Effects of misfit stresses on the structure and transport properties of grain boundaries in high-T_c superconducting films

S. V. Bobylev, I. A. Ovid'ko,* and A. G. Sheinerman
Institute for Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vas. Ostrov, St. Petersburg 199178, Russia
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A theoretical model is suggested that describes the effect of misfit stresses on the structure and the transport properties of tilt boundaries in high-transition-temperature superconducting films. It is theoretically revealed here that misfit stresses are capable of inducing structural transformations of tilt boundaries, which give rise to local changes of grain-boundary misorientation and corresponding changes of the critical current density across grain boundaries.

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I. INTRODUCTION

Polycrystalline high-transition-temperature (T_c) superconductors exhibit low values of the critical current density J_c compared to their single crystalline counterparts; see, e.g., Refs. 1–7. The dramatic suppression of J_c due to grain boundaries is related to their role as Josephson layers in high-T_c superconductors, where nanoscale coherency length is of the same order as grain-boundary thickness. The weak-link behavior of grain boundaries, on the one hand, is undesired for high-current applications of high-T_c cuprates and, on the other hand, forms a basis for use of polycrystalline thin-film cuprates in low-current microelectronics. In addition to technologically motivated interest in the grain-boundary effect on J_c, physics of this effect is of high importance for understanding the fundamentals of high-T_c superconductivity.

The experimentally documented behavioral peculiarities of grain boundaries in high-T_c cuprates, in particular, are as follows.

(i) There is a dramatic discrepancy between the transport properties of low- and high-angle boundaries; see, e.g., Refs. 1–7. Thus, J_c across low-angle boundaries shows a sharp exponential drop with rising boundary misorientation θ, while the critical current density across high-angle boundaries is weakly dependent on θ and is lower by two or three orders than the critical current density in the bulk phase.[1–7]

(ii) The doping-induced enhancement of J_c has been detected in Ca-doped YBaCuO films.[8]

(iii) High-quality twist boundaries have been fabricated in BiSrCaCuO superconductors, which are characterized by boundary cores of zero thickness and exhibit the enhanced transport properties.[9–11] Such boundaries carry critical current as high as their constituent single crystals.[9–11]

(iv) Grain-boundary structures undergo transformations that are capable of strongly influencing their transport properties.[12–15] Thus, the splitting and amorphization of dislocation cores composing low-angle boundaries in high-T_c cuprates have been experimentally observed.[12,13] Amorphization and chemical-composition inhomogeneities at high-angle boundary cores have been detected in experiments; see, e.g., Refs. 14 and 15.

(v) Spatial variations of the critical current have been detected in BiSrCaCuO tapes; most of the supercurrent flows through the thin layer of superconductor next to the silver sheet (see Ref. 16 and references therein).

Several theoretical models have been suggested describing the structural and behavioral features of grain boundaries in high-T_c superconductors. In particular, the following factors have been considered as those responsible for the effects of grain boundaries on high-T_c superconductivity: (a) stress fields of grain-boundary dislocations and crystallographic disorder within grain-boundary cores;[17–19] (b) deviations from bulk stoichiometry in vicinities of grain boundaries;[20–22] (c) the combined effects of d symmetry of the superconducting order parameter and the faceted microstructure of grain boundaries;[23] (d) electric-charge inhomogeneities (band bending).[7,8,24–26] Nevertheless, the key mechanism(s) of the J_c suppression at grain boundaries in high-T_c cuprates is (are) still the subject of controversy.

In any event, there are no doubts in the crucial influence of the structure of grain boundaries on their transport properties. In this context, a theoretical analysis of experimentally detected[5,7,12–15] structural transformations of grain boundaries in high-T_c superconductors is of utmost interest. In Ref. 27 the splitting and amorphization of dislocation cores at low-angle boundaries in YBaCuO superconductors have been naturally described as those induced by relaxation of intrinsic stresses of such boundaries. At the same time, in addition to intrinsic stresses of grain boundaries, dilatation stresses are generated in films due to lattice-parameter mismatch and thermal-expansion mismatch between films and substrates. The dilatation misfit stresses in superconducting thin-film cuprates (as with conventional films[28–30]) can strongly influence grain-boundary structures. (Also, dilatation-misfit stresses, as it has been demonstrated in experiments[31] with LaSrCuO superconducting films, are capable of essentially enhancing critical temperature in single crystalline films.) In Ref. 32, structural transformations of low-angle tilt boundaries in thin-film cuprates due to misfit stresses have been briefly discussed. It has been theoretically revealed that misfit stresses are capable of decreasing the mean boundary misorientation and, as a corollary, enhancing the transport properties of tilt boundaries in thin-film cuprates, compared to bulk samples.[32] The transformations of the tilt-boundary structures under consideration effectively accommodate misfit stresses in polycrystalline films. That is, the transformations in question effectively competes with the conventional mechanism for misfit-stress relaxation occurring via the formation of rows of misfit dislocations at interphase (film/substrate) boundaries.

In the model of Ref. 32, for the sake of simplicity, tilt-boundary structures have been assumed to be transformed into tilt-boundary structures with misorientation parameters being constant along boundary planes. However, in general, the effect of misfit stresses on the grain-boundary structures and their misorientation parameters is more complicated than that briefly described in Ref. 32. Thus, following experimental data reported in Ref. 33, misorientation of grain boundaries varies along boundary planes in polycrystalline films. This can be naturally associated with the action of misfit stresses on boundary dislocations. The main aim of this paper is to theoretically describe (a) variations of tilt-boundary misorientation parameters (along boundary planes) due to misfit stresses and (b) the influence of such spatial variations on the critical current density J_c across tilt boundaries in high-T_c superconducting films. Also, we will analyze the conditions at which the misfit stress accommodation through the transformations of the tilt-boundary structures in polycrystalline films is more effective (energetically favorable) than that through formation of "conventional" misfit dislocations.

