

## Orientation order in nanoparticles in composite films

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A theoretical model is suggested that describes the effects of misfit stresses on the crystal lattice orientation in nanoparticles in composite films. Formulas for the energy that characterizes the elastic interaction between misfit stresses and different kinds of nanoparticles in composite films are revealed. It is found that misfit stresses tend to cause the orientation order (associated with a preferred orientation of crystal lattices) in nanoparticles embedded into a film matrix.

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### I. INTRODUCTION

Solid films exhibiting functional physical properties represent the subject of intensive studies motivated by their diverse technological applications and interest to the fundamentals of physical phenomena occurring in these films. Both the structure and physical properties of films are strongly influenced by misfit stresses generated due to lattice-parameter mismatch between films and substrates. For instance, misfit stresses cause the formation of misfit dislocations, disclinations, and their configurations in continuous and island films whose properties are very sensitive to the presence of these defects; see, e.g., Refs. 1–12. In recent years, composite films which contain nanoparticles (in particular, quantum dots) have attracted tremendous attention motivated by a range of new technological applications; see, e.g., Refs. 13–16. Structural characteristics of nanoparticles serving as stress sources are sensitive to misfit stresses in composite films. In particular, misfit stresses can influence the crystal lattice orientation in nanoparticles, which in its turn affects the functional physical properties of nanoparticles and their ensembles. The main aim of this paper is to suggest a theoretical model which describes the effect of misfit stresses on the crystal lattice orientation in nanoparticles in composite films.

### II. EFFECT OF MISFIT STRESSES ON CRYSTAL LATTICE ORIENTATION IN NANOPARTICLES IN COMPOSITE FILMS. GENERAL MODEL

In general, nanoparticles in a composite film represent stress sources due to crystal-lattice mismatch between nanoparticles and a film matrix. The theory of the equilibrium structure and elastic behavior of particles in a matrix under no-loading conditions was developed many years ago; see, e.g., pioneering works<sup>17,18</sup> and books.<sup>19,20</sup> Also, the strengthening effects of particles on dislocation slip deformation occurring in response to a shear stress in composite solids have been theoretically examined; see, e.g., Refs. 21 and 22. In this paper, we will focus our attention on the effects of tensile and compressive misfit stresses on the crystal lattice orientation in nanoparticles embedded into a film matrix.

Nanoparticles as stress sources in a composite film are characterized by the proper plastic distortion tensor  $\beta_{ij}^*$  (or plastic strain tensor  $\epsilon_{ij}^*$ ) with dilatation and shear compo-

nents. These components are defined in the coordinate system  $X'Y'Z'$  attached to the nanoparticle crystal lattice (Fig. 1). In particular, nanoparticles with a pure dilatation plastic distortion are characterized by the plastic distortion tensor written in the coordinate system  $X'Y'Z'$  (Fig. 1) in the following form:

$$\hat{\beta}^* = \begin{pmatrix} \beta_{x'x'}^* & 0 & 0 \\ 0 & \beta_{y'y'}^* & 0 \\ 0 & 0 & \beta_{z'z'}^* \end{pmatrix}. \quad (1)$$

Here  $\beta_{ii}^*$  ( $i=x',y',z'$ ) are the plastic distortion components which have constant values within a nanoparticle and equal to 0 outside it. Nanoparticle with a pure dilatation can be divided into the three categories: nanoparticles with one-axis, two- and three-axes plastic distortion tensor having one, two and three nonzero diagonal component(s)  $\beta_{ii}^* \neq 0$ , respectively.

The plastic distortion tensor that characterizes nanoparticles with a pure shear distortion can be written in the coordinate system  $X'Y'Z'$  (Fig. 1) in the following general form:

$$\hat{\beta}^* = \begin{pmatrix} 0 & \beta_{x'y'}^* & \beta_{x'z'}^* \\ \beta_{y'x'}^* & 0 & \beta_{y'z'}^* \\ \beta_{z'x'}^* & \beta_{z'y'}^* & 0 \end{pmatrix}. \quad (2)$$

