INFLUENCE OF DISPERSION ON LOCAL PHYSICAL, MAGNETIC AND THERMODYNAMIC PROPERTIES OF BCC Fe AND ITS BINARY ALLOYS

A. Udovsky
Baikov Institute of metallurgy and Materials Science of RAS, Moscow, Russia
udovsky@imet.ac.ru

The results of quantum mechanical calculations of the total binding energy and the mean magnetic moment (MMM) as a function of the volume of the bcc Fe are analyzed. To take into account the anisotropy of the spin density, the concepts of the partial magnetic moments (PMM) of atoms for pure Fe located in different crystallographic directions on 1\(\rightarrow\)4 coordination spheres (CS) are introduced. Within the framework of this model, the relationship between PMM and static displacements (SD) of Fe atoms located around the impurity atom in binary bcc- metal alloys of the Fe- (Cr, V, Mo, W) systems with a dimensional factor (DF) is established.

The presence of DF leads to the appearance of local pressures, which lower the PMM and MMM of the matrix atoms. It is obvious that the relaxation of SD of Fe atoms located in the 1–3 CS relative to the impurity atom in the vicinity of the small-angular boundary (SAB) occurs in the space of the small-angular boundary (SAB) of the grain.

With a considerable dispersion of the matrix, the number of "surface" atoms can be comparable to the number of atoms located in the core of the sub-grain. Assuming the conjugacy of the crystal lattices formed by the "surface" atoms and the core atoms, it is possible to introduce the concepts of the surface (quasi-two-dimensional) and bulk phases, interpreting their appearance as a "stratification" of the general phase.

This allows us to use the thermodynamic relationship for the heat capacity \(C_p\) of a two-phase ("surface" and bulk) system taking into account the "frozen" kinetics in the measurement of \(C_p(T)\) in the interval from zero to \(T<\theta_B\). Measurement processing \(C_p(T)\) it is possible to calculate the Debye temperatures, elastic moduli, PMM, and MMM atoms for both the surface and bulk phases.

**Keywords**: Ferritic steels, magnetism, stability bcc -Fe, dispersion, thermodynamic approach, "surface" and "bulk" phases, static atomic displacements, partial magnetic moments, local Debye temperature.

**Introduction**

Comparison, first, of the diffusion properties as a function of the ferrite temperature (alloy F82H = Fe + 8CrTaV) and austenitic steels and,
secondly, induced normalized radioactivity as a function of the residence
time for various pure chemical elements under the action of the neutron
flux spectrum after a stoppage reactor shows at elevated temperatures (0.5
$T$ melt) significant advantages of ferritic steels (1).

So, for example, the holding time to a significant (by 10-11 orders)
decrease in the induced activity for nickel is more than 100 years, for
chromium a little more than 2 years, and for Fe – about 20 years.

The base alloys for the fuel cell shells of the 4th generation reactors
are Cr solutions in the bcc phase of the Fe. In recent decades, to increase
the strength during the operation of ferritic alloys at high temperatures,
the steel has been alloyed additionally with molybdenum and / or
tungsten, and dispersed particles of oxides have been introduced to
prevent the growth of ferrite grain.

As follows from the analysis of the data shown in Fig. 1, at a
temperature of 1000 K, the Gibbs energy of formation ($\Delta G_f$) of yttrium
and zirconium oxides is an order of magnitude higher than $\Delta G_f$ of
chromium nitride $\Delta G_f$(CrN,1000K) $\approx$ –40 kJ/atom, already on smaller
values of the enthalpy of formation of chromium carbides $\Delta H_f$(Cr$_{23}$C$_6$) =
$-11.86$ kJ/atom, $\Delta H_f$(Cr$_7$C$_3$) = $-14.4$ kJ/atom (3) and the enthalpy of meta-
stable cementite formation $\Delta H_f$(Fe$_3$C) = $+21.7$ kJ/atom.

Thus, the thermodynamic stability of oxides is 10-20 times greater
than that of carbides iron and chromium nitrides.

Although the question of the chemical compatibility of zirconia
with the bcc – phase of Fe has in principle been solved to a certain extent
(6), nevertheless the question as to how much the dispersion of ZrO$_2$
affects the phase equilibrium remains open.
Fig. 1. Gibbs energy of formation of oxides and nitrides as a function of temperature (2).

Moreover, the nature of the behavior of nanoparticles and the nature of their contact between the crystal lattice and the interaction with the crystal lattice of the matrix is also not clear. This is due, in particular, to the complex behavior and nature of the stability of the fluorite phase of the $\text{ZrO}_2$ in the presence of anion vacancies in its crystal lattice and the possible dissolution of iron atoms in the cation sub-lattice of the fluorite phase. The latter leads to an increase in the number of oxygen structural vacancies in the presence of atoms of different valences in the cation sub-lattice. Therefore, the purpose of this paper is to elucidate the effect of dispersion on the behavior of the crystal lattice of the ferrite matrix, i.e. Fe-bcc base solutions of the Fe- (Cr, V, Mo, W) systems.

The relationship between magnetism and the structural properties of bcc-phase of the Fe

Ever since the times of C. Zener and R. Weiss, it is known that magnetism stabilizes the bcc lattice of Fe more loosely in comparison with the fcc lattice. In the last 20 years, this has been confirmed by numerous quantum-mechanical calculations.

