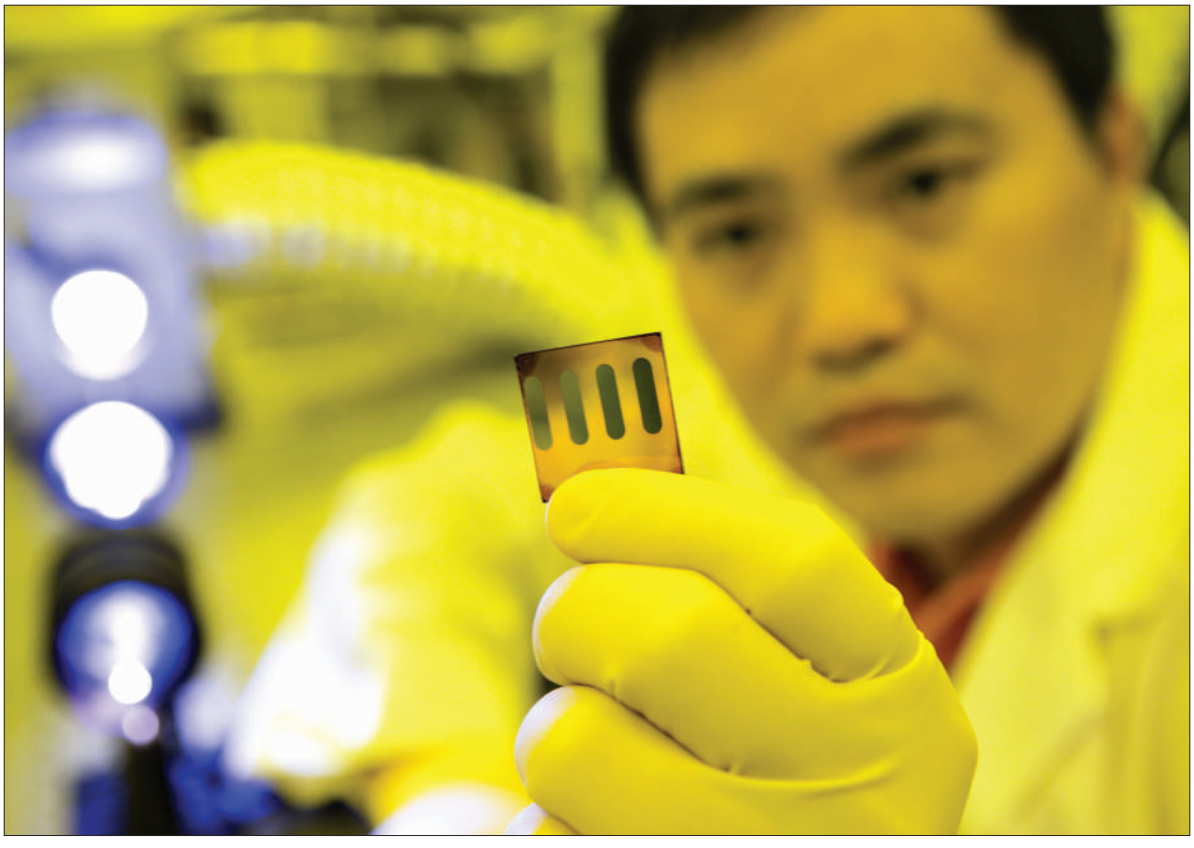

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Research Article
Determination of the Modulus of Elasticity from Size Factor and Temperature

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Abstract

Background and Objective: The study of elastic moduli (bulk or nanoscale) of materials in extreme conditions is a complex and volumetric task requiring separate consideration. Therefore, the need arose for a universal method that allows one to study the elastic properties of materials using first-principle methods. A method was proposed in this study for estimating the energy of the samples external surfaces and for taking into account their influence on the internal state of the electron-ion system. **Materials and Methods:** The temperature dependences of the elastic moduli of materials (metals, high-entropy alloy, ceramic materials, borides, nitrides, dielectrics and eutectic systems, etc.) are calculated from the first principles and analytically presented with taking into account the size factor. The dependence of the elastic moduli on temperature and size, for single-phase samples, are described by the same law in the form of two factors that separately depend on the temperature and size of the material. **Results:** With increasing temperature, as well as reducing the size of the sample, the elastic moduli decrease. **Conclusion:** The constants, included in these formulas, depend on the basic parameters of bulk materials. The calculated values of the melting temperature of nanoplates (single-phase and two-phase) are consistent with experimental data.