II. BICRYSTALLINE FILM WITH A TILT BOUNDARY: A MODEL

Let us consider a model film/substrate system consisting of a bicrystalline film of thickness H and a semi-infinite substrate. The film and substrate are assumed to be isotopic solids having the same values of the shear modulus G and the same values of Poisson ratio ν. The film/substrate boundary is characterized by the misfit parameter

$$f=\frac{2(a_f-a_s)}{a_f+a_s}, \tag{1}$$

where a_s and a_f are the crystal lattice parameters of the substrate and the film, respectively.

The film/substrate boundary creates misfit stresses occurring due to a misfit (geometric mismatch) between adjacent crystalline lattices of the film and the substrate. These stresses affect grain-boundary dislocations, either causing them to move towards the film free surface [where dislocations disappear; see Figs. 1(a) and 1(b)] or causing generation of new dislocations and motion of the new and preexistent dislocations towards the film/substrate boundary [Figs. 1(a) and 1(c)], depending on geometric parameters of the system.[29,30,32] The new dislocation configurations [Figs. 1(b) and 1(c)] contribute to accommodation of the misfit stresses, in which case their formation is driven by a release of the elastic energy. Previous works[29,30,32] have described the effect in question as that resulting in a transformation of the structure of a grain-boundary in a spatially homogeneous way. In other words, a structural transformation of a grain boundary due to misfit stresses has been described as that associated with a spatially homogeneous change of the den-

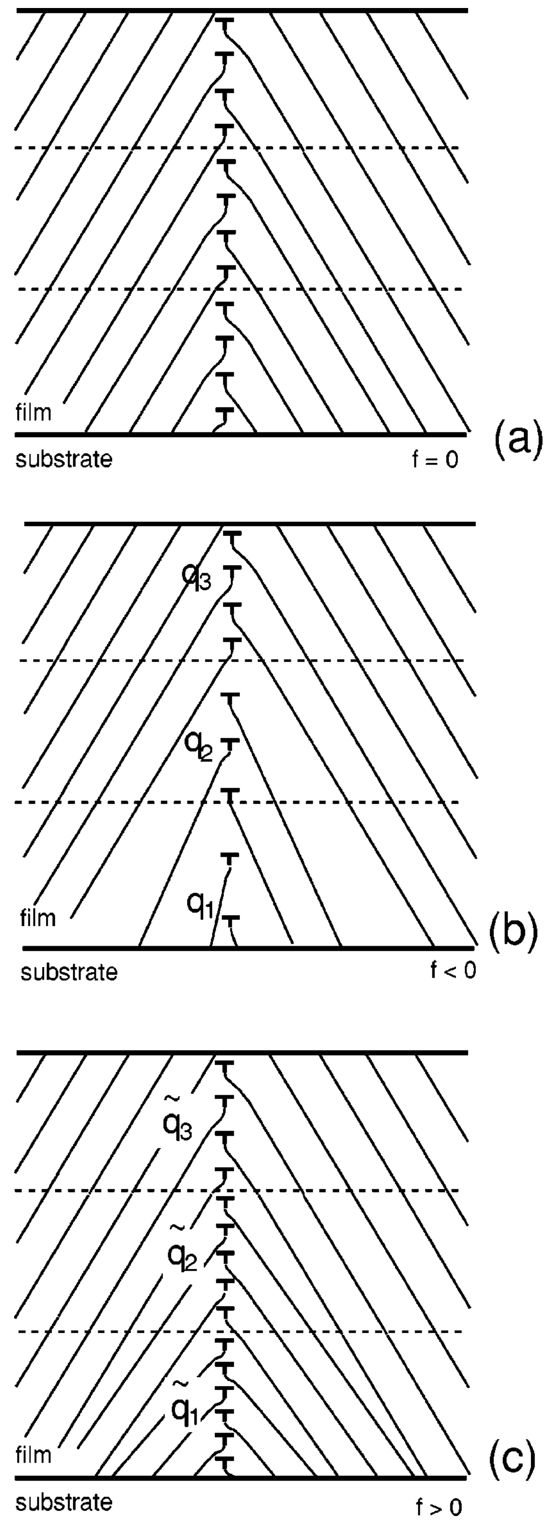

FIG. 1. Transformations of tilt-boundary structure in bicrystalline film due to the effect of misfit stresses. Tilt boundary transforms from its initial state (a) into final state with (b) low or (c) high density of inhomogeneously distributed dislocations. The final state (b) is realized via climb of grain-boundary dislocations towards the film free surface where the dislocations disappear. The final state (c) results from the initial state via generation of new dislocations at the film free surface and climb of the new and preexistent grain-boundary dislocations towards the film/substrate boundary.

sity of grain boundary dislocations. The transformation in question gives rise to both a spatially homogeneous change of boundary misorientation and the generation of a disclination, a rotational defect. The disclination is located at the junction of the grain boundary and the interphase boundary and is characterized by disclination strength $\omega=\theta_f-\theta_i$, with θ_f and θ_i being the boundary misorientation in final and initial states of grain boundary, respectively.[32] In general, however, the influence of misfit stresses on spatial positions of grain-boundary dislocations in a film varies along the boundary; the effect is strong in the vicinity of the film/substrate boundary and becomes weaker as the distance from the film/substrate boundary increases [Figs. 1(b) and 1(c)]. This is related to the fact that a contribution of a (misfit) dislocation to relaxation of misfit stresses decreases, when the distance between the dislocation and the film free surface decreases; see, e.g., Refs. 34–36.