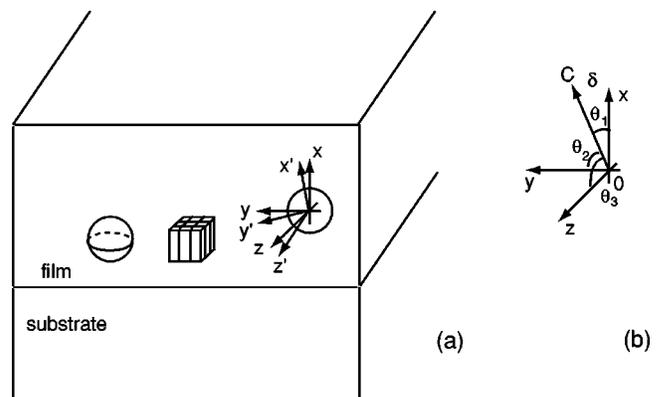


FIG. 1. Nanoparticles in a composite film. (a) Spherical and cubic nanoparticles. (b) Definition of the rotation axis  $C$  in the  $XYZ$  coordinate system.

Examples of nanoparticles with a pure shear plastic distortion are those with gliding dislocation loops (Orowan loops) (Ref. 20) at interphase boundaries dividing these nanoparticles and a film matrix. In this case, the plastic distortion tensor given by Eq. (2) has just one nonzero component. It characterizes the plastic shear of the nanoparticle material relative to the film matrix.

Nanoparticles as stress sources in a composite film deposited onto a substrate elastically interact with misfit stresses occurring due to crystal-lattice mismatch at the film/substrate boundary. In most cases, the energy  $W$  that characterizes the elastic interaction between the nanoparticles and misfit stresses is sensitive to the crystal lattice orientation in the nanoparticles. In these circumstances, the interaction tends to cause the preferred orientations of crystal lattices and, therefore, the orientation order of the nanoparticles in a composite film. Below we will calculate the energy  $W$  of the interaction between nanoparticles and misfit stresses in exemplary cases of spherical and cubic nanoparticles characterized by one-axis, two- and three-axes dilatation as well as nanoparticles surrounded by either one or two sets of dislocation loops causing a plastic shear distortion. In doing so, for definiteness and simplicity, we will consider nanoparticles distant enough from the film free surface, in which case the surface effects do not come into play. (In Sec. IV of this paper, the surface effects on the elastic energy of nanoparticles are estimated. These effects are shown to be essential in the only very thin layer (with thickness being about the nanoparticle diameter) close to the film free surface.)

Let us consider a model film/substrate system consisting of a composite film and a semi-infinite substrate [Fig. 1(a)]. The film and substrate are assumed to be elastically isotropic solids with the same values of the shear modulus  $G$  and the same values of Poisson ratio  $\nu$ . Misfit stresses occur in the film due to a dilatation misfit (geometric mismatch) between adjacent crystal lattices of the film and the substrate. For definiteness, here and in the following we consider the film and the substrate matched at  $(Y,Z)$  plane (Fig. 1) where they have square crystal lattices with the same crystallographic orientation. In this situation, the film/substrate boundary is characterized by two misfit parameters,  $f_y$  and  $f_z$ , given as  $f_y=f_z=(a_s-a_f)/a_f$ ,<sup>23</sup> where  $a_s$  and  $a_f$  are the crystal lattice parameters in the  $(Y,Z)$  plane of the film and the substrate, respectively. In the coordinate system  $XYZ$  [Fig. 1(a)] attached to the film crystal lattice, the misfit stress field in the film is given as

$$\begin{aligned}\sigma_{yy}^m &= 2G(f_y + \nu f_z)/(1 - \nu), \\ \sigma_{zz}^m &= 2G(\nu f_y + f_z)/(1 - \nu).\end{aligned}\quad (3)$$

Now let us consider a nanoparticle in the film. The crystal lattice orientation of the nanoparticle relative to the coordinate system  $XYZ$  [Fig. 1(a)] is characterized by the rotation matrix  $\mathbf{A}$ . It is parametrized by cosines of the three angles  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  determining the orientation of the rotation axis  $C$  in three-dimensional space and by the angle  $\delta$  characterizing the rotation of the nanoparticle crystal lattice relative to the axis  $C$  [Fig. 1(b)] as follows (Ref. 24):

$$\begin{aligned}\mathbf{A} &= \cos \delta \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + (1 - \cos \delta) \begin{pmatrix} c_1^2 & c_1 c_2 & c_1 c_3 \\ c_2 c_1 & c_2^2 & c_2 c_3 \\ c_3 c_1 & c_3 c_2 & c_3^2 \end{pmatrix} \\ &+ \sin \delta \begin{pmatrix} 0 & -c_3 & c_2 \\ c_3 & 0 & -c_1 \\ -c_2 & c_1 & 0 \end{pmatrix}.\end{aligned}\quad (4)$$