Key words: Energy of the electron-ion system, pseudopotential, nanoplate, surface energy, nanoscale materials

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INTRODUCTION

When calculating the stiffness and strength of various structures, to assess the residual stresses, fatigue strength, wear resistance and other operational properties of materials, knowledge of the values of their elastic constants is required. One of the main requirements for composites, the products of which are used in extreme operating conditions in internal combustion engines, gas pipes, aircraft jet engines-is their performance at high temperatures.

For reliable estimation of the stress-strain state of working blades based on Ni_3Al and TiAl intermetallic compounds, there is no information on the temperature dependence of the elastic modulus of materials[1].

From the works of a computational experiment concerning borides where, using the theory of the density functional, the bulk modulus and anisotropic elastic constants for TiB_2 were calculated[2,3]. But, these studies do not consider the dependence of mechanical characteristics on temperature for transition metal borides and even more so for LaB_6-M e B_2 systems. This is due to the complexity of accounting for the thermal part of the energy of the system. With increasing temperature, the thermal vibrations of atoms do not obey the harmonic approximation.

Taking into account non-harmonic terms is a rather complicated task in the framework of quantum-mechanical calculations, but the question of the dependence of mechanical characteristics on temperature remains relevant. As for the estimation of the elastic modulus of nanoscale materials, there are opposite data.

A method for determining the elastic modulus of a material of micro and nanoparticles based on an interconnected analysis of the results of experimental indentation and numerical computer simulation was proposed[4].

A review of methods for determining the mechanical properties of nanostructures is presented by Shushkov and Vakhrushev[5]. Some authors showed a tendency to increase the elastic modulus with a decrease in size. However, there are opposite results as well[6-10]. In view of the fact that the results are ambiguous and sometimes contradictory, this study aimed to evaluate the temperature dependence of the elastic modulus on the size of nanostructures and to develop a generalized, accurate method for determining the elastic properties of nanomaterials and nanoparticles.

MATERIALS AND METHODS

The purpose of the work is to study the temperature dependence of the elastic modulus taking into account the size factor based on the first principles computational experiment (a priori pseudopotential method) for a different class of materials[11].

The method of "a priori pseudopotential" (authoring) was tested on different materials to calculate the basic parameters, the value of which is consistent with the experiment (maximum error 5-7%)[12,13]. The basic parameters include the following: type of crystal lattice, lattice parameters, elastic moduli (volumetric, linear), characteristic parameters (concentration and temperature at the eutectic point) of quasibinary eutectics (based on carbides, borides, nitrides, semiconductors and metals, etc.), theoretical strength, etc.

The work is a theoretical study in the field of solid state physics, performed at the Frantsevich Institute of Materials Science of the National Academy of Sciences of Ukraine in the Department of "Mathematical Modeling in Materials Science" for 2018-2019 as part of the thematic plans

THEORY AND CALCULATION METHODS

It is believed that the surface energy of a nanoparticle plays a major role in changing its physical and mechanical properties. For bulk samples, the fraction of surface energy is small compared to volumetric energy, therefore, it can be neglected and for sufficiently small particles the values of these energies are comparable.

The presence of an external surface leads to an increase in the total energy of the electron-ion system of crystals. Therefore, in the transition from bulk crystals to nanocrystals, it is first of all necessary to estimate the size of the contribution of the energy of the external surface compared to the energy of the bulk.

Previously, it was developed a method for taking into account the influence of the size factor on the physical properties of nanoparticles with a diamond-like structure[14,15], based on the interaction energy of close-packed atomic planes[16].

Strength characteristics will be determined through the energy of the electron-ion system per one-unit cell. This approach is successful when calculating the energy of carbides, borides of transition metals[17].

