are relatively irrational (see formulae (13) and (14)). In this case, a tilt boundary is quasiperiodic with its mass density expressed as:

$$\rho(x) = \sum_{p_1,p_2} \rho_{p_1p_2} exp\{i2\pi(p_1x/d'_A + p_2x/d'_B) + i\varphi_1 + i\varphi_2\} \tag{15}$$

where p_1 and p_2 are integers, φ_1 and φ_2 are the phases.

In terms of structural–unit model, a quasiperiodic tilt boundary with infinite length can be modeled as a quasiperiodic consequence of $\tilde{r}$ units A and $\tilde{s}$ units B with $\tilde{r}$ and $\tilde{s}$ being infinite and $\tilde{r}/\tilde{s}$ being irrational [13, 14]. Minority units A in the quasiperiodic consequence are separated by either n' or $n' + 1$ units B, where n' is the smallest positive integer such that $1/(n' + 1) < \tilde{r}/\tilde{s} < 1/n'$ (Fig.6). For given $\tilde{r}/\tilde{s}$, the quasiperiodic ordering in arrangement of $\tilde{r}A$ and $\tilde{s}B$ units provides the smoothest arrangement of minority units with corresponding boundary dislocations. Since such dislocations repel each other, their smoothest arrangement related to quasiperiodicity of tilt boundary provides minimization of its elastic energy (associated with elastic fields of the dislocations) [13].

Let us consider a quasiperiodic tilt boundary with a finite length, which is naturally defined as a finite–length fragment of an infinite quasiperiodic boundary characterized by irrational values of $\tilde{r}/\tilde{s}$ and $\theta + \kappa$. For given finite length l misorientation θ and inclination κ, one finds the characteristic finite numbers r and s, of structural units as those satisfying relationships (11)–(14) with H substituted by l. In this event, the rational value of r/s should be closest to irrational value of $\tilde{r}/\tilde{s}$. Ordering in arrangement of A and B units in quasiperiodic boundary with finite length is caused by the demand that elastic energy of the boundary is minimal for given r/s or, in other words, that arrangement of minority units with corresponding grain boundary dislocations) is smoothest for given r/s.

Let us consider briefly the properties (stress field, symmetry and grain boundary sliding) of infinite quasiperiodic tilt boundaries.

Stress field. In general, stress field components of quasiperiodic tilt boundaries are more homogeneously distributed along boundary planes as compared with periodic boundaries [15, 16].

Symmetry. Grain boundary dislocations. A DSC lattice of a quasiperiodic tilt boundary is simply a line lattice parallel to the tilt axsis [13, 17]. Since Burgers vectors of grain boundary dislocations are those of a DSC lattice, such dislocations can have any Burgers vector component normal to the boundary plane or perpendicular to the tilt axis in the boundary plane [13, 15].

Grain boundary sliding. Due to the symmetry reflected in a DSC lattice, a free energy of a quasiperiodic tilt boundary is invariant, in particular, at relative displacements of adjacent grains in the direction perpendicular to the tilt axis in the boundary plane [18, 19]. These relative displacements are realized via such rearrangements ($A \leftrightarrow B$) of structural units that preserve the quasiperiodic ordering of the boundary [19]. Energetic barriers for such rearrangements are essentially lower than those for $A \leftrightarrow B$ rearrangements in a periodic boundary. Summing up, quasiperiodic tilt boundaries are capable of effectively carrying integrain sliding even without any involvement of grain boundary defects (dislocations). This special attribute distinguishes quasiperiodic from periodic boundaries.

4.2. QUASIPERIODIC TILT BOUNDARIES IN NANOSTRUCTURED POLYCRYSTALS

Let us consider conditions at which quasiperiodic boundaries with finite lengths are formed in polycrystalline and nanocrystalline materials. First, for example, we examine formation of grain boundaries in the highly nonequilibrium process of compacting of crystalline nanoparticles. Let a straight tilt boundary with length l be formed in cold welding of two crystalline particles. In general, inclination κ, misorientation θ and length l of this boundary can have arbitrary values as those determined by randomly varied geometric parameters of particles and their contact. Randomly-varied-in-specimen values of geometric parameters κ, θ and l of tilt boundaries, in turn, determine randomly-varied-in-specimen values of structural parameters r and s of tilt boundaries. In these circumstances, the two following basic situations can occur: (1) s/r is integer, and (2) s/r is non-integer. Since cold welding of particles is a highly nonequilibrium process, rA units and sB units in both situations (1) and (2) usually are disorderedly arranged in boundary sharing two just welded particles. More than that, the third following situation is also possible: a tilt boundary can contain structural units of other type(s), neither A or B. In all these events, a tilt boundary should be treated as a nonequilibrium (or defected) boundary.