Here  $c_1 = \cos \theta_1$ ,  $c_2 = \cos \theta_2$ ,  $c_3 = \cos \theta_3$ . The angles obey the following equation:  $c_1^2 + c_2^2 + c_3^2 = 1$ .

Let us consider the energy  $W$  that characterizes the elastic interaction between nanoparticles and misfit stresses occurring due to lattice-mismatch at the film/substrate boundary in a composite film. According to the general calculation scheme,<sup>20</sup> the energy of the elastic interaction between two defects is calculated as the work spent to the generation of one defect in the stress field created by another defect. In our partial case [Fig. 1(a)], a nanoparticle plays the role of one defect, and the film/substrate boundary plays the role of another defect. In this case, following the approach,<sup>20</sup> the interaction energy  $W$  is written in the linear elasticity approximation as follows:

$$W = - \int_V \beta_{i'j'} \sigma_{i'j'}^m dV'. \quad (5)$$

Here  $V$  is the volume of the elastic medium,  $\beta_{i'j'}$  is the plastic distortion tensor of a nanoparticle, and  $\sigma_{i'j'}^m$  is the misfit stress tensor. Both the tensors  $\beta_{i'j'}$  and  $\sigma_{i'j'}^m$  are written in the coordinate system  $X'Y'Z'$  attached to the nanoparticle crystal lattice [Fig. 1(a)].

In its general form, Eq. (5) is valid both for isotropic and anisotropic crystals containing arbitrary defects, sources of internal stresses.<sup>20</sup> Also, Mura<sup>20</sup> showed that this approach can be used in a description of defects in elastically inhomogeneous composite solids, in particular, composites which contain nanoparticles with elastic constants different from those of a surrounding matrix. In this paper, for the sake of simplicity, we will use Eq. (5) in the framework of the isotropic elasticity theory applied to a description of composite solids which contain nanoparticles, a film matrix and substrate assumed to be elastically isotropic solids with the same values of elastic constants. In doing so, substitution of the plastic distortion tensor  $\beta_{i'j'}^*$ , characterizing different types of nanoparticles to general formula (5) will allow us to calculate the interaction energy  $W$  in these partial cases. An analysis of the partial cases of formula (5) will show the preferred orientations of crystal lattices of the different types of nanoparticles in a composite film.

### III. EFFECT OF MISFIT STRESSES ON CRYSTAL LATTICE ORIENTATION IN NANOPARTICLES IN COMPOSITE FILMS. PARTIAL CASES

*Nanoparticle with one-axis plastic dilatation.* Such a nanoparticle is characterized by one non-zero component of the plastic distortion tensor. This component is given as

$$\beta_{x'x'}^* = \begin{cases} \epsilon^* & \text{if } (x', y', z') \in V^{incl} \\ 0 & \text{if } (x', y', z') \notin V^{incl} \end{cases}$$

With  $\beta_{x'x'}^*$ , substituted to formula (5), we find the interaction energy

$$W = -\frac{2G(1+\nu)}{(1-\nu)} \epsilon^* f V^{incl} \{ [c_1 c_2 (1 - \cos \delta) + c_3 \sin \delta]^2 + [c_1 c_3 (1 - \cos \delta) - c_2 \sin \delta]^2 \}. \quad (6)$$

Here  $V^{incl}$  is the nanoparticle (nanoinclusion) volume. For  $\epsilon^* f > 0$ , the energy  $W$  given by formula (6) has a minimum:

$$W_{min} = -\frac{2G(1+\nu)}{(1-\nu)} \epsilon^* f V^{incl}, \quad (7)$$

if the dilatation axis of the nanoparticle is parallel to the film/substrate boundary ( $\theta_1 = \pi/2, \delta = \pi/2$ ). For  $\epsilon^* f < 0$ , the above orientation corresponds to a maximum of the interaction energy  $W$ . In the case of  $\epsilon^* f < 0$ , the interaction energy reaches its minimum  $W_{min} = 0$ , if the dilatation axis is perpendicular to the film/substrate boundary plane.

