10. PROPERTIES OF DEFECTS IN NANOSTRUCTURED MATERIALS

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For the prediction of the mechanical properties of nanostructured materials (nanocrystals, nanocomposites, nanoscaled films), the behavior of the various defects (dislocations, disclinations, grain boundaries, etc.) plays an important role. To analyze the behavior of defects, it is often necessary to find their elastic fields and energies of these defects.

In nanostructured materials, the elastic properties of defects are strongly modified by the interaction with interfaces. The results of calculating elastic fields for conventional dislocations and disclinations, and Somigliana dislocations in small particles, nanograined materials, and nanoscaled heterophase films are reported here.

On the basis of these results, the stability of defects in nanostructured materials is discussed, and the existence of various critical scales connected with defect strain energy relaxation is predicted. Special attention is paid to the generation of pentagonal symmetry in small particles (which is explained in terms of disclinations) and to the relaxation of misfit strains in thin films (which is connected with the nucleation and motion of misfit dislocations). The other mechanism of strain energy relief in nanoscale film is associated with multiple twinning and is peculiar, for example, to domain formation in ferroelastic and ferroelectric epitaxial films. In this case, analysis of defect properties explains the development of domain patterns with film thickness.

The continuum description of defects in nanoscaled materials is demonstrated to be useful in estimates of stored energy and volume change in nanocrystals, in the analysis of the structural stability of nanomaterials, in the explanation of the yield stress anomalies in the region of nanoscales, etc.

Editor's note: The following outline and figures were used as viewgraphs during Professor Romanov's presentation.

Introduction: The Role of the Theory of Defects in Materials Science and Solid State Physics

- the theory of defects is a natural language for the description of structure-sensitive properties of solids
- the theory of defects is a bridge connecting materials science with solid state physics

History of the Development of the Theory of Defects in the Soviet Union and Russia (see Table 10.1)

Table 10.1
History of the Theory of Defects

Name	Years	Results
Frenkel	1930s	A model for one-dimensional dislocations A model for point defect formation
Indenbom	1950s 1960s	Theory of dislocation-induced internal stresses Various applications of the theory of defects
Orlov	1950s 1960s	Applications of defect theory to the problems of the physics of strength and plasticity; Defect kinetics
Slezov	1960s	Theory of segregation and coalescence in the ensemble of point defects
Kosevich	1960s	Mechanics of defects in crystals
Predvoditelev	1970s	Computer modeling of defects
Krivoglaz	1970s	Theory of X-ray diffraction in crystals with defects
Lyubov	1970s	Diffusion and point defects
Orlov	1970s	Theory of radiation-induced defects
Vladimirov	1980s	Cooperative effects in defect ensembles, disclinations
Rybin	1980s	Grain boundaries, disclinations
Likhachev	1980s	Defects in amorphous structures
Ovid'ko	1980s 1990s	Defects in glasses, quasicrystals, liquid crystals Quasiperiodic grain boundaries, nanocrystals
Romanov	1980s 1990s	Theory of disclinations in solids, defect kinetics Defects in small particles, thin films and nanocrystals
Gryaznov	1980s 1990s	Pentagonal symmetry in small particles Stability of defects in nanocrystals

Defects in Small Particles and Nanostructured Materials

- size effects and characteristic scales in defect structure of solids
- modeling of grain and phase boundaries in crystalline materials
- stability of dislocations and disclinations in small particles and nanocrystals
- misfit and threading dislocations in growing thin films

Figure 10.1 indicates the various scale lengths of defects and material structures.

