PHYSICAL CHEMISTRY OF NANOSTRUCTURED SYSTEMS

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LECTURE No. 4

PROPERTIES OF NANOSTRUCTURED MATERIALS

INTRODUCTION

Physical-chemistry of solid-state nanostructures is a bridge between:

- Atomic Physics
- Physical chemistry of the concentrated state

Наноструктура - очень маленький фрагмент твердого тела. Что при таких малых размерах свойства наноструктур сильно отличаются от свойств сыпучих материалов.

INTRODUCTION

What is Nonotechnology?

What is Nonoscience?

Stability:
- ✔ Kinetic
- ✔ Thermodynamic factors

OBJECTIVES

- To analyse physico-chemical properties of nanostructured materials.
- To explain size effect of nanoparticles on the chemical and thermodynamic properties.

OUTLINE

- Physico-chemical properties of nanostructured materials.
- Size effect of nanoparticles on the chemical and thermodynamic properties.

Factors, influencing the properties of nanostructured materials (with decreasing of size of nanoparticles):

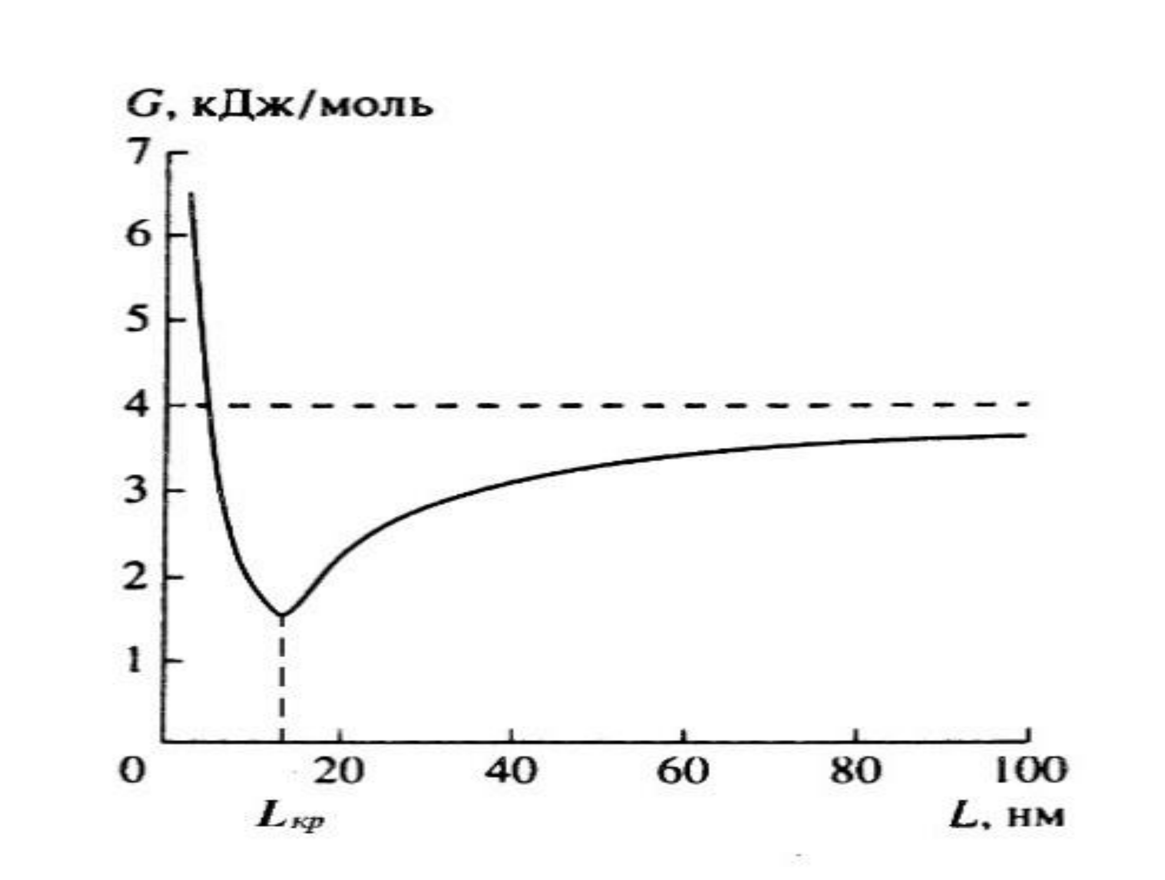
- A change in the thermodynamic state of nanosystems
- The appearance of quantum-size effects
  - ✔ excess energy and
  - ✔ high physico-chemical activity

The formation of nanoparticles from atoms is accompanied by two processes:

- Formation of metallic nuclei of different sizes
- Interaction between the particles, which facilitates the creation of ensembles representing nanostructures from them.