*Nanoparticle with two-axes plastic dilatation.* Non zero components of the plastic distortion tensor are given as

$$\beta_{y'y'}^* = \beta_{z'z'}^* = \begin{cases} \epsilon^* & \text{if } (x', y', z') \in V^{incl} \\ 0 & \text{if } (x', y', z') \notin V^{incl} \end{cases}$$

With these components substituted into formula (5), we get

$$W = -\frac{2G(1+\nu)}{(1-\nu)} \epsilon^* f V^{incl} \{ [c_2^2 (1 - \cos \delta) + \cos \delta]^2 + [c_2 c_3 (1 - \cos \delta) - c_1 \sin \delta]^2 + [c_2 c_3 (1 - \cos \delta) + c_1 \sin \delta]^2 + [c_3^2 (1 - \cos \delta) + \cos \delta]^2 \}. \quad (8)$$

For  $\epsilon^* f > 0$ , the interaction energy given by formula (8) reaches its minimum, if the dilatation axes of the nanoparticle are parallel to the film/substrate boundary plane ( $\theta_1 = 0$ ):

$$W_{min} = -\frac{4G(1+\nu)}{(1-\nu)} \epsilon^* f V^{incl}. \quad (9)$$

For  $\epsilon^* f < 0$ , the above orientation of the nanoparticle crystal lattice corresponds to a maximum of the interaction energy  $W$ . In the case of  $\epsilon^* f < 0$ , a minimum of the interaction energy

$$W_{min} = -\frac{2G(1+\nu)}{(1-\nu)} \epsilon^* f V^{incl}$$

corresponds to the nanoparticle orientations having one of the dilatation axes to be perpendicular to the film/substrate boundary.

*Nanoparticle with three-axes plastic dilatation.* In this case, the plastic distortion tensor has the three non-zero components

$$\beta_{x'x'}^* = \beta_{y'y'}^* = \beta_{z'z'}^* = \begin{cases} \epsilon^* & \text{if } (x', y', z') \in V^{incl} \\ 0 & \text{if } (x', y', z') \notin V^{incl} \end{cases}$$

With these components substituted into formula (5), one finds that

$$W = -\frac{4G(1+\nu)}{(1-\nu)} \epsilon^* f V^{incl}. \quad (10)$$

The interaction energy given by Eq. (10) is independent of the crystal lattice orientation of the nanoparticle.

*Nanoparticle with one set of gliding dislocation loops.* For definiteness, let us consider a nanoparticle with one set of gliding dislocation loops continuously distributed at the interphase boundary that divides the nanoparticle and a film matrix. In this case, the plastic distortion tensor is as follows:

$$\beta_{y'y'}^* = \begin{cases} \gamma^* & \text{if } (x', y', z') \in V^{incl} \\ 0 & \text{if } (x', y', z') \notin V^{incl} \end{cases}$$

where  $\gamma^*$  is the plastic shear of the nanoparticle material relative to the film matrix material. With  $\beta_{y'y'}^*$ , substituted into formula (5), we find the interaction energy

$$W = -\frac{2G(1+\nu)}{(1-\nu)} \gamma^* f V^{incl} \{ [c_2^2 (1 - \cos \delta) + \cos \delta] \times [c_1 c_2 (1 - \cos \delta) + c_3 \sin \delta] + [c_1 c_3 (1 - \cos \delta) - c_2 \sin \delta] [c_2 c_3 (1 - \cos \delta) + c_1 \sin \delta] \}. \quad (11)$$

The interaction energy  $W$  given by formula (11) reaches one of its minima, if the axis normal to the shear plane is misoriented by  $\pi/4$  relative to the film/substrate boundary.