In this paper we will consider spatially inhomogeneous distributions of dislocations at grain boundaries in films, resulted from the effect of misfit stresses [Figs. 1(b) and 1(c)]. In doing so, here we model, in the first approximation, a tilt grain boundary (perpendicular to the film/substrate boundary) in a film as that consisting of N ($N>1$) fragments each characterized by the density ρ_i of grain-boundary dislocations, where $i=1,\ldots,N$ and $\rho_i\neq\rho_j$, if $i\neq j$ (see Fig. 2). The dislocation density ρ_i of the ith grain-boundary fragment is unambiguously related to misorientation of the fragment. (In the case of low-angle boundaries consisting of periodically arranged lattice dislocations, misorientation θ of the boundary is in the Frank relationship with parameters of the lattice dislocations.[37] In the case of high-angle boundaries, the density of grain-boundary dislocations relates to deviations of boundary misorientation from that of low-energy grain boundaries; for details, see Ref. 37.) Therefore, various fragments of the grain boundary are characterized by various values θ_i of boundary misorientation. Junctions of boundary fragments with various misorientation angles represent line cores of grain-boundary disclinations, rotational defects; see, e.g., Refs. 38 and 39. More precisely, a disclination at the junction of tilt-boundary fragments with misorientation angles θ_i and θ_{i+1}, respectively, is the wedge disclination with strength $\omega_i=\theta_{i+1}-\theta_i$.

Thus, in the framework of our model, a structural transformation of a tilt grain boundary due to misfit stresses in a bicrystalline film is described as that associated with a spatially inhomogeneous change of the density of grain-boundary dislocations. The transformation in question gives rise to formation of N ($N>1$) boundary fragments separated by N grain-boundary disclinations (Fig. 2). For the sake of simplicity, boundary fragments are assumed to be of the same length H/N, in which case grain-boundary disclinations are arranged periodically (Fig. 2). Also, in the following we consider only the elastic-energy contribution to the total energy of the superconducting film with a tilt boundary, in which case we neglect the contribution associated with the spatial dependence of the superconducting order parameter. This assumption is based on the fact that diffusion-mediated structural transformations (in particular, the transformations described in this paper) commonly occur in as-deposited films during some relaxation time interval at relatively high temperatures. At the same time, the superconducting state is realized in a cuprate film at low temperatures at which the diffusion is suppressed and, therefore, the film structure (resulted from the transformations occurring at high temperatures) is frozen. In these circumstances, the energy that characterizes the superconducting state of the film does not affect the frozen grain-boundary structure in the cuprate film. With this taken into account, in our further analysis of the diffusion-mediated transformations of grain-boundary structures in the film, we will neglect the contribution of the superconducting-state energy to the total energy of the film.

III. ELASTIC-ENERGY DENSITY OF TILT BOUNDARIES WITH SPATIALLY INHOMOGENEOUS MISORIENTATIONS

Let us find values ω_i ($i=1,\ldots,N$) of the disclination strengths that correspond to equilibrium of the disclination ensemble at a grain boundary with spatially inhomogeneous misorientation (Fig. 2), that is, to the minimum of the energy density that characterizes grain-boundary disclinations as defects compensating for, in part, misfit stresses generated at the film/substrate boundary. To do so, let us compare energetic characteristics of two physical states, namely, the initial state of the tilt boundary (with spatially homogeneous misorientation) that does not contribute to relaxation of misfit stresses [Fig. 1(a)], and the final state of the tilt boundary (with spatially inhomogeneous misorientation) that contains disclinations contributing to relaxation of misfit stresses (Fig. 2). The difference ΔW between the energy densities (energies per unit length of disclinations in the final state) W_f and W_i of the tilt boundary in, respectively, final and initial states consists of three basic terms,

$$\Delta W=W^{\Delta}+W^{\Delta-\Delta}+W^{\Delta-f}. \tag{2}$$

Here W^{Δ} denotes the sum proper energy density of disclinations, $W^{\Delta-\Delta}$ is the energy density that characterizes interaction between disclinations, and $W^{\Delta-f}$ is the energy density that characterizes interaction between disclinations and misfit stresses. [Contributions to ΔW, associated with the screened stress fields of dislocations composing each boundary fragment are not taken into account in formula (2), because such contributions are essentially small compared to contributions, W^{Δ}, $W^{\Delta-\Delta}$, and $W^{\Delta-f}$, associated with long-range stress fields of disclinations.]

According to the theory of disclinations,[40] the proper energy density W_i^{Δ} of the ith disclination specified by strength ω_i and distant by d_i from the film free surface is given as

$$W_i^{\Delta}=\frac{D\omega_i^2 d_i^2}{2}, \tag{3}$$

where $D=G/[2\pi(1-\nu)]$. With disclinations numerated by $i=1,\ldots,N$ (where $i=1$ and $i=N$ correspond to disclinations nearest to the film/substrate boundary and the film free surface, respectively), distance d_i figuring on the right-hand side of formula (3) can be written as follows:

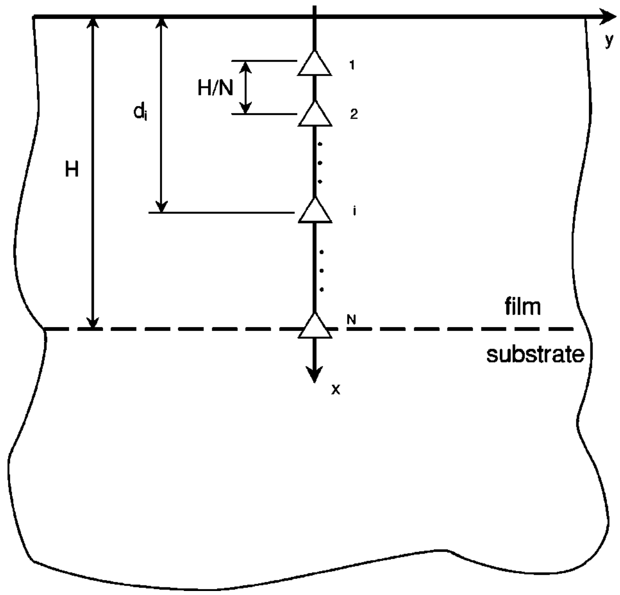

FIG. 2. Tilt boundary in thin film consists of N fragments with misorientations θ_i $(i=1,\ldots,N)$. Wedge disclinations (triangles) are located at junctions of tilt-boundary fragments with various values of misorientation.