Physico-chemical properties

Change in the free Gibbs energy (G)



Physico-chemical properties

Electrical resistivity

$$\ln\left(\frac{\rho}{\rho_\infty}\right) = \frac{l_\infty}{D}\ln\frac{1}{q}$$

$0 < q < 1$

Where:

- ρ_∞ is the electrical resistivity of a coarse grain substance,
- l_∞ is the mean free path of electrons in a single crystal,
- q is the coefficient of electron scattering during the transition of grain boundaries (межзеренных границ)

Physico-chemical properties

Mechanical properties

Tensile strength and hardness:

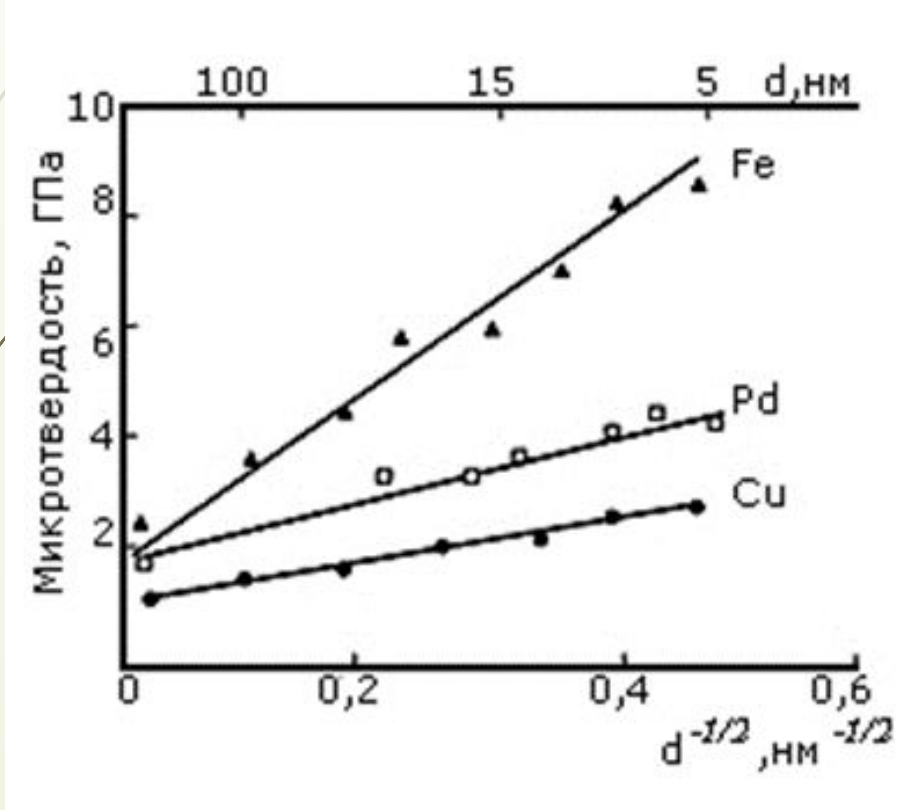
$$\sigma_T = \sigma_T^0 + k\overline{d}^{-\frac{1}{2}}$$ (Hall-Petch equation)

Where:

- σ_T^0 is strength of a single crystal,
- k is a coefficient of strength (specific for each material),
- d is an average grain size.