FORMULATION OF THE PROBLEM

The problem is solved in following stages:

- Assessment of the energy of the outer surface of a nanoscale material and its effect on the internal state of the electron-ion system
- Calculation of physical characteristics taking into account the dimensional factor

- The influence of the dimensional factor on the temperature dependence of physical characteristics:

  - Metals, multi-element metal equiatomic alloys (HEAs), ceramic materials, carbides, borides, nitrides
  - Quasibinary eutectic systems based on carbides, borides, metals and dielectrics etc

Energy of the outer surface and its influence on electron-ion system of nanoplate: In the ideal case (a sample of material that is infinite along the three coordinate axes), let the energy per unit cell be Φ_0. The energy of the electron-ion system Φ_0 is calculated by using the pseudopotential method. For a material whose size is limited by at least one coordinate, when calculating the energy of a unit cell, the energy of external surfaces must also be taken into account. In the case of a nanoplate, there are 2 closing (atomic) surfaces.

A semi-infinite sample is considered in which the free surface coincides with the basal plane of the plate.

The main thing in calculating the physical characteristics of nanoparticles in the form of a nanoplate is the assumption that the outer surfaces of the nanoparticles have energy $\Phi_1/2$ (the surface of the nanoparticle has positive energy), where, Φ_1 is the energy of the electron-ion system per atomic plane parallel to the surface of the plate in the unit cell.

As an example, let us consider LaB_6 and MeB_2 nanocrystals, where is one "representative element" of LaB_6 or MeB_2 (Me-are transition metals of the IV-VI group) per unit cell. In this case, the energy of the outer surface can be determined based on the total energy of the electron-ion system of the unit cell. It distributed the total energy of the electron-ion system per one unit cell evenly along the faces. For MeB_2, the total face are will be:

$$S = 4 \cdot a \cdot c. + 2a^2 \cdot \sqrt{3}$$

Then for the energy density along the outer surface of the cell we have:

$$\rho = \Phi_0 \frac{MeB_2}{4 \cdot a \cdot c. + 2a^2 \cdot \sqrt{3}} \quad (1)$$

where, Φ_0 (MEB_2) is the energy of the electron-ion system of one MeB_2 cell, a and c are the parameters of the hexagonal lattice. The surface energy per basal planes will be:

$$\Phi_1 = S_1 \rho = a^2 \sqrt{3} \cdot \rho$$

In the case of crystals with a cubic structure (LaB_6), the energy per area of one face is (a_0 is the lattice parameter):

$$\Phi_1 = S_1 \ \rho = a_0^2 \cdot \rho, \ \rho = \Phi_0 \frac{LaB_6}{6 \cdot a_0^2} \quad (2)$$

In those cases when the "representative element" is an atom, the energy of the electron-ion system of the atom must be multiplied by the number of atoms of the unit cell.

The energy of the electron-ion system of one-unit cell inside the crystal always has a negative sign, the surface energy has a negative sign with respect to an infinitely distant point and is positive in comparison with the energy inside the crystal. The influence of the external surface on the internal states of ions and electrons is estimated by averaging the energy of neighbouring unit cells.

To estimate the energy of a nanocrystal, use the averaging technique to estimate the energy of crystals having close-packed atomic planes[14,15], only with the difference that energy is averaged over two neighbouring cells and not over atomic planes.

To determine the energy of a unit cell in the presence of a free surface, the following averaging over 2 neighbouring cells is proposed. Consider a nanoplate having a limited size in thickness.

Let, the energy in the 0th order be equal Φ_o for the first and second cells and the free surface has energy ($-\Phi_1/2$). The energy of the first cell is defined as the arithmetic mean:

$$\Phi_I = \frac{1}{2}(\Phi_0 + \Phi_0 - \frac{\Phi_1}{2}) = \Phi_0 - \frac{\Phi_1}{2^2} \quad (3)$$

For the 2nd cell, the energy is determined based on the specified value of the energy of the 1st cell:

$$\Phi_{II} = \frac{1}{2}(\Phi_I + \Phi_0) = \Phi_0 - \frac{\Phi_1}{2^3} \quad (4)$$

And for the ith cell:

$$\Phi_i = \Phi_0 - \frac{\Phi_1}{2^{i+1}} \quad (5)$$

Thus, the distribution of surface energy in the cells is obtained depending on the distance from the outer surface (implicitly expressed in the unit cell number).

If the object has a limited size along the spatial axis z, then the influence of the energy of the second free surface must be taken into account. Let, this surface have energy ($-\Phi_1/2$). The

method for calculating the energy distribution of unit cells, taking into account the 2nd external surface is the same as for the first. As a result, it turns out for the ith unit cell:

$$\Phi_i = \Phi_0 - \Phi_1 \frac{1}{2^{i+1}} - \Phi_2 \frac{1}{2^{j+2-i}} - \frac{1}{j \cdot 2^{j+1}}(\Phi_1 + \Phi_2) \quad (6)$$

where, j is the number of unit cells in the nanoparticle along the z-axis.