$$d_i=\frac{iH}{N},\quad i=1,2,\ldots,N, \tag{4}$$

where H denotes the film thickness and N is the number of disclinations. From Eqs. (3) and (4) we get

$$W^{\Delta}=\frac{DH^2}{2N^2}\sum_{i=1}^{N} i^2\omega_i^2. \tag{5}$$

In accordance with the theory of disclinations,[40] the energy density that characterizes interaction between disclinations in its general form is given as

$$W^{\Delta-\Delta}=\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{k=1\\k\neq i}}^{N} W_{ik}^{\Delta-\Delta}, \tag{6}$$

where the energy density $W_{ik}^{\Delta-\Delta}$ characterizes interaction between the ith and kth disclinations. In the situation discussed (Fig. 2), the energy density $W_{ik}^{\Delta-\Delta}$ can be written as follows:[40]

$$W_{ik}^{\Delta-\Delta}=D\omega_i\omega_k\left[d_i d_k+\frac{(d_i-d_k)^2}{2}\ln\left|\frac{d_i-d_k}{d_i+d_k}\right|\right]. \tag{7}$$

With Eq. (7) substituted into Eq. (6) and formula (4) taken into account, we find the following formula for $W^{\Delta-\Delta}$:

$$W^{\Delta-\Delta}=\frac{DH^2}{2N^2}\sum_{i=1}^{N}\sum_{\substack{k=1\\k\neq i}}^{N}\left[ik+\frac{(i-k)^2}{2}\ln\left|\frac{i-k}{i+k}\right|\right]\omega_i\omega_k. \tag{8}$$

The energy density $W_i^{\Delta-f}$ that characterizes interaction of the misfit stresses $\sigma^f=4\pi D(1+\nu)$ and the ith disclination (with strength ω_i) distant by d_i from the film free surface is given as[41]

$$W_i^{\Delta-f}=\omega_i\int_{d_i}^{0}x\sigma^f dx=-4\pi D(1+\nu)f\frac{\omega_i d_i^2}{2}. \tag{9}$$

From formula (9) we find the total energy density $W^{\Delta-f}=\Sigma_{i=1}^{N}W_i^{\Delta-f}$ to be as follows:

$$W^{\Delta-f}=-2\pi D(1+\nu)f\frac{H^2}{N^2}\sum_{i=1}^{N} i^2\omega_i. \tag{10}$$

From expressions (5), (8), and (10) we have the following formula for the characteristic difference between the energy densities of final and initial states of the tilt boundary in a film,

$$\Delta W=\frac{DH^2}{2N^2}\left\{\sum_{i=1}^{N}\left[\sum_{\substack{k=1\\k\neq i}}^{N}\left\{ik+\frac{(i-k)^2}{2}\ln\left|\frac{i-k}{i+k}\right|\right\}\omega_i\omega_k+i^2\omega_i^2\right]\right.$$
$$\left.-4\pi(1+\nu)f\sum_{i=1}^{N} i^2\omega_i\right\}. \tag{11}$$

In order to find minimum of function ΔW, one should differentiate this function with respect to ω_j (at fixed j). In doing so, we get the following system of equations: $\partial(\Delta W)/\partial\omega_j=0$, where $j=1,2,\ldots,N$. This system of equations, with formula (11) taken into consideration, gives rise to equations

$$2\sum_{\substack{k=1\\k\neq j}}^{N}\left[jk+\frac{(j-k)^2}{2}\ln\left|\frac{j-k}{j+k}\right|\right]\alpha_k+2j^2\alpha_j=j^2,$$
$$j=1,2,\ldots,N, \tag{12}$$

where

$$\alpha_k=\frac{\omega_k}{4\pi(1+\nu)f}. \tag{13}$$

Equations (12) are self-consistent in the following sense. They compose the complete set of the relationships between independent variables α_k [or ω_k, see formula (13)], which allows one to find the set of values of α_k (or ω_k), which corresponds to minimum of the characteristic energy difference ΔW.

Values of α_k are in the following relationships with misorientations θ_i that characterize tilt-boundary fragments (Fig. 2): $\theta_i=\theta'+\Delta\theta_i$, where

$$\Delta\theta_i=4\pi(1+\nu)f\sum_{k=i}^{N}\alpha_k,\quad i=1,2,\ldots,N. \tag{14}$$

Here θ' is the misorientation of the tilt boundary in its initial state [Fig. 1(a)].

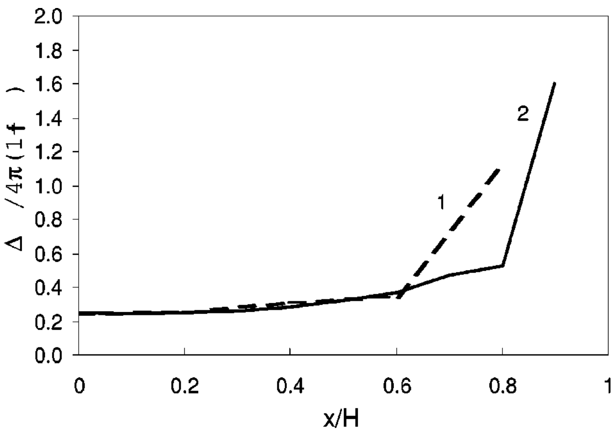

FIG. 3. Dependence of $\Delta\theta$ on x/H for $N=5$ (curve 1) and $N=10$ (solid curve 2).