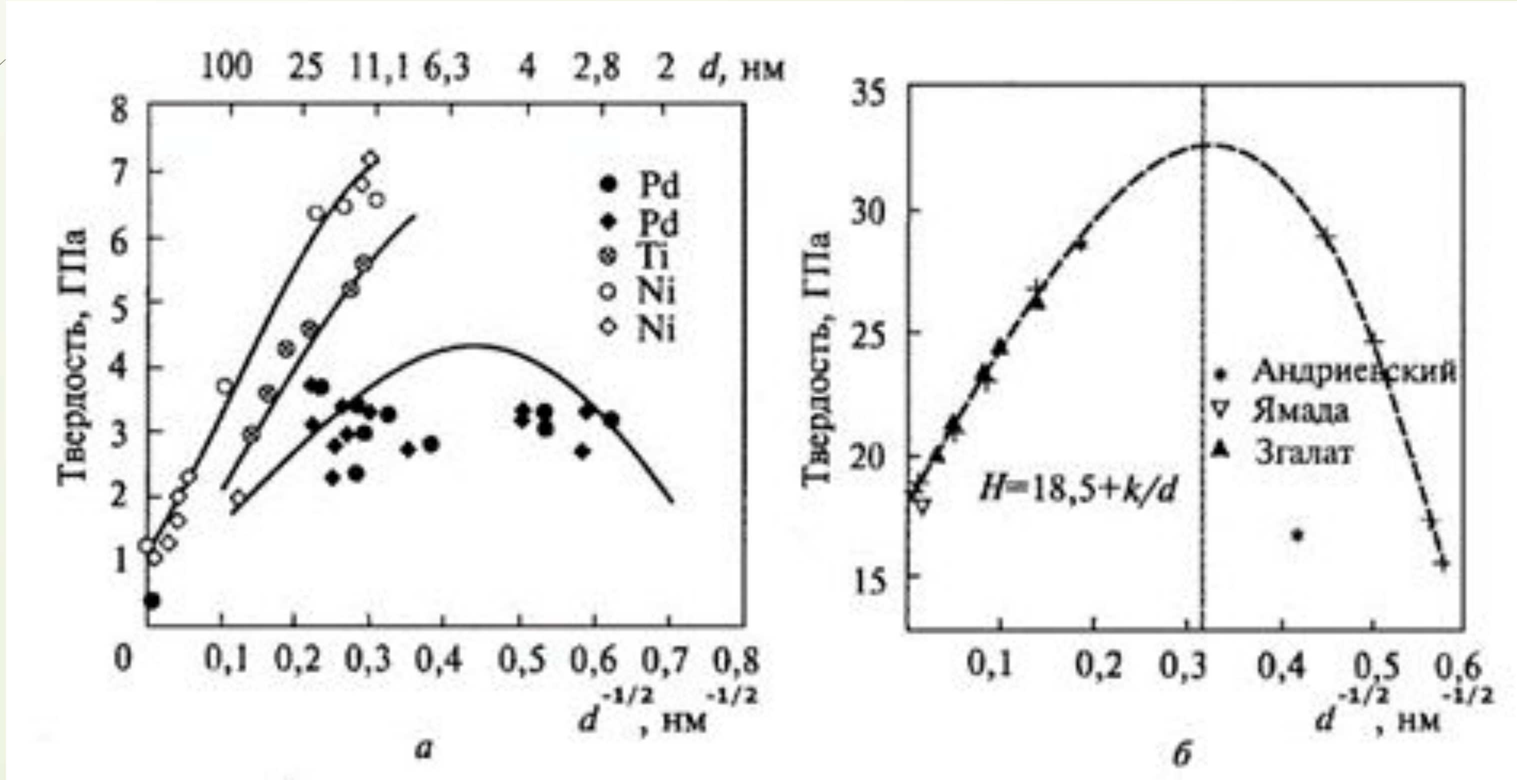
Physico-chemical properties

Effect of grain size (d) on the micro hardness of metals



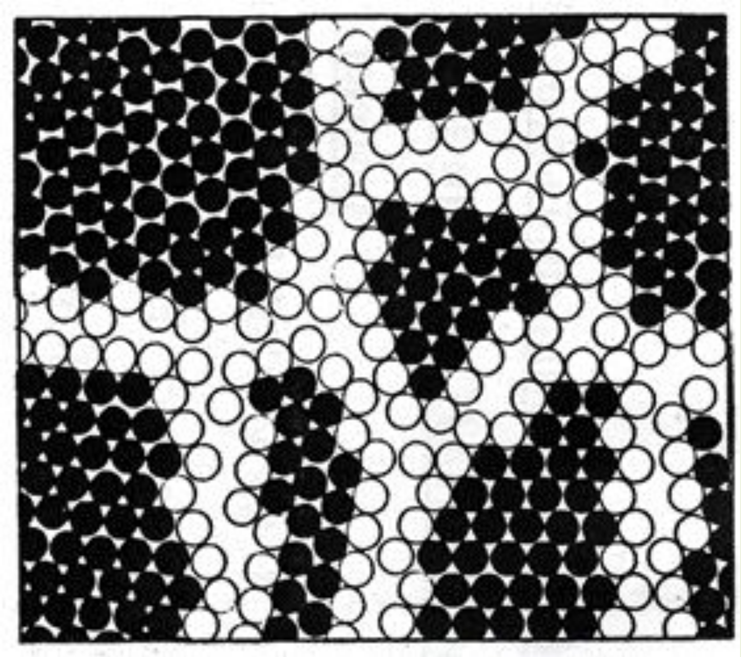
Physico-chemical properties

Effect of grain size (d) on the micro hardness of metals (a) and ceramics (b)



Physico-chemical properties

Internal stresses (grain boundaries as determining role)



Two-dimensional model of nanocrystalline material.

- ○ Nanocrystallites with different orientations
- ● Interphase boundaries (межзеренных границ)

Physico-chemical properties

The study of experimental data and reactions of atoms, clusters and nanoparticles of various elements of the periodic system allows us to formulate the following definition:

Размерные эффекты в химии – это явление, выражающееся в качественном изменении физико-химических свойств и реакционной способности в зависимости от количества атомов или молекул в частице вещества, происходящее в интервале менее 100 атомно-молекулярных диаметров.