However, relaxation processes driven by decrease in elastic energy of a tilt boundary, after some relaxation period, will result in equilibrium, ordered arrangement of structural units, A and B, in this boundary. In a relaxed state, ordering in arrangement of A and B units is either periodic or quasiperiodic, depending on the characteristic numbers r and s. If s/r is integer (situation (1)), a boundary is periodic. If s/r is non-integer (situation (2)), a periodic arrangement is impossible, and structural units of a tilt boundary of finite extent are quasiperiodically arranged.

Of utmost interest is the question: how many periodic and quasiperiodic boundaries do exist in compacted aggregates of particles, in particular, in nanostructured materials? Let us estimate ratio ν_p/ν_q of densities, ν_p and ν_q, of respectively periodic and quasiperiodic tilt boundaries [3] existing in a nanostructured material with the grain sizes in the range from 5 to 20 nm. For every tilt boundary in such a material, the quantity $r + s$ of structural units ranges tentatively nanostructured polycrystals is determinitive. This allows us to view that nanostructured polycrystals with quasiperiodic grain boundaries as representing a new type of nanostructured materials with the structure and properties being different from those of conventional nanocrystalline materials with disordered and/or periodic boundaries (and of other nanostructured solids).

In order to emphasize the fact that the nanoscale structure and quasiperiodic elements are the definitive structural features of nanostructured polycrystals with quasiperiodic grain boundaries, we shall call such polycrystals as quasinanocrystalline materials.

Synthesis of quasinanocrystalline materials is an open technological problem. In any event, however, nanostructured polycrystals synthesized by presently available methods can be effectively treated as composites consisting of the quasinanocrystalline phase and the conventional nanocrystalline phase. Therefore, the notion of quasinanocrystalline materials is of importance in analysis of both the structure and the macroscopic properties of such nanostructured polycrystals. In this context, we will study in next subsection a contribution of quasiperiodic boundaries to the plastic properties of nanostructured polycrystals.

4.4. QUASIPERIODIC BOUNDARIES AND PLASTIC FLOW IN NANOSTRUCTURED POLYCRYSTALS

Let us discuss the features of plastic flow in nanostructured polycrystals related to quasiperiodic boundaries. In nanostructured solids, in which the activity of mobile lattice dislocations in nanocrystallites is low (owing to image forces that act on lattice dislocations near surfaces and hence in confined media [22]), grain boundary sliding provides an essential contribution to plastic deformation processes, e.g. [23–25]. The grain boundary sliding in quasiperiodic boundaries occurs via rearrangements of structural units or via motion of grain boundary dislocations having the features which differ from boundary dislocations in periodic boundaries. In particular, the spectrum of admissible Burgers vectors of boundary dislocations (or, in other terms, DSC lattice) in quasiperiodic boundaries usually is essentially richer than that in periodic boundaries [13, 17]. For instance, as shown in [13], dislocations in a quasiperiodic tilt boundary can have any Burgers vector component b' perpendicular to the tilt axis in the boundary plane (in contrast to periodic boundaries in which dislocation Burgers vectors are quantized). For definiteness, hereafter we confine ourself to analysis of boundary dislocations characterized by small Burgers vectors of b'-type in quasiperiodic tilt boundaries, since (as shown below) they are easily generated and easily move in quasiperiodic tilt boundaries, causing specific plastic properties of the boundaries.

As to details, let us consider a dislocation in a quasiperiodic tilt boundary, having the Burgers vector b' which is perpendicular to the tilt axis in the boundary plane and obeys the inequality: $b' << b$, where b is the characteristic Burgers vector of dislocations in periodic boundaries. Dislocations with (small) Burgers vectors b' can be generated in a quasiperiodic tilt boundary by Frank-Read sources at critical shear stresses $T' = Gb'/L$ (here L denotes the Frank-Read source length and G the shear modulus, e.g. [26]) being essentially smaller than the critical shear stress $T = Gb/L$ which activates Frank-Read sources in a periodic boundary. Say, for $b = a/10$ [27], $b' = a/50$ and $L = 10a$ (here a denotes the crystal lattice parameter), we find $T' = G/500 << T = G/100$.