*Cubic nanoparticle surrounded by two sets of discrete gliding dislocation loops.* Let us consider a cubic nanoparticle surrounded by two sets of discrete gliding dislocation loops located at the interphase boundary dividing the nanoparticle and a film matrix. Following Ref. 20, such a cubic particle has two parallel facets with networks of screw dislocations (serving as dislocation models of low-angle twist boundaries<sup>25</sup>) and four facets with edge dislocation rows (serving as models of low-angle tilt boundaries<sup>25</sup>). The plastic distortion of the gliding dislocation loop, which lies in plane parallel to  $X'o'Z'$  plane and has coordinate  $y'_0$  and Burgers vector  $\mathbf{b}^I = \pm b \mathbf{e}_{z'}$ , is given as<sup>20</sup>

$$\beta_{y'z'}^{*I} = -\text{sgn}^I b \delta(y' - y'_0) H \quad (0 \leq x' \leq R, 0 \leq z' \leq R). \quad (12)$$

The plastic distortion of the gliding dislocation loop, which lies in plane parallel to  $X'o'Y'$  plane and has coordinate  $z'_0$  and Burgers vector  $\mathbf{b}^{II} = \pm b \mathbf{e}_{y'}$ , is given as<sup>20</sup>

$$\beta_{z'y'}^{*II} = -\text{sgn}^{II} b \delta(z' - z'_0) H \quad (0 \leq x' \leq R, 0 \leq y' \leq R). \quad (13)$$

In formulas (12) and (13),  $\text{sgn}^I$  is the sign of projections of Burgers vectors that characterize dislocation loops belonging to the dislocation set  $I$  on axis  $o'Z'$ ,  $\text{sgn}^{II}$  is the sign of projections of Burgers vectors that characterize dislocation loops belonging to the set  $II$  on axis  $o'Y'$ ,  $\delta(y')$  and  $\delta(z')$

denote the  $\delta$  functions,  $H$  is the Heaviside function, and  $R$  is the size (edge length) of the cubic nanoparticle.

With Eqs. (12) and (13) substituted into formula (5), after some algebra, we find the interaction energy

$$W = -\frac{4G(1+\nu)}{(1-\nu)}fNbR^2(\text{sgn}^I + \text{sgn}^{II})\{[c_2^2(1-\cos\delta) + \cos\delta][c_2c_3(1-\cos\delta) - c_1\sin\delta] + [c_3^2(1-\cos\delta) + \cos\delta][c_2c_3(1-\cos\delta) + c_1\sin\delta]\}. \quad (14)$$

Here  $b$  denotes the Burgers vector magnitude, and  $N$  the number of dislocation loops belonging to set I (or II).

An analysis of formula (14) shows that the interaction energy  $W=0$  in the two following cases: (1) the nanoparticle facets with screw dislocation networks are parallel to the film/substrate boundary (the rotation axis  $C$  coincides with axis  $X$ :  $\theta_1=0, \theta_2=\theta_3=\pi/2$ , and  $\delta$  is arbitrary); and (2) the rotation axis  $C$  coincides with either axis  $Y$  or  $Z$  ( $\theta_2=0, \theta_1=\theta_3=\pi/2$  or  $\theta_3=0, \theta_1=\theta_2=\pi/2$ , respectively). Also, notice that the interaction is absent ( $W=0$ ) at any value of the rotation angle and any position of the rotation axis, if gliding dislocation loops which belong to the different dislocation sets have opposite signs ( $\text{sgn}^I = -\text{sgn}^{II}$ ). If the gliding dislocation loops which belong to the different sets have the same sign ( $\text{sgn}^I = \text{sgn}^{II}$ ), the interaction energy  $W$  is either positive or negative. The dependences of  $W$  on parameters characterizing the crystal lattice orientation of the nanoparticle are presented in Fig. 2. As follows from Fig. 2, the interaction energy has its minimum at  $f \cdot \text{sgn}^{I,II} < 0$  (or maximum at  $f \cdot \text{sgn}^{I,II} > 0$ ), provided that the nanoparticle facets with screw dislocation segments are perpendicular to the film/substrate boundary and the nanoparticle facets with edge dislocation segments make angle  $\pi/4$  with the film/substrate boundary plane.