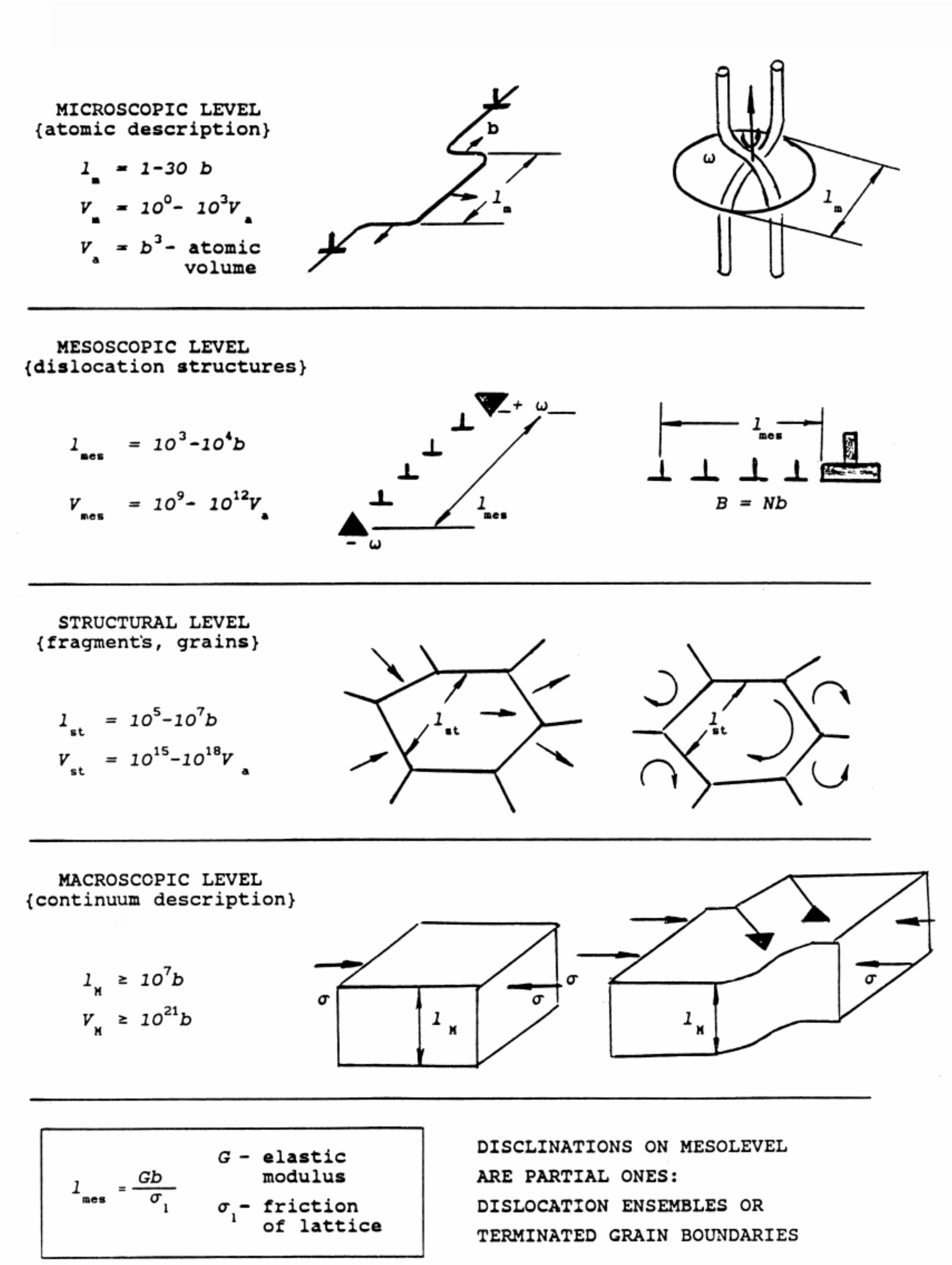

Fig. 10.1. Defects and scale levels.

The energy balance of defects within materials, and hence their ultimate stability, will vary according to the nature of the interfaces. Figure 10.2 gives a schematic representation of coherent, semicoherent and incoherent interfaces.