Believing that: $\Phi_1 = \Phi_2 = K^{*p}\,\Phi_0$, we get:

$$\Phi_i = \Phi_0 - K_P^*\,\Phi_0 \frac{1}{2^{i+1}} - K_P^*\,\Phi_0 \frac{1}{2^{j+2-i}} - K_P^* \frac{1}{j \cdot 2^j}\Phi_0 \quad (7)$$

K_P is a coefficient which depends on the unit cell parameters of the material.

The last term in Eq. 7 provides the law of conservation of the total energy of the system with a limited number of unit cells along the z-axis.

To determine the average energy of the nanoplate, it is summarized in Eq. 7 for all unit cells along the z-axis and divided by the number of unit cells j.

The result for a nanoplate with an infinite basal plane:

$$\bar{\Phi} \approx \Phi_0 (1 - \frac{K_P^*}{j}) \quad (8)$$

The number of layers is j = d/c, where, d is the thickness of the nanoplate, c is the unit cell parameter along the z-axis (for LaB_6, the lattice parameter is a_0 for MeB_2, c).

As a result, for the average energy of the electron-ion system of a nanoplate with a thickness d, obtained data is:

$$\Phi_P = \Phi_0 (1 - \frac{K_P}{d}) \quad (9)$$

where, Φ_0 is the energy of the electron-ionic system of the elementary lattice of a bulk crystal, $K_p = K_P^*.c$.

In the case of a nanoparticle, the form of an infinitely nanobar or a limited nanobar, the average energy of the electron-ion system is determined by the same formula in Eq. 9, but with different coefficients K_S (infinite nanobar) and K_Ω (limited nanobar), which depend on the crystal lattice parameters of the nanoparticle.

Given that the linear elastic modulus is determined through the 2nd derivatives of the energy of the electron-ion system with respect to the lattice parameter and the derivatives with respect to the lattice parameter of $1\text{-}K_P/d$ are equal to 0, it turns out:

$$E_d = E_0 (1\text{-}K_p.d^{-1}) \quad (10)$$

where, E_0 is the elastic modulus of the bulk material at T = 0K.

Temperature dependence of physical characteristics: The second part of the problem is the study of the temperature dependence of the elastic moduli of a nanocrystal.

To identify the dependence of mechanical characteristics on temperature, it is necessary to calculate the energy values of the electron-ion system of the materials at different temperatures. In the framework of the pseudopotential method, this means finding the change in the volume of unit cells of crystals at temperatures other than 0, i.e., to obtain an explicit dependence of the total energy on the lattice or volume parameters at a non-zero temperature.

With increasing temperature, the thermal vibrations of atoms cease to obey the harmonic approximation. The developed model[17-19] within the framework of quantum mechanical calculations makes it possible to study the effect of high temperatures on the tensile strength of borides and eutectic systems.

To take into account the non-harmonic terms in the total energy of the electron-ion system of materials must use the quasi-harmonic approximation method[19], the essence of which is as follows:

- The minimum energy U (Ω) of the electron-ion system determines the lattice volume (Ω) in the equilibrium state of the crystal
- The total energy $U^* = U_0 + U_T$ of the system is calculated at non-zero temperatures ($T \neq 0$). The average value of thermal energy associated with lattice vibrations is determined by the ratio:

$$U_T = \sum_q \frac{\hbar\omega_q}{\exp\frac{\hbar\omega_q}{kT} - 1}$$

  where, the summation is over all types of oscillations and ω_q is the oscillation frequency (according to the Einstein model $\omega_q = \omega$ for all q). The oscillation frequency is determined through force constants using the pseudopotential method[18,19]
- The new value of the volume of the crystal lattice is determined from the equation:

$$U^*_{min}(\Omega_0, T) = U(\Omega_1)$$

As a result, the temperature dependence of the unit cell volume is obtained.

For each volume value (corresponding to a given temperature), the energy of the electron-ion system is calculated. Using standard methods[20], stresses and elastic moduli are calculated.