Dependences of $\Delta\theta_i$ (that characterize misfit-stress-induced deviations of tilt-boundary misorientation from its initial value θ') on boundary coordinate x can be numerically calculated in accordance with formulas (12)–(14) at given values of the characteristic parameters. [The computer calculation algorithm automatically provides the aforediscussed self-consistency of Eqs. (12).] For illustration, the numerically calculated dependences $\Delta\theta_i(x)$, for $N=5$ and $=10$, are shown in Fig. 3. In doing so, functions $\Delta\theta(x)$ shown in Fig. 3 are presented as those resulted from the corresponding linear spline interpolation. From Fig. 3 it follows that the deviation functions $\Delta\theta(x)$ have their maximums in vicinity of the film/substrate boundary and decrease as the distance from the film free surface decreases.

Now let us consider the sign of ΔW. With solutions of system (12) substituted into formula (11), we directly find that, for any N, the characteristic difference ΔW between the energy densities of final and initial states of the tilt boundary is negative and decreases with rising N. As a corollary, the final state of the tilt boundary characterized by spatially inhomogeneous misorientation (see, e.g., Figs. 1(b), 1(c), and 2) is energetically favorable.

IV. DISCLINATION AND DISLOCATION MECHANISMS FOR MISFIT STRESS ACCOMMODATION IN POLYCRYSTALLINE FILMS

According to theoretical estimates given in the preceding section, the formation of disclinations (associated with spatially inhomogeneous boundary misorientation; see Figs. 1 and 2) at tilt boundaries is energetically favorable compared to the coherent state of a polycrystalline film/substrate composite. In these circumstances, the formation of disclinations is capable of causing effective relaxation of misfit stresses in high-T_c superconducting films and competing with the conventional misfit-stress relaxation through the formation of misfit dislocations at film/substrate interfaces. This statement is directly and indirectly supported by experiments[42–45] with polycrystalline films. Thus, Refs. 42–44 have reported on experimental observation of misfit disclinations at junctions of grain and twin boundaries in Ge films on Si substrates. Misfit disclination dipoles and quadropole configurations have been experimentally observed in epitaxial rhombohedral ferroelectric films.[45] A theoretical description of such misfit disclination configurations in ferroelectric films has been done in Ref. 46.

The role of grain-boundary disclinations as misfit defects is expected to be very effective in nanocrystalline films and coatings[29,30] where the volume fraction of the grain-boundary phase is extremely large. This is indirectly supported by data of experiments dealing with measurements of residual stresses in nanocrystalline films and coatings. So, as noted in Ref. 47, residual stresses, are low in nanocrystalline cermet coatings, resulting in a capability for producing very thick coatings. So, nanocrystalline coatings were fabricated up to 0.65 cm thick and could probably be made with arbitrary thickness.[47] At the same time, in a conventional polycrystalline cermet coating, stress buildup limits coating thickness to typically 500–800 μm. This is naturally explained as the fact caused by the action of a misfit-stress-relaxation micromechanism (in our model, the formation of grain-boundary misfit disclinations), which is strongly related to the existence of high-density ensembles of grain boundaries in nanocrystalline films, and is different from and more effective than the conventional relaxation of misfit stresses through the formation of misfit dislocations at film/substrate interface.

The relaxation of misfit stresses through the formation of conventional misfit dislocations in high-T_c superconducting films is possible only for small misfit-parameter values, such as in the case of YBaCuO film growth on $LaAlO_3$ or $SrTiO_3$; see Ref. 48. Even in these cases, one frequently observes low-angle grain boundaries. When the misfit parameter is much larger, as in the case of YBaCuO film growth on MgO or ZrO_2, the high-T_c superconducting films are no longer single crystalline; grain boundaries are formed in such films.[48] These experimental data indicate that the formation of grain boundaries accompanies growth of high-T_c superconducting films on substrates, for large misfit-parameter values, in which case grain boundaries are capable of causing more effective relaxation of misfit stresses than conventional misfit dislocations.

In context of this paper, with the experimental data considered in Refs. 42–45, 47, and 48, it is interesting to reveal the conditions at which the disclination mechanism for misfit-stress accommodation is more effective than the dislocation mechanism related to the formation of conventional misfit dislocations at film/substrate interfaces. To do so, in the rest of this section, we will analyze and compare energetic characteristics of the formation of grain-boundary disclinations and that of conventional misfit dislocations in polycrystalline films deposited onto crystalline substrates.

The film/substrate system commonly "chooses" either disclination [Figs. 1(b), 1(c), and 2] or dislocation mechanism for misfit-stress accommodation at low values of the film thickness when the coherent state becomes energetically unfavorable. In these circumstances, we focus our consideration on the cases with one ("first") misfit disclination [Fig. 4(a)] and one ("first") conventional misfit dislocation [Fig. 4(b)] located at the film/substrate interface. Let ΔW^{ω} be the

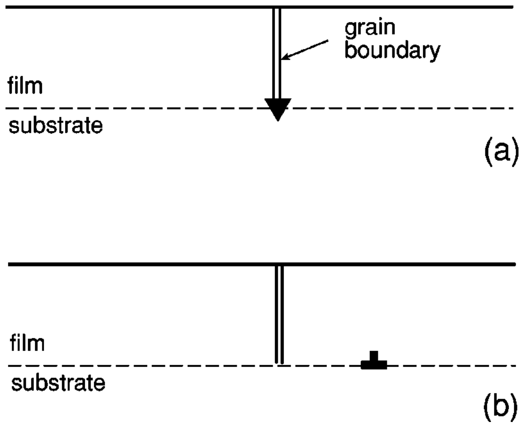

FIG. 4. Generation of (a) one misfit disclination at junction of grain and interphase boundaries, and (b) one ("first") conventional misfit dislocation at interphase boundary.

difference of the energy density between the state with one misfit grain-boundary disclination and the coherent (misfit-defect-free) state of the film/substrate system. That is, $\Delta W^{\omega}=\Delta W|_{N=1}$. Let ΔW^{d} be the difference of the energy density between the state with one conventional misfit dislocation and the coherent state of the film/substrate system. In the situation discussed, the condition $\Delta W^{\omega}<\Delta W^{d}$ is the criterion for the formation of misfit grain-boundary disclinations to be more energetically favorable than that of conventional misfit dislocations.