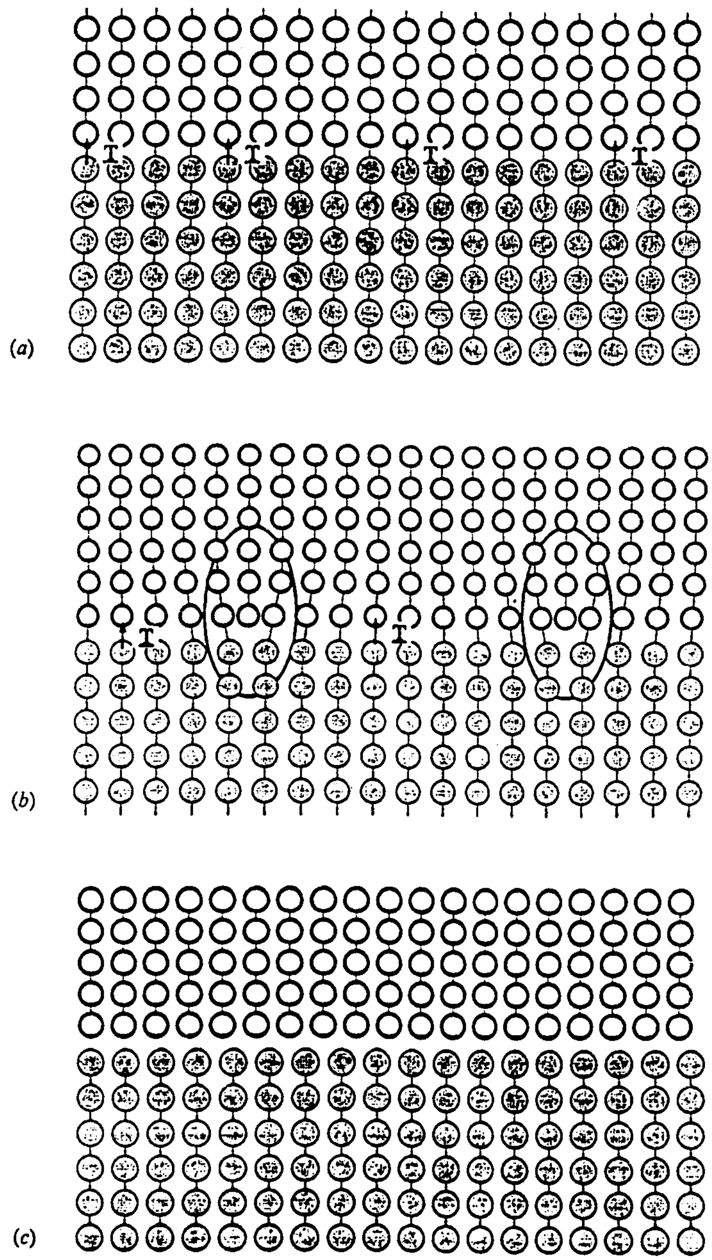

Fig. 10.2. Structure of interfaces (schematic): (a) coherent, (b) semicoherent, (c) incoherent. From G.Gutekunst, J. Mayer, and M. Ruhle, 1997, *Philosophical Magazine A, Vol. 75, No. 5, 1329-1355.*

Figure 10.3 gives the conditions for establishing the stability of a location and the critical size of a nanocrystallite, L.

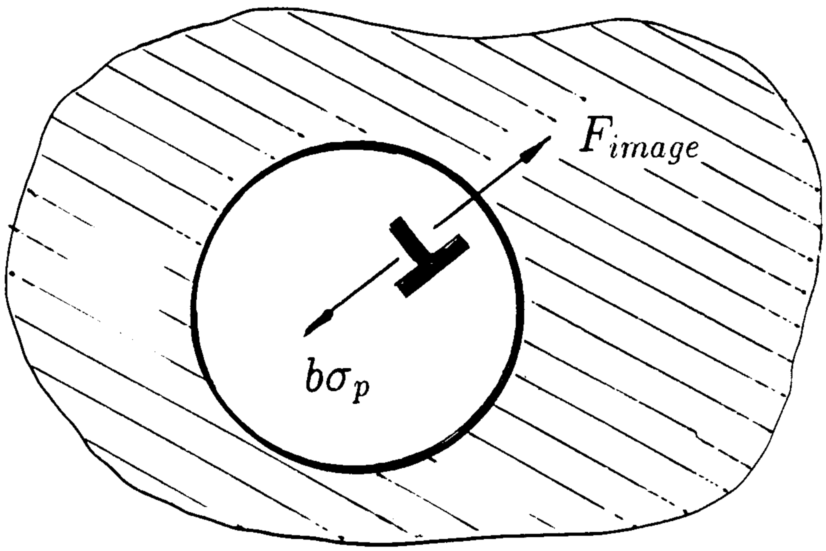

Fig. 10.3. Dislocation stability in nanocrystallites.

Condition for Dislocation Stability:

$F_{image} \leq b\sigma_p$

Parameters of the Problem:

σ_p	— Peierls stress
$G^{(m)} = \sum_{i=1}^{N} \int_i G^{(m)}$	— Effective elastic modulus of matrix
V_e	— Volume of dislocation stability in a nanocrystallite
Λ	— Critical size of a nanocrystallite

Estimation for the Critical Size:

$\Lambda \cong Gb/\sigma_p \cong 10 - 10^2$ nm

More Precise Results for $\Gamma \cong 1$:

$\Lambda \cong [\vartheta_0 + \vartheta_1(\Gamma - 1)]Gb/\sigma_p$

$\vartheta_0 = 0$; $\vartheta_1 \cong 0.1\text{sgn}(\Gamma - 1)$ for sphere with coherent boundary

$\vartheta_0 \cong 0.04$; $\vartheta_1 \cong -0.05$ for the cylinder with slipping interface

Table 10.2 lists some of the critical parameters for various metallic materials.