#### IV. EFFECTS OF NANOPARTICLE FACETS AND FILM FREE SURFACE ON CRYSTAL LATTICE ORIENTATION IN NANOPARTICLES

Nanoparticles are often faceted in nanocomposite solids, because there are energetically favorable orientations of nanoparticle facets; see, e.g., Refs. 26 and 27. This faceting effect is in competition with the effect of misfit stresses on the crystal lattice orientation in nanoparticles. To describe the competition between the effects in question, we will estimate and compare their energy characteristics. The effect of misfit stresses is characterized by the difference  $\Delta W = W_{max} - W_{min}$  between maximum ( $W_{max}$ ) and minimum ( $W_{min}$ ) values of the energy  $W$  that specifies the elastic interaction of nanoparticles and misfit stresses in a composite film. In the exemplary case of one-axis dilatation nanoparticle having the form of a sphere with radius  $R_{sph}$ , from formulas (6) and (7) we find  $\Delta W$  to be given as

$$|\Delta W| = \frac{8\pi G(1+\nu)}{3(1-\nu)}\varepsilon^*fR_{sph}^3. \quad (15)$$

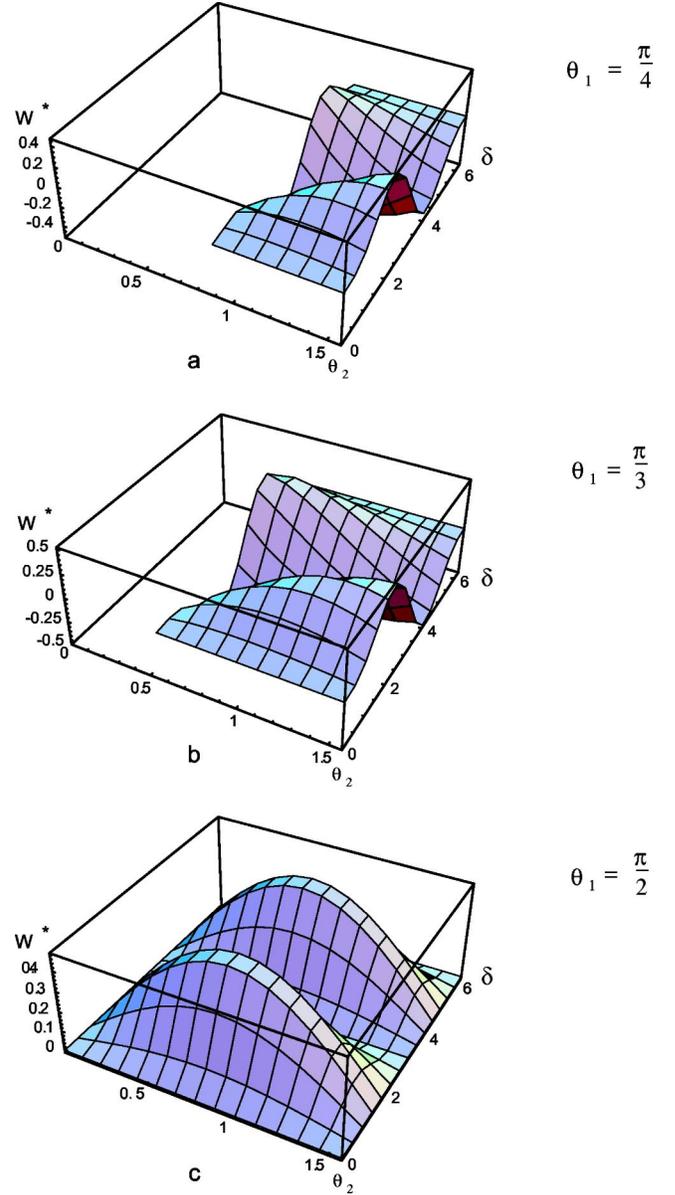


FIG. 2. (Color online) Dependence of the interaction energy  $W^*$  [in units of  $2G(1+\nu)/(1-\nu)fNbR^2(\text{sgn}^I + \text{sgn}^{II})$ ] on angles  $\theta_2$  and  $\delta$ , for (a)  $\theta_1 = \pi/4$ , (b)  $\theta_1 = \pi/3$ , and (c)  $\theta_1 = \pi/2$ .

Values of  $\Delta W$ , for  $\varepsilon^* = 0.01$ ,  $f = 0.01$ ,  $\nu = 0.3$ ,  $G = 20$  and 100 GPa, and different values of  $R_{sph}$ , are presented in Table I. For comparison, values of the proper elastic energy  $E^I$  of one-axis dilatation nanoparticle of spherical form<sup>20</sup> are presented in Table I, too.