Types of size effects

- Internal: associated with specific changes in the volume and surface properties of both individual particles and the ensembles obtained because of their self-organization.

- External: dimensionally dependent response to an external field or the action of forces independent of the internal effect.

Types of size effects

The study of internal dimensional effects is aimed on the studying of:

- ✔ The electronic and structural properties of clusters,
- ✔ The effect on chemical activity, the ionization potential, the binding energy between atoms in a particle and between particles, and
- ✔ The crystallographic structure.

The melting point as a function of the particle size and its geometry.

- Thermodynamic representations

$$T_b - T_m = \left[\frac{2T_b}{\Delta H \, \rho_s \, r_s}\right]\left[\gamma_s - \gamma_l\left(\frac{\rho_s}{\rho_l}\right)^{\frac{2}{3}}\right]$$

- System dimensions are infinite.
- Equilibrium and perfect crystals.

Where:

- r_s is the radius of the particle,
- ΔH is the molar latent heat of fusion,
- Y is the surface energy,
- ρ is the density.

The melting point as a function of the particle size and its geometry.

- Vibrations of atoms: Lindemann criteria.

$$[illegible] = \frac{[illegible]}{[illegible]} \qquad 2 \le \alpha \le 4$$

Where:

δ_S: are atoms on the surface,

δv : atoms inside the nanoparticle.

The melting point as a function of the particle size and its geometry.

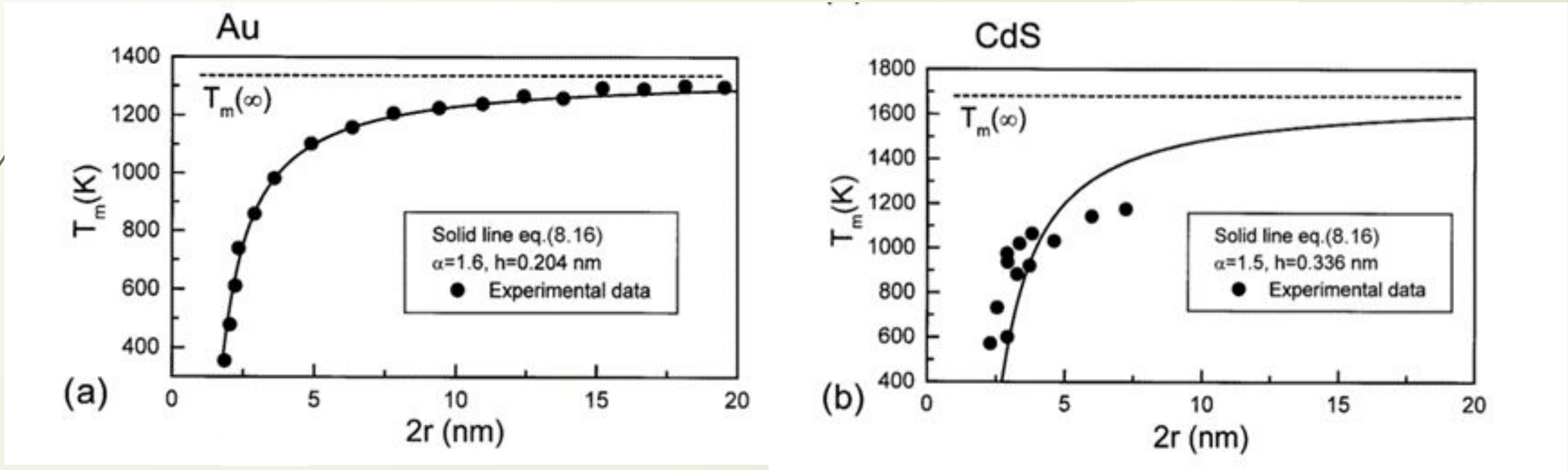
- Vibrations of atoms: Lindemann criteria.

$$\frac{T_m(r)}{T_m(\infty)} = \exp\left[-(\alpha - 1)\left(\frac{r}{3h} - 1\right)^{-1}\right]$$

Where:
- Tm (r) and Tm (∞) are the melting points of a nanocrystal and a compact metal,
- h the height of the monolayer of atoms in the crystal structure,
- r is the size of the nanoparticle.

The melting point as a function of the particle size and its geometry.

- Vibrations of atoms: Lindemann criteria.



Control questions

1. What are the main factors that influence in the properties of nanomaterials?.
2. Mention the steps of nanostructures formation.
3. Why is important the particle size.
4. Explain the behavior of the mechanical properties with decreasing of size in nanostructured materials.
5. Describe the size effect on the melting point of nanostructured materials.
6. Analyze the models that explain the dependence of melting point on the size of metallic nanoparticles.

THANK YOU FOR YOUR ATTENTION!