As a result of these calculations, the dependence of the relative values of the elastic moduli on temperature for all the materials under study was obtained by using the following[11]:

$$\frac{E(T)}{E_0} = 1 - 0.2 \cdot \frac{T}{T_{max}} - 0.25 \cdot \left(\frac{T}{T_{max}}\right)^2 \quad (11)$$

T_{max} is the melting temperature of the bulk material. For a nanoparticle with size d, the elastic moduli are determined from the relation:

$$E_d(T_i) = E(T_i) \cdot (1 - (K_p \cdot d^{-1})_{T=T_i})$$

Coefficient K_p linearly depends on the crystal lattice parameters (a, c) and if it assumed that the nanoparticle expands uniformly with increasing temperature, then:

$$\left(\frac{K_P}{d}\right)_{T=T_i} = \left(\frac{K_P}{d}\right)_{T=0}$$

It follows that the temperature dependence of the elastic modulus of nanoparticles can be estimated from the relation:

$$E_d(T) = E_0 \cdot (1 - K_P \cdot d^{-1}) \cdot 1 - 0.2 \cdot \left(\frac{T}{(T_d)_{max}} - 0.25 \cdot \frac{T}{(T_d)_{max}}\right)^2 \quad (12)$$

where, $(T_d)_{max}$ is the melting temperature of a nanoparticle with a linear size d.

From the standpoint of thermodynamics, the transition from a solid to a liquid state, with an increase in temperature, begins with the appearance on the surface of an infinitely small liquid layer, when the inside remains solid. From the Gibbs-Tolman-Koenig-Buff equation, where the curved surface of the condensed phase is considered, it can obtain the relation for estimating the melting temperature of a nanoparticle (with radius R)[21]:

$$T_{max}(R) = T_{max} \exp\left(\frac{-4\delta}{\delta + 2R}\right) \quad (13)$$

where, R is the radius of the nanoparticle, δ is the Tolman constant, equal in order of magnitude to the thickness of the surface layer ($R >> \delta$).

In the case of a nanoplate, the melting temperature is estimated by the formula:

$$T_{max}(d) = T_{max} \exp\frac{-4c}{c+d} \quad (14)$$

Using Eq. 14 to estimate the melting temperature of a gold nanoplate with a thickness of d = 10 nm, leads to the value $T_{max}(d) = 1136$ K, which is 36 K higher than the melting temperature of gold nanoparticles with a radius of R = 5 nm[21].

This discrepancy has a simple physical explanation. A nanoplate having nanoscale only in thickness has physical characteristics closer to bulk materials than nanoparticles (having nanoscale in 3 directions)[14].

The basic formula for assessing the influence of the size factor on the temperature dependence of the Young's modulus is:

$$E_d(T) = E_0 \cdot (1 - K_P \cdot d^{-1}) \cdot \left(1 - 0.2 \cdot \frac{T}{T(d)} - 0.25 \cdot \frac{T}{T(d)}\right)^2 \quad (15)$$

Where:

$$T(d) = T_{max} \exp\left(\frac{-4c}{c+d}\right) \quad (16)$$

where, E_0 and T_{max} are Young's modulus and the melting temperature of bulk material (metals, HEAs, dielectrics, semiconductors, borides, carbides and nitrides, etc.).

The K_P coefficient is determined from the type and lattice parameters of the material. For a cubic lattice (with parameter a) $K_P = a/6$, in the case of a hexagonal lattice (with parameters a and c) $K_P = c \bullet a^2\sqrt{3}/(a \bullet c + 2a^2\sqrt{3})$.

Small-scale eutectic systems: When passing to eutectic systems with a limited size, it is necessary to take into account that in this case not only the melting temperature of the eutectic changes, but also the concentration of the components depending on the size of the object[22].