The faceting effect is characterized by the difference  $\Delta W^f = W_{max}^f - W_{min}^f$  between maximum ( $W_{max}^f$ ) and minimum ( $W_{min}^f$ ) values of the energy that specifies facet orientations of the nanoparticle/matrix boundary. In the exemplary case of a nanoparticle having the form of a sphere with radius  $R_{sph}$ , we have:  $W^f \approx 4\pi\gamma_s R_{sph}^2$ . The faceting energy difference is given as

$$\Delta W^f = 4\pi\Delta\gamma_s R_{sph}^2, \quad (16)$$

TABLE I. Energy characteristics of nanoparticles embedded into a mismatched film on a substrate.  $4\pi\Delta\gamma_s R_{sph}^2$  is the energy difference that characterizes the faceting effect,  $E^I$  is the proper elastic energy of one-axis dilatation nanoparticle of the spherical form, and  $|\Delta W|$  is the energy difference that characterizes the effect of misfit stresses on the crystal lattice orientation in one-axis dilatation nanoparticle of the spherical form (for details, see the text).

$R_{sph} \rightarrow$ energies $\downarrow$	10 nm	20 nm	40 nm	60 nm
	$G = 2 \times 10^{10} \text{ N/m}^2$ (20 GPa), $\Delta\gamma_s = 0.06 \text{ J/m}^2$ ( $\approx 4 \text{ meV/\text{Å}^2}$ )			
$4\pi\Delta\gamma_s R_{sph}^2$	$7.5 \times 10^{-17} \text{ J}$	$3 \times 10^{-16} \text{ J}$	$1.2 \times 10^{-15} \text{ J}$	$2.7 \times 10^{-15} \text{ J}$
$E^I$	$6.3 \times 10^{-18} \text{ J}$	$5.1 \times 10^{-17} \text{ J}$	$4.1 \times 10^{-16} \text{ J}$	$1.37 \times 10^{-15} \text{ J}$
$ \Delta W $	$3.1 \times 10^{-17} \text{ J}$	$2.5 \times 10^{-16} \text{ J}$	$1.9 \times 10^{-15} \text{ J}$	$6.7 \times 10^{-15} \text{ J}$
	$G = 10 \times 10^{10} \text{ N/m}^2$ (100 GPa), $\Delta\gamma_s = 0.06 \text{ J/m}^2$ ( $\approx 4 \text{ meV/\text{Å}^2}$ )			
$4\pi\Delta\gamma_s R_{sph}^2$	$7.5 \times 10^{-17} \text{ J}$	$3 \times 10^{-16} \text{ J}$	$1.2 \times 10^{-15} \text{ J}$	$2.7 \times 10^{-15} \text{ J}$
$E^I$	$3.1 \times 10^{-17} \text{ J}$	$2.5 \times 10^{-16} \text{ J}$	$2.0 \times 10^{-15} \text{ J}$	$6.9 \times 10^{-15} \text{ J}$
$ \Delta W $	$1.5 \times 10^{-16} \text{ J}$	$1.2 \times 10^{-15} \text{ J}$	$9.9 \times 10^{-15} \text{ J}$	$3.4 \times 10^{-14} \text{ J}$

where  $\Delta\gamma_s$  is the difference between maximum and minimum energy densities (per unit area) of facets. With data<sup>27</sup> for  $\Delta\gamma_s$  that characterize InAs nanoparticles in the As matrix, we have calculated values of  $\Delta W^f$ . These values, for different values of  $R_{sph}$ , are presented in Table I.

As follows from formulas (15) and (16), the energy characteristics  $\Delta W^f$  and  $\Delta W$  of the faceting effect and the effect of misfit stresses on crystal lattice orientation, respectively, exhibit different dependences on  $R_{sph}$  and  $G$ . When the nanoparticle radius  $R_{sph}$  and/or the shear modulus  $G$  grow, the energy difference  $\Delta W$  rapidly increases. In particular,  $\Delta W$  is proportional to  $R_{sph}^3$ . At the same time,  $\Delta W^f$  slowly increases with rising  $R_{sph}$  and does not depend on  $G$ . In particular,  $\Delta W^f$  is proportional to  $R_{sph}^2$ . In this context, as illustrated by data presented in Table I, the effect of misfit stresses is dominant in wide ranges of parameters characterizing composite films which contain one-axis dilatation nanoparticles. A similar behavior is exhibited by other kinds of nanoparticles examined in this paper.