Table 10.2

Dislocation Stability in Various Nanocrystallites

	Cu	**Al**	**Ni**	**∝-Fe**
G (GPa)	33	28	95	85
b (nm)	0.256	0.286	0.249	0.248
σ_p (10^{-2} GPa)	1.67	6.56	8.7	45.5
Λ (nm), sphere	38	18	16	3
Λ (nm), cylinder	24	11	10	2

Figure 10.4 gives a hierarchy of stability scales for defects in nanocrystallites.

1. **ELECTROSTATIC INSTABILITY:** (generation of mobile defects under electron beam) — $\Lambda_e \leq 1 - 2$ nm
2. **IMAGE INSTABILITY:** (cleaning of the nanoparticle volume from dislocations) — $\Lambda = 10 - 50$ nm
3. **MISFIT INSTABILITY:** (appearence of misfit dislocations in thin films or coated nanocrystallites) — $h_c = 1 - 100$ nm
4. **PENTAGONAL INSTABILITY:** (transition of noncrystallographic nuclei in true crystals) — $A^* = 1 - 10$ nm
5. **RELAXATION INSTABILITY:** (formation of defects in nanocrystallites with pentagonal symmetry) — $A_r \geq 2 - 5$ nm

Fig. 10.4. Hierarchy of stability scales for defects in nanocrystallites.

Figure 10.5 is a high resolution micrograph of a decahedral small particle of Pd.

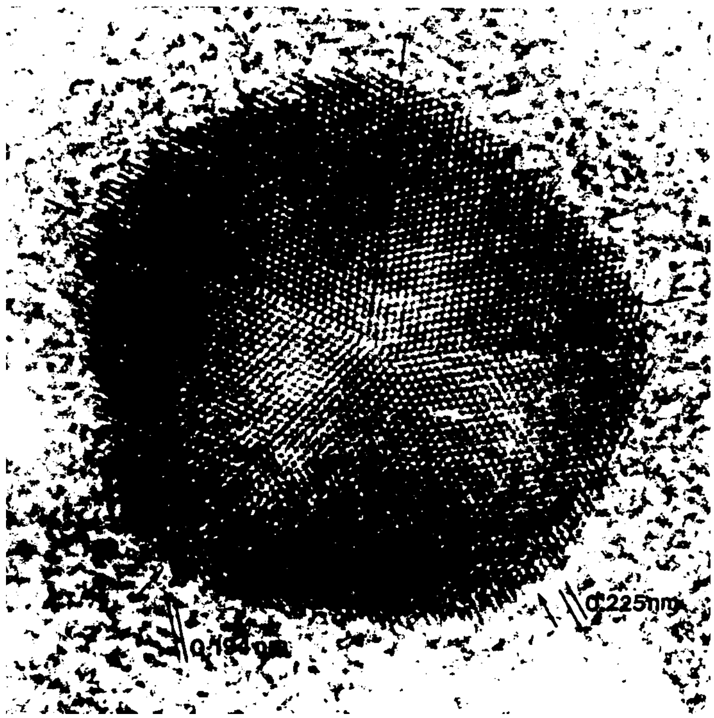

Fig. 10.5. Structure of small particles. High-resolution micrograph of a decahedral small particle of Pd. There is a splitting of the pentagonal axis (Renou & Penisson).

Possible Directions for Future Developments and Applications of the Theory of Defects for Nanostructured Materials

Analysis of defect interactions at the nanometer scale (computer and analytical modeling)

Investigations of the influence of defects on physical and mechanical properties of nanostructured materials

Predictions of structure-property relationships for nanostructured materials including the results of the modeling in the chain: processing—characterization—applications

The following are particular problems associated with nanostructured materials:

- theory of defect interactions with triple lines in nanocrystals
- clarification of deformation and fracture mechanisms in nanocrystals
- development and stability of defect structure in functional materials of modern nano- and microelectronics
- behavior of defects in fullerenes and other atomic clusters