In contrast to the above materials for eutectic systems (for example, LaB_6-MeB_2), when the size factor is taken into account, the melting temperature is estimated based on the interfacial interaction energy taking into account the presence of an external boundary-the junction of two components forming a nanoplate, which has a volume $\Omega_{AB} = C_E \Omega_A + (1-C_E) \Omega_B$, C_E is the eutectic concentration for bulk materials and the unit cell volumes of the components is Ω_A and Ω_B, respectively. If we assign a cubic structure with parameter a_v to a virtual cell, then we can write:

$$\Omega_{AB} = a_v^3,\ a_v = \left[0,5(a_0^3 C_E + (1-C_E)a^2 c\sqrt{3})\right]^{1/3} \quad (17)$$

After determining the energy of the area of one face, it can obtained the final formulas for the energy of interaction of representative elements, taking into account the size factor:

$$\begin{aligned} \bar{U}_{AA} &= U^0_{AA}(1-K_{AA}\cdot d^{-1}) \\ \bar{U}_{BB} &= U^0_{BB}(1-K_{BB}\cdot d^{-1}) \\ U_{AB} &= U^0_{AB}(1-K_{AB}\cdot d^{-1}) \end{aligned} \quad (18)$$

With coefficients:

$$K_{AA} = \frac{a_0}{6},\ K_{BB} = \frac{c\cdot a^2\sqrt{3}}{4\cdot a\cdot c + 2a^2\cdot\sqrt{3}},\ K_{AB} = 0,072\,a_v \quad (19)$$

By using Eq. 18 and 19, we obtain:

$$U^0_{AA} = \Phi_0,\ K_{AA} = K_P$$

Also, applies to the coefficients and the interaction energy of component B and the energy of inter-component interaction between A and B.

The method for calculating the eutectic concentration and temperature for small-scale eutectic systems is the same as for bulk materials, but only with new values of the interaction energy between the representative elements of the components (Eq. 18). In relation (Eq. 18), an increase in the mean square displacement of atoms at small sizes and a decrease in the Debye temperature are taken into account in implicit form. Based on the results of calculations by using the approximating function, relations are derived that describe the relationship between the concentration and temperature of the eutectic on the plate size of two-component composites[22]:

$$C_E(d) = (1-0.05\exp(\frac{-0.01d}{r_B}))\cdot C_E^0 \quad (20)$$

$$T_E(d) = (1-0.26\exp(\frac{-0.01d}{r_B}))\cdot T_E^0 \quad (21)$$

where, r_B = 0,0529 nm (Bohr radius), C_E (d), T_E (d) are the eutectic concentration and temperature for the composite with thickness d and C_{E0}, T_{E0} are the corresponding values for bulk composites.

It follows from Eq. 21 that at d = 4 nm, the melting temperature of the eutectic composition of the Au-Ge system is T_E (d)≈579 K (for bulk material T_E = 634 K) and C_E (d) = 0,9965 C_E^0. Those, a change in concentration with a change in the thickness of the plate is small and can be neglected[23].

A decrease in the size of the composite leads to an increase in the concentration fraction of the strengthening phase and to a decrease in the eutectic temperature. The course of the relative change in the eutectic concentration and temperature versus the size of the composite is the same for different two-component systems.

Temperature dependence of the elastic modulus of nanoscale eutectic systems: In order to derive the temperature dependence of the elastic modulus of eutectic systems taking into account the size factor, the following step-by-step approach to solving the problem is needed:

- The calculation of the elastic modulus of the bulk composite at T = 0K

  The calculation of the physical characteristics of eutectic systems, taking into account the insolubility of the components, leads to the calculation of the corresponding characteristics of the components. To assess the elastic moduli of a eutectic system, it is perfectly acceptable to use the mixture rule:

$$E_{0\,K,} = \delta_A E_{0,A} + \delta_B E_{0,B} \quad (22)$$

  where, $E_{0,A}$, δ_A and $E_{0,B}$, δ_B are the elastic moduli and volume fractions of the A and B components in the bulk material. Volume fractions are directly related to component concentrations[18]
- Calculation of the elastic modulus of a composite having a limited size in one direction (nanoplate) at T = 0K

  It is assumed that the outer surfaces of the plate coincide with the basal plane MeB_2 and the (001) LaB_6 plane.

  The components in the alloy do not dissolve and retain their structure.