Now let us estimate the effect of the film free surface (image forces) on the elastic energy of nanoparticles dispersed in a composite film [Fig. 1(a)]. In the framework of our model, elastic moduli of the nanoparticles and the film matrix are assumed to have the same values. In these circumstances, in order to quantitatively characterize the free surface effect, it is sufficient to calculate the proper elastic energy of a nanoparticle (inclusion) embedded into an elastic half-space. The free surface effect should cause a dependence of this energy on the distance between the nanoparticle and the free surface. In calculation of the proper elastic energy of the nanoparticle shown in Fig. 1(a), the following boundary conditions are realized on the half-space free surface:  $\sigma_{xj}(x=0) = 0$ , where  $j = x, y, z$ .

Let us consider the simplest case of a spherical nanoparticle with three-axes dilatation. In calculation of its proper elastic energy, we will use the method<sup>28</sup> of surface virtual dislocation loops. (This method is based on the general scheme<sup>29,30</sup> of surface virtual defects that describe the image forces.) In doing so, after some algebra, we find the follow-

ing formula for the elastic energy of a spherical nanoparticle with three-axes plastic distortion:

$$E = E^\infty + E^{surf} = \frac{8\pi(1+\nu)}{3(1-\nu)} G \varepsilon^{*2} R_{sph}^3 - \frac{4\pi(1+\nu)^2}{9(1-\nu)} G \varepsilon^{*2} R_{sph}^3 \left( \frac{R_{sph}}{h} \right)^3, \quad (17)$$

where  $R_{sph}$  is the nanoparticle radius, and  $h$  is the distance between the nanoparticle center and the film free surface. Formula (17) is valid at  $h \geq R_{sph}$ .

The first term on the right-hand side of formula (17) is the energy of the spherical nanoparticle in an infinite solid. The second term on the right-hand side of formula (17) is the energy that characterizes the elastic interaction between the nanoparticle and the film free surface or, in other words, describes the effect of the image forces on the elastic energy of the nanoparticle. Numerical calculations using formula (17), for  $\nu = 0.3$ , show that ratio  $E^{surf}/E^\infty = 0.22$  in the limiting case of  $h = R_{sph}$  and rapidly falls with rising  $h$ . For instance,  $E^{surf}/E^\infty = 0.03$  at  $h = 2R_{sph}$ . The above estimate is indicative of the fact that the free surface effect on the elastic behavior of spherical nanoparticles with three-axes plastic distortion is essential in the only very thin layer (with thickness being about the nanoparticle diameter) close to the film free surface. In general, this statement is valid for all the types of nanoparticles considered in this paper, because these nanoparticles induce short-range stress fields causing the only short-range interaction between the nanoparticles and the film free surface. In particular, the film free surface effect is negligible in the case of quantum dots grown on the film/substrate boundary and distant enough from the film free surface.

For nanoparticles with dislocated interphase boundaries, the structure of edges, where different dislocation arrays meet, can be different from that in the rest of these boundaries. (A similar effect occurs in low-angle grain boundaries with nanoscale facets in high- $T_c$  superconductors; see ex-

perimental data<sup>31</sup> and a theoretical model.<sup>32</sup>) Notice that this difference is able to affect the only local crystal lattice orientation of nanoparticle regions adjacent to the edges. However, the edge effect hardly influences the mean crystal lattice orientation in dislocated nanoparticles. This edge effect will be the subject of further studies of authors.

## V. CONCLUDING REMARKS

Thus, in this paper, we have theoretically examined the elastic interaction between nanoparticles and misfit stresses in composite films which contain nanoparticles [Fig. 1(a)]. It is shown that misfit stresses tend to cause the preferred orientation of crystal lattices in nanoparticles in a composite film. The preferred orientation depends on both the proper plastic distortion tensor characterizing nanoparticles and the misfit parameters characterizing the film/substrate boundary.

As a corollary, the elastic interaction tends to cause the orientation order of crystal lattices in nanoparticles in composite films. This effect should be definitely taken into consideration in further experimental and theoretical study of composite films with embedded nanoparticles, because of its fundamental significance and potential use in technological applications.

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