From formula (10) we find the following expression for $\Delta W^{\omega}(=\Delta W|_{N=1})$:

$$\Delta W^{\omega}=\frac{DH^{2}}{2}[\omega^{2}-4\pi(1+\nu)f\omega]. \tag{15}$$

The disclination strength ω given by the condition $(\partial\Delta W^{\omega}/\partial\omega=0)$ of minimum of ΔW^{ω} is as follows: $\omega=2\pi(1+\nu)f$. In this situation, the minimal value $\Delta W^{\omega}_{min}=\Delta W^{\omega}[\omega=2\pi(1+\nu)f]$ of the energy density difference ΔW^{ω} is given as

$$\Delta W^{\omega}_{min}=-2DH^{2}\pi^{2}(1+\nu)^{2}f^{2}. \tag{16}$$

The difference ΔW^{d} of the energy density between the state with one misfit dislocation [Fig. 4(b)] and the coherent state consists of the following three terms: the proper elastic energy of the misfit dislocation, the energy that characterizes the interaction between the misfit dislocation and misfit stresses, and the energy density of the dislocation core. Following Ref. 49, the energy density ΔW^{d} is given as

$$\Delta W^{d}=\frac{Db^{2}}{2}\left\{\ln\frac{2H}{b}+\frac{1}{2}-8\pi(1+\nu)f\frac{H}{b}\right\}. \tag{17}$$

With formulas (16) and (17), the condition $\Delta W^{\omega}_{min}=\Delta W^{d}$ leads to the following equation for the film thickness H:

$$t^{2}-4t+\ln\frac{2H}{b}+\frac{1}{2}=0, \tag{18}$$

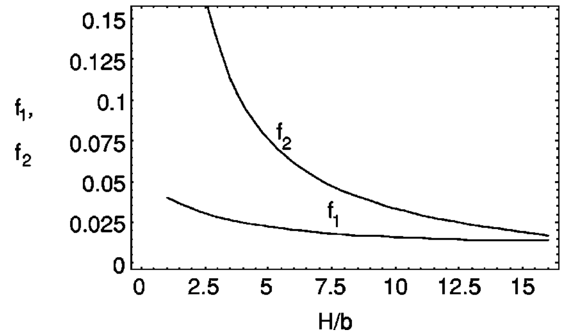

FIG. 5. Dependences of critical misfit parameters f_1 and f_2 on film thickness H/b.

where $t=2\pi(1+\nu)fH/b$. This equation does not have any solution for $H>(b/2)\exp(7/2)\approx 17b$. In this case ($H>17b$), $\Delta W^{\omega}_{min}<\Delta W^{d}$ at any value of misfit parameter f. If $H<17b$, we have $\Delta W^{\omega}_{min}<\Delta W^{d}$ at either $f<f_1$ or $f>f_2$, where

$$f_{1,2}=\frac{2\mp\sqrt{\dfrac{7}{2}-\ln\dfrac{2H}{b}}}{2\pi(1+\nu)H/b}. \tag{19}$$

Dependences of f_1 and f_2 on the film thickness H/b, given by formula (19) in the case with $\nu=0.3$, are shown in Fig. 5. As it follows from formulas (18) and (19) as well as Fig. 5, $\Delta W^{\omega}_{min}<\Delta W^{d}$ in wide ranges of values of both the misfit parameter f and the film thickness H. In particular, the formation of misfit disclinations is energetically favorable ($\Delta W^{\omega}_{min}<\Delta W^{d}$) at the beginning of deposition of films (at $H=b$, which corresponds to one-atom-layered film) if the misfit parameter $f<0.02$.

Thus, according to our theoretical estimations given in this section, the formation of misfit disclination at grain boundaries [Figs. 1(b), 1(c), 2, and 4(a)] in thin polycrystalline films is more energetically favorable than that of conventional misfit dislocations [Fig. 4(b)] in wide ranges of parameters (film thickness, misfit parameter) that characterize polycrystalline film/substrate systems. This statement is directly and indirectly supported by data of experiments considered in Refs. 42–45, 47, and 48, which deal with observation of misfit disclinations and/or predominant formation of grain boundaries over conventional misfit dislocations in solid films. Formula (18) predicts the formation of grain boundaries with intrinsic misfit disclinations to be more energetically favorable than that of conventional misfit dislocations in films with the thickness $H>17b$ at any value of the misfit parameter. This is an agreement with the experimentally documented fact (see Ref. 48 and references therein) that the grained structure with mixed, c- and a-axis, grain orientations as well as a/c grain boundaries tends to be intensively formed in YBaCuO films with rising film thickness. At the same time, growth of c-axis films with the dominant single crystalline structure occurs at low values of the film thickness.[48]

Our analysis of the disclination [Fig. 4(a)] and dislocation [Fig. 4(b)] mechanisms for misfit-stress accommodation has been based on comparison of the energetic characteristics, ΔW^{ω}_{min} and ΔW^{d}, that describe polycrystalline films growing at weakly nonequilibrium conditions. Real films are often fabricated at highly nonequilibrium conditions, in which case kinetic factors are capable of essentially influencing their defect structure. In particular, both misfit disclinations at grain boundaries and conventional misfit dislocations can co-exist, as it has been observed in experiments.[43] A detailed theoretical analysis of all the structural and behavioral peculiarities of polycrystalline films with misfit disclinations and dislocations is beyond the scope of this paper. In this section we just have demonstrated that the formation of misfit disclinations at grain boundaries as a mechanism for misfit-stress accommodation in polycrystalline films can effectively compete with the formation of conventional misfit dislocations. The following section deals with a theoretical examination of the influence of tilt boundary transformations associated with the formation of misfit disclinations on the transport properties of high-T_c superconducting polycrystalline films.