  The elastic modulus of the nanoplate, taking into account changes in the eutectic concentration, will be:

$$E_K(d) = \delta_A(d)\,E_A(d) + \delta_B(d)\,E_B(d) \quad (23)$$

  Where:

$$E_A(d) = (\frac{1-K_{AA}}{d})E_{0,A},\ E_B(d) = (\frac{1-K_{BB}}{d})E_{0,B} \quad (24)$$

For LaB_6-MeB_2 (Me-Ti, Zr, Hf) systems, the $K_{AA} \approx K_{BB}$ and then the elastic modulus of the nanoplate at T = 0 K is determined from the following relation:

$$E_{K,d} \approx \frac{1-K_{BB}}{d} \cdot E_{0,K} \quad (25)$$

- The temperature dependence of the elastic modulus of small-sized eutectic systems is determined from the relation:

$$E_{K,d}(T) = E_{K,d} \cdot \frac{1-0.2 \cdot T}{T_E(d)-0} 0.25 \cdot \frac{T}{T_E(d)^2} \quad (26)$$

Or taking into account the ratio by using Eq. 25:

$$E_{K,d}(T) \approx \frac{1-K_{BB}}{d} \cdot E_{0,K} \frac{\cdot 1-0.2 \cdot T}{T_E(d)} - 0.25 \cdot (\frac{T}{T_E(d)})^2 \quad (27)$$

The melting temperature of the $T_E(d)$ is determined by the Eq. 21

RESULTS AND DISCUSSION

Using Eq. 16 and 21, one can calculate the melting temperature of a nanoplate depending on its thickness for the eutectic system.

The calculated results are presented in Table 1. For some materials, basic parameters are also given (type and parameters of crystal lattices and elastic moduli calculated from first principles) as well as experimental values of the melting temperature of the components that make up the eutectic.

Figure 1 and 2 showed the temperature dependences of the normalized Young's modulus $E/E_{T=0}$ on the temperature and size of the materials.

Compared to single-phase objects, in eutectics with decreasing plate size, the melting temperature and the elastic moduli decrease significantly. In two-phase systems, a decrease in the size of an object enhances the influence of external surfaces on the interphase boundaries and weakens their bonds, which explained the low values of the melting temperature of the nanoplate and the elastic modulus by increasing the total energy of the electron-ion system.

In the studies on the dependence of the elastic modulus on the size factor, there are plenty of opposite data. In some studies (experimental and theoretical), data were obtained on the growth of the elastic modulus with decreasing sample size[6-8].

The obtained results for the larger nanostructures fairly agreed to the values reported in the literature for the macroscopic elastic modulus of the corresponding materials[7].

The authors[26] argued that the method also gives the correct results for smaller sizes, when it is known that measuring the characteristics of nanoparticles with small sizes is difficult to solve.

In studies based on simple theoretical models[6,8] for TiO_2, Si, Ag, Au and Cu and Si, Ge, an increase in the elastic moduli with a decrease in the size of the nanoparticles was obtained. In previous study[9,10], a decrease in Young's modulus with a decrease in particle size is observed.

In the work[9], the presented dependence of the elastic moduli on the shape and size of nanoparticles (Al, Cu, Pd, Pt) with sizes less than 30 nm is completely identical to the previously obtained dependence of theoretical strength on the shape and size of diamond-like nanoparticles[14,27]. In works[14,27], a decrease in the theoretical strength of diamond-like materials with a decrease in their size was proved. This result does not contradict physical laws, since we are dealing with theoretical strength, which is the maximum value for a given material with an ideal structure.

The presented approaches and methods in favor of the work are also supported by the consistency of calculated and experimental data on the melting temperature of nanoplates (single-phase and two-phase).

The developed methods for the temperature dependence of the strength characteristics for borides, carbides and

Table 1: Basic parameters of materials are a, c (lattice parameters), T_{max} and T(d) (melting temperature of bulk materials and nanomaterials), E_0 and E_d (Young's modulus of bulk materials and nanomaterials)

Parameters	Crystal cell	(a, c) nm	T_{max}, K	T(d), K d = 10	T(d), K d = 5	E_0, GPa	E_d, GPa d = 10	E_d, GPa d = 5
NiCoCrFe	fcc	0.3561	1861	1622,9	1426,3	216,61	210,81	205,60
AlNiCoCrFe	bcc	0.2890	1675	1497,5	1346,6	187,23	185,08	183,12
LaB_6	CaB_6	0.4177	2800	2385	2056	495,64	474,82	454,00
TiB_2	hex	0.301,0.3245	3280	2881	2535	587,08	582,70	578,19

T_{max}, K[24,25]