Dislocations with small Burgers vectors b', generated in a quasiperiodic tilt boundary at low values T' of the shear stress, form pile-ups which are capable of effectively moving in the boundary at the same low values of the shear stress (owing to the effect of stress concentration in dislocation pile-up heads, e.g. [26]). As a result, boundary sliding processes intensively occur (via motion of dislocation pile-ups) in quasiperiodic tilt boundaries at low shear stresses T', in which case such boundaries serve as plastic elements of a nanostructured polycrystal.

Let us estimate a contribution of quasiperiodic tilt boundaries to plastic properties of nanocrystalline materials comprising both periodic and quasiperiodic grain boundaries. In doing so, we model such materials as composites consisting of the matrix, being a nanocrystalline solid with periodic boundaries, and the quasiperiodic tilt boundary phase elements. In the first approximation, the yield stress S of a nanocrystalline material modeled as the composite can be estimated with the help of the standard additive mixing formula for mechanical characteristics of composites as follows:

$$S = \psi S' + (1 - \psi) S'' \tag{16}$$

where ψ is the volume fraction of the quasiperiodic tilt boundary phase, S' and S'' are the yield stresses of the quasiperiodic tilt boundary phase and the matrix, respectively.

Let us discuss consequently values of S', S'' and ψ appearing on the r.h.s of formula (16). In the light of our previous analysis, S' is determined by the critical shear stress T' which activates Frank-Read sources in quasiperiodic tilt boundaries: $S' = T'/M$, where M is the standard orientation factor.

In our model all the features of the nanoscale structure of the nanocrystalline material are assumed to be related to only the presence of a high-density ensemble of quasiperiodic tilt boundaries in the material. Therefore, we consider the yield stress S'' of the matrix to be the same as for polycrystalline solids with periodic grain boundaries, in which case S'' depends on the grain size d in the standard Hall-Petch form:

$$S'' = S^* + kd^{-1/2} \tag{17}$$

Here S^* denotes the intrinsic stress resisting crystal lattice dislocation motion and k the Hall-Petch constant.

The volume fraction ψ of the quasiperiodic boundary phase can be represented as $\psi = gh$, where g is the volume fraction of quasiperiodic tilt boundaries in the grain boundary phase and h is the volume fraction of the grain boundary phase in the nanostructured polycrystal. In nanostructured polycrystals $h \approx 9a/d$ [28]. Then we find

$$\psi \approx 9ga/d \tag{18}$$

With (17) and (18) substituted to (16), one obtains the following approximate formula:

$$S \approx S^* + kd^{-1/2} + 9ga(T'/M - S^*)d^{-1} - 9gakd^{-3/2} \tag{19}$$

For characteristic values of $a \approx 3 \cdot 10^{-10}m$, $T' \approx G/500$, $M \approx 0.5$, $G \approx 65GPa$, $S^* \approx 66MPa (\approx G/1000)$, $k \approx 26447MPa \cdot nm^{1/2}$ (see data [29] for Fe) and $g = 0.1, 0.5$ and 1, the dependences $S(d)$ defined by formula (19) are shown in Fig.7, where d ranges from 3 to $500nm$. The curves 1, 2 and 3 correspond to $g = 0.1, 0.5$ and 1, respectively. (The case $g = 1$ describes quasinanocrystalline materials with quasiperiodic tilt boundaries.)

For $d \approx 3 - 20nm$, S (curves 1, 2 and 3 in Fig.7) is the yield stress of nanocrystalline materials with quasiperiodic boundaries. For $d > 20nm$, S (curves 1, 2 and 3 in Fig.7) plays the role as the yield stress of polycrystalline solids with quasiperiodic boundaries. The dependencies S(d) with different values of parameter g have similar features which are as follows. For large values of d, the dependences $S(d)$ (Fig.7) are close to the standard Hall-Petch relationship (dashed line in Fig.7). For small values of d, the dependences $S(d)$ deviate from the Hall-Petch relationship. Similar deviations are inherent to dependencies (observed experimentally; for a review, see [24, 25]) for mechanical characteristics (yield stress, microhardeness) of real nanostructured polycrystals. This allows us to think that the presence of quasiperiodic boundaries in nanostructured polycrystals is capable of effectively contributing to the experimentally observed deviations of the yield stress dependence on d from the Hall-Petch relationship.

4.5. INTERFACES IN QUASICRYSTALS

Quasicrystals are solids with long–range quasiperiodic translational ordering and non–crystallographic rotational symmetries, e.g. [1–3]. Quasicrystals (synthesized as aggregates of quasicrystalline grains [30] or nanoparticles [31]) usually contain high–density ensembles of interfaces. Quasiperiodicity in grains/nanoparticles imposes a quasiperiodic translational order to exist in such interfaces [32]. Theoretical and experimental examinations of quasiperiodic interfaces are just at the starting point.