V. CRITICAL CURRENT DENSITY ACROSS TILT BOUNDARIES WITH SPATIALLY INHOMOGENEOUS MISORIENTATIONS

Let us estimate changes of the transport properties of tilt boundaries due to the misfit-stress-induced transformations of their structures (Fig. 1). For the exemplary case of [001]-tilt boundaries in YBaCuO superconductors at a temperature $T=4.2$ K, the dependence of the critical current density J_c across boundaries on tilt misorientation θ can be written as follows:[3,50]

$$J_c = J_0 \exp\left[-\frac{\theta}{\theta_0}\right], \tag{20}$$

where $\theta \approx 6.3°$ and $J_0 \approx 2\times10^7$ A/cm^2 for typical critical densities in the bulk phase. With formula (20) taken into consideration, we find the critical density across a tilt boundary with a spatially inhomogeneous misorientation (Fig. 2) to be given as

$$J_c = \frac{J_0}{N}\sum_{i=1}^{N} \exp\left[-\frac{\theta' + \Delta\theta_i}{\theta_0}\right]. \tag{21}$$

[From formulas (14), (20), and (21) we find the following dependence of ratio $J_c/\tilde{J}_c$ on misfit parameter f:

$$J_c/\tilde{J}_c = \frac{1}{N}\sum_{i=1}^{N} \exp\left[-\frac{4\pi(1+\nu) f \sum_{k=i}^{N} \alpha_k}{\theta_0}\right], \tag{22}$$

where $\tilde{J}_c = J_0 \exp[-\theta'/\theta_0]$ is the critical current density across a tilt boundary in its initial state [Fig. 1(a)] with the spatially homogeneous misorientation θ'. This ratio characterizes changes of the transport properties of tilt boundaries due to misfit-stress-induced transformations of boundary structures (Fig. 1).

For illustration, we have calculated with the help of formula (22) the dependences of $J_c/\tilde{J}_c$ on misfit parameter f, in the cases of $\theta' = 15°$ [Fig. 6(a)] and $=3°$ [Fig. 6(b)], for $\nu = 0.3$ and $N=3$, 5, 10, 25, and 50 The dependences (Fig. 6) indicate that misfit stresses are capable of strongly affecting (increasing or decreasing) values of the critical current density J_c across tilt boundaries in YBaCuO superconducting films. In doing so, the number N of tilt boundary fragments with various misorientations weakly influences values of $J_c/\tilde{J}_c$ in wide ranges of the misfit parameter. In fact, all the curves in Fig. 6(b) (for $\theta' = 3°$) are very similar, in which case it is difficult to graphically distinguish them.

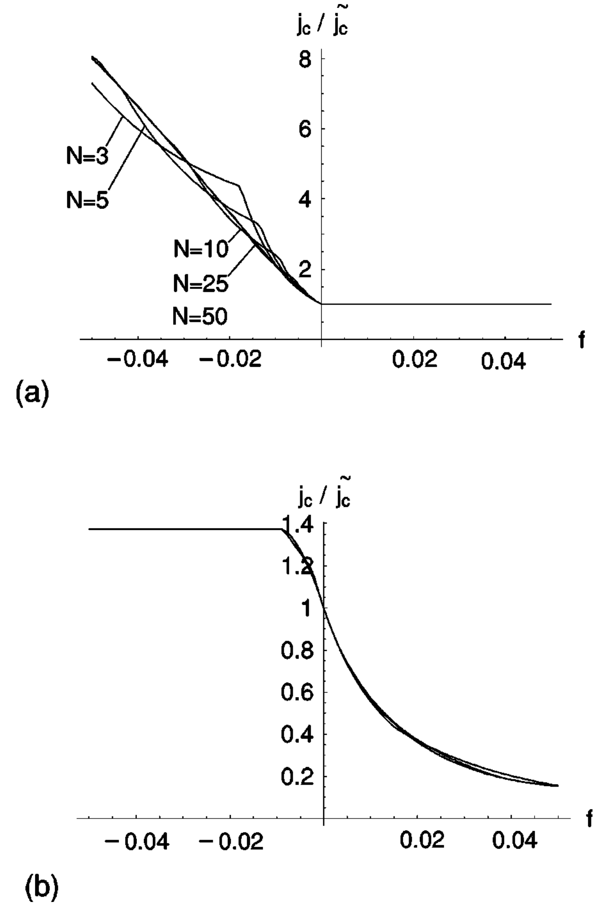

FIG. 6. Dependences of ratio $J_c/\tilde{J}_c$ on misorientation θ, for tilt boundary with initial misorientation (a) $\theta' = 15°$ and (b) $\theta' = 3°$, for $N=3$, 5, 10, 25, and 50 (see text).

In calculation of the dependences of $J_c/\tilde{J}_c$ on θ (Fig. 6), we have taken into account the following. Tilt boundaries with misorientation angles $\theta' = 3°$ and 15° are low-angle tilt boundaries consisting of lattice dislocations. In these circumstances, their structural transformations (Fig. 1) (induced by misfit stresses) occur via either generation or disappearance of lattice dislocations and rearrangements of dislocation ensembles along boundary planes. Such structural transformations do not remove the tilt boundaries with misorientation angles $\theta' = 3°$ and 15° from the class of low-angle boundaries, which is specified by misorientation ranging from 0° to tentatively 15°. With this taken into account, the minimum and maximum values of local misorientation $\theta' + \theta_i$ ($i=1,\ldots,10$) of fragments of grain boundaries, resulted from misfit-stress-induced transformations [Figs. 1(b), 1(c), and 2], are supposed to be 0° and 15°, respectively. More precisely, if the sum $\theta' + \theta_i$, which specifies the ith boundary fragment and corresponds to the minimum of ΔW given by formula (11) is higher than 15° (lower than 0°), it is supposed to be equal to 15° (0°, respectively).