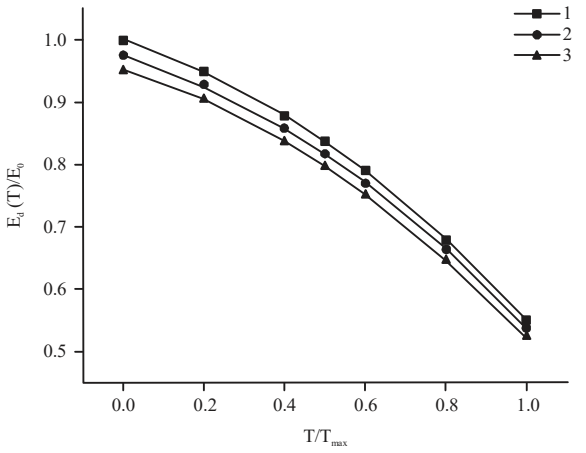

Fig. 1: Dependence of the normalized Young's modulus E_d (T)/E_0 on T/T_{max} (d) for different values of the plate thickness *d* for high-entropy alloy NiCoCrFe

(1) for a bulk material (the thickness tends to infinity), (2) d = 10 nm and (3) d = 5 nm. (E_0 is the modulus of elasticity of the bulk material at T = 0 K, T_{max} (d) is the melting temperature of the plate, depending on the size of its thickness)

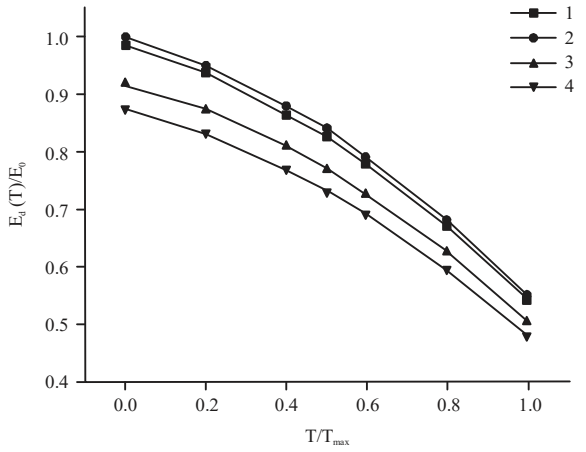

Fig. 2: Dependence of the normalized Young's modulus E_d (T)/E_0on T/T_{max} (d) for different values of the plate thickness d for

(1) bulk LaB_6 material, (2) LaB_6 nanoplates with a thickness d = 5 nm, (3) for the LaB_6-TiB_2 system with thickness d = 10 nm and (4) LaB_6-TiB_2 with thickness d = 5 nm

eutectic systems are also successfully used for metals, where the calculated and experimental data coincide[28].

In the transition from bulk materials to nanoparticles, its external surfaces become the main defects. Atoms on the surface are weakly interconnected and have positive energy compared to the energies of internal atoms. On average, this leads to a noticeable increase in the electron-ion system, i.e., to a decrease in the bond strength of atoms, if only the number of external atoms is comparable to the number of internal atoms. In this case, the theoretical strength and elastic moduli decrease.

CONCLUSION

Elastic characteristics are not structurally sensitive as strength, which means that from the first principles, the calculated elastic moduli are characteristics of real (i.e., defective) materials.

With a decrease in the grain size in the materials, the movement of the dislocation becomes more complicated, which leads to an increase in the yield strength, hardness, but not the elastic modulus.

The obtained analytical formulas have significant practical value.

These formulas make it possible to obtain the elastic modulus of different materials (metals, HEAs, semiconductors, dielectrics, borides, carbides, nitrides and eutectic quasi-binary composites based on metals, carbides and borides, etc.) depending on the temperature and size of the plate thickness, at the presence of basic parameters of the bulk materials under study (lattice parameter and elastic modulus).

SIGNIFICANCE STATEMENT

Representation of the dependence of the elastic modulus on the crystal temperature in form E (T)/E_0 as a function of temperature ratio (T_{max}/T) removes the need to clarify the crystallographic directions of the elastic moduli. The temperature dependence of the normalized elastic modulus is the same for different materials and in different crystallographic directions.

The implementation of the developed methodology for determining the temperature dependence of the elastic modulus taking into account the dimensional factor of materials does not depend on the type of pseudopotential applied. To calculate the total energy of the electron-ion system, any pseudopotential (or the corresponding software package) that adequately describes the electron-ion interaction in the material can be used.

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