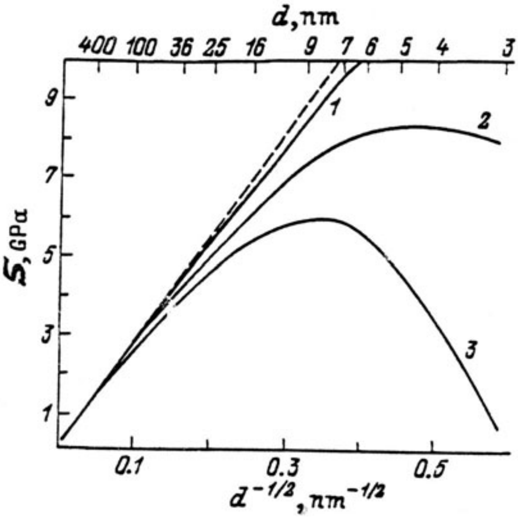

Fig.7. Dependence of the yield stress S on grain size d for $g = 0.1$ (curve 1), $g = 0.5$ (curve 2) and $g = 1$ (curve 3). The standard Hall–Petch dependence $S(d)$ is shown as dashed line.

4.6. CONCLUDING REMARKS

To briefly summarize this section, theoretical analysis indicates about quasiperiodic tilt boundaries as inherent elements of nanostructural polycrystals. Of course, this statement needs to be verified experimentally. However, at that moment, existence of quasiperiodic grain boundaries in nanostructured polycrystals can not and should not be ignored.

5. Disordered Interfaces in Nanostructured Materials

Disordered interfaces are usually formed in nanostructured polycrystals just synthesized in highly nonequilibrium conditions, e.g. [23]. Such interfaces contain high–density ensembles of interfacial defects and serve as sources of internal stresses in just synthesized nanostructured polycrystals [23]. After some relaxation period, disordered interfaces transform into ordered, periodic or quasiperiodic, ones. This process is accompanied by relaxation of internal stresses, leading to decrease of the elastic energy stored in a nanostructured polycrystal. For more details about disordered interfaces in nanostructured polycrystals, see lecture [33] and references therein.

Now let us turn to discussion of nanoamorphous alloys (firstly synthesized in 1989 [34]) which represent a new class of nanostructured materials. Nanoamorphous alloys are synthesized as high–pressure compacted aggregates of amorphous nanoparticles divided by disordered (amorphous) interfaces characterized by higher free–volume density [34, 35]. Just synthesized nanoamorphous alloys specified by nano–scale inhomogeneities of free–volume density can gradually transform into homogeneous amorphous alloys [35, 36].

So, disordered interfaces are unstable elements of the nanostructured materials structure. Disordered interfaces in nanostructured polycrystals transform into periodic or quasiperiodic interfaces. Disordered interfaces in nanoamorphous alloys gradually disappear (diffusionally spread), in which case the nanoamorphous phase transforms into the homogeneous amorphous one.

6. Conclusion

The basic conclusions of this lecture are as follows:

(*a*) Quasiperiodic film–substrate interfaces and quasiperiodic tilt boundaries are inherent structural elements of nanostructured materials.

(*b*) Quasiperiodic interfaces represent the special type of ordered interfaces with both the structure and the properties being different from those of periodically ordered interfaces.

(*c*) Quasiperiodic film–substrate interfaces are capable of contributing to mobility of island films.

(*d*) Quasiperiodic tilt boundaries serve as plastic deformation elements in nanostructured polycrystals. Their contribution induces deviations of the yield stress dependence on the grain size from the standard Hall–Petch relationship.

(*e*) Quasinanocrystalline materials (consisting of nanocrystallites and only quasiperiodic interfaces) represent a new class of nanostructured materials.

The following points of development in studies of quasiperiodic interfaces are of primary interest:

(*i*) Experimental identification of quasiperiodic interfaces in thin films, nanostructured and polycrystalline materials.

(*ii*) Experimental and theoretical examinations of the properties (in particular, migration, conductivity, magnetic characteristics) of quasiperiodic interfaces as well as contribution of quasiperiodic interfaces to the macroscopic properties of thin films, nanostructured and polycrystalline materials.

(*iii*) Synthesis of quasinanocrystalline materials.

(*iv*) Theoretical analysis of quasiperiodicity in twist and twist–tilt boundaries in nanostructured and polycrystalline materials.

7. References

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