It is important to note that the action of misfit stresses, in general, leads to the J_c enhancement. This occurs owing to the highly nonlinear character of dependence (20) of J_c on tilt-boundary misorientation θ. More precisely, an increase of J_c due to misfit-stress-induced decrease of θ by value of $\Delta\theta$ is higher than a decrease of J_c due to misfit-stress-induced increase of θ by the same value of $\Delta\theta$. That is,

$$J_c(\theta-\Delta\theta)/J_c(\theta+\Delta\theta) = \exp\left(\frac{2\Delta\theta}{\theta_0}\right) > 1. \tag{23}$$

Relationship (23) quantitatively reflects the fact that, in general, misfit stresses lead to the J_c enhancement.

The effect of misfit stresses is strong in vicinity of the film/substrate boundary and decreases with approaching the film free surface (see Fig. 3). Therefore, with relationship (23) taken into account, our model predicts a high (moderate, respectively) enhancement of J_c near the film/substrate boundary (the film free surface, respectively). This is in agreement with experimental data[16] indicating that most of the supercurrent in BiSrCaCuO tapes flows through the thin layer next to the interphase (BiSrCaCuO/silver) boundary.

VI. DISCUSSION AND CONCLUDING REMARKS

In this paper a theoretical model has been suggested describing misfit-stress-induced transformations of boundary-dislocation structures at tilt boundaries in high-T_c superconducting films. In the framework of the model suggested, boundary dislocations at tilt boundaries in films are rearranged (Fig. 1), in which case the new dislocation configurations effectively contribute to accommodation of misfit stresses. The rearrangements of grain-boundary dislocations are driven by a release of the elastic-energy density of the film and give rise to changes of tilt-boundary misorientation. In doing so, the influence of misfit stresses on spatial positions of grain-boundary dislocations in the film varies along the boundary. The effect is strong in vicinity of the film/substrate boundary and becomes weaker as the distance from the film/substrate boundary increases. As a corollary, distribution of grain-boundary dislocations and boundary misorientation vary along the grain boundary (see Figs. 1(b), 1(c), and 2).

The structure of tilt boundaries, resulted from misfit-stress-induced transformations (Fig. 1), causes the properties of such boundaries to be different from those in the case where misfit stresses are absent. In particular, misfit stresses can strongly influence the structure-dependent transport properties of grain boundaries in high-T_c superconducting films. Here we have considered the effect of misfit stresses on the critical current density J_c across tilt boundaries in the case of low-angle boundaries in YBaCuO films. In particular, it has been demonstrated that misfit-stress-induced transformations of tilt boundaries [Fig. 1(b)] are capable of causing essential enhancement of J_c in polycrystalline high-T_c cuprate films. The most significant enhancement of J_c is predicted to occur near the film/substrate boundary. This is in agreement with experimental data[16] indicating that most of the supercurrent in BiSrCaCuO tapes flows through the thin layer next to the interphase (BiSrCaCuO/silver) boundary.

The misfit-stress-driven transformations of tilt-boundary structures (Fig. 1) require grain-boundary dislocations to climb towards the film free surface or the film/substrate boundary, in which case the dislocations should overcome some energetic barriers related to emission or absorption of point defects at the dislocations cores.[51] Pressure and thermal treatment are capable of enhancing the climbing of dislocations and, therefore, according to our model, increasing J_c. In this context, recent experimental data[52] on a significant enhancement of J_c by hot pressing in Bi-2223/Ag multifilamentary tapes can indicate in favor of the model suggested in this paper.

Current models[17–26] of the grain-boundary effect on high-T_c superconductivity are based on the representation of low-angle tilt boundaries as periodic walls of perfect dislocations [Fig. 1(a)]. However, in the light of both experiments[12–15,33] and theoretical analysis given in this paper, the transformations of low-angle tilt boundaries (Fig. 1) should be definitely taken into consideration of the effects of grain-boundary strain fields and core structures on high-T_c superconductivity in thin films. In particular, the Ginzburg-Landau formulation[19,22] of the problem is worth being modified in the situation discussed (tilt boundaries in high-T_c superconducting films) in order to take into account the misfit-stress-induced structural transformations of low-angle tilt boundaries in high-T_c superconductors.

Actually, grain-boundary disclinations (Fig. 2) generated due to the effects of misfit stresses induce spatially inhomogeneous strain fields ϵ_{ik} that are screened at length scales essentially exceeding those of dislocations at periodic-dislocation walls. So, the strain fields of the ith disclination distant by d_i from the film free surface is characterized by the screening length $\approx d_i$. In particular, the screening length of strain fields generated by a disclination located at the film/substrate interface is close to the film thickness H. At the same time, strain fields of dislocations at periodically arranged dislocation walls are screened at length scales close to the dislocation wall period, which commonly $\ll H$. In these circumstances, long-range effects of grain boundaries, associated with long-range strain fields of the disclinations, should be taken into account in the framework of the Ginzburg-Landau description of the transport properties of grain boundaries in cuprates. For instance, these effects are worth being taken into consideration in the Ginzburg-Landau approach[19] operating with the strain-induced shift of critical temperature $T_c = T_{c0} - C_{ik}\epsilon_{ik}$, where C_{ik} is the tensor describing sensitivity of T_c to strains. Long-range strains of grain-boundary disclinations are capable of essentially modifying results[19] describing the high-T_c superconducting properties of low-angle boundaries as those associated with short-range strain fields of periodic-dislocation walls. Also, the long-range effects in question are worth being taken into account in the Ginzburg-Landau description[22] of the transport properties of grain boundaries, operating with the suppression of the superconducting order parameter due to the hole-depletion zones in the vicinity of grain boundaries. In doing so, long-range strain fields of grain-boundary disclinations are important, because they are capable of influencing the oxygen concentration in cuprates[26] and, therefore, the hole concentration near boundaries, which plays the role of the key characteristics of grain boundaries in the framework of the approach.[22] A detailed cumbersome analysis of the long-range effects discussed is beyond the scope of this paper, the results of which can be used as input in such analysis in the future.

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*Email address: ovidko@def.ipme.ru

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