Fig. 2 shows the results of calculations performed by Kabliman using the WIEN2K package, the dependences of the total binding energy and the mean magnetic moment as a function of the atomic volume for the ferromagnetic (FM) bcc phase of the Fe. The results obtained
demonstrate a sharp increase in the mean magnetic moment of iron atoms with increasing volume, and consequently, of inter-atomic distances, relative to the equilibrium value of the volume.

Fig. 2. Dependence of the total binding energy (triangles) and the mean magnetic moment (circles) as a function of the atomic volume for the ferromagnetic bcc phase FM-Fe.

It should be taken into account that the distribution of the spin density in the real space of the osc lattice of iron is a tensor characteristic. This is evidenced by the results obtained by Nobel laureate Clifford Shull (4), from the experimental data on the scattering of polarized neutrons (Fig. 3) and processed by applying the inverse Fourier transform, which are represented on the plane of type (100) – the left part of Fig. 3 and plane constructed on the vectors [100] and [110] of the unit cell—the right-hand side of Fig. 3. The Fig. 4 helps to understand on which fragments of crystallographic planes the bcc crystal lattice represents a
family of spin-density cross sections in Fig. 3. The asymmetry of the contour lines of the spin density – Fig. 3 shows that the 3d electron density is distributed asymmetrically around the ion skeletons of the Fe atoms.

In order to reflect to some extent the tensor character of the spin density, in work (5), an expanded cell containing 8 cells of cells and consequently including 16 iron atoms was introduced; secondly, the partial magnetic moments of atoms located relative to the center of the expanded cell on different coordination spheres (CS)

Third, in the same work, a method was developed for calculating the partial magnetic moments (PMM) of atoms. For this purpose, the relative distances in units of the parameter $\text{osc}$ of the lattice were considered: the distances from the center of the extended cell to the atoms located on the first four coordination spheres

$$\rho_1 = R_{111}/a = \sqrt{3}/2; \quad \rho_2 = 1; \quad \rho_3 = \sqrt{2}; \quad \rho_4 = \sqrt{3}$$

(1)

Fig. 3. Distribution of the magnetic moment density obtained from the inverse Fourier transform of the experimental data on the scattering of polarized neutrons on a plane of the (100) type and on the plane constructed on the [001] and [110] cells of the cell. The asymmetry of the contour lines shows that the 3d electron density is distributed asymmetrically around the ion cores of the Fe atoms. The values of the spin density are given in units of $[\mu \text{B/Å}^3]$ from the Landolt_Borstein-Text book (4).

Magnetic moment density distribution obtained from the Fourier inversion of the data of Fig. 3a over (a) the (100) face and (b) the (110) diagonal plane of the Fe unit cell. The asymmetric contour lines show that the 3d electrons are asymmetrically distributed around the Fe nucleus. The values of spin-density are given in units $[\mu \text{B/Å}^3]-(4)$. 

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Fig. 4. The extracted fragment of the crystal lattice, explaining Fig. 3, containing the planes constructed on the vectors <100> and <001>, and on the vectors <001> and <110>.

Using relations (1), a small parameter was obtained

\[ \Delta \rho_{12} = \text{mod}(\rho_1) - \text{mod}(\rho_2) = -0.134 \ll 1 \]  

and expansions in the small parameter \( \Delta \rho_{12} \) of the dependence of the partial magnetic moment with respect to the decomposition point \( \rho_2 \) are carried out.

\[
m(\rho_1 = \rho_2 - \Delta \rho_{12}) \approx m(\rho_2) - \left( \frac{\partial m_2(\rho)}{\partial \rho} \right)_{\rho_2} \Delta \rho_{12} = \]

\[
m(\rho_2) \left[ 1 - \left( \frac{\partial \ln m_2[V(\rho)]}{\partial \ln V} \right)_{V(\rho_2)} \cdot \frac{\partial \ln V}{\partial \ln \rho} \right] \Delta \rho_{12} \approx m(\rho_2) \left[ 1 - 3\Gamma_m[V(\rho_2)] \cdot \Delta \rho_{12} \right]. \]

The transition to the last equation in (3) is due to the introduction in (5) of the partial Grüneisen magnetic parameters, which are equal to (4):

\[ \Gamma_{m_2} = \Gamma_m[V(\rho_2)] = \left( \frac{\partial \ln m_2[V(\rho)]}{\partial \ln V} \right)_{V(\rho_2)}. \]  

The details of the calculations of the remaining partial magnetic moments of atoms located on the first four coordination spheres are
presented in [5], in which the partial magnetic Grüneisen parameters were calculated, which are equal in accordance with relation (4) analogously to atoms located in other coordination spheres

\[ \Gamma_{m,i} = \Gamma_m[V(\rho_i)] = \left( \frac{\partial \ln m_i[V(\rho_i)]}{\partial \ln V} \right)_{V(\rho_i)}, \quad i = 1, 2, 3, 4. \]  

Relations (5) were introduced in (5) by analogy with the definition of the Grüneisen parameter for the Debye temperature, which is equal to the logarithmic derivative with respect to the volume from the logarithm of the Debye temperature. The results of calculations of the partial magnetic moments and the partial Grüneisen magnetic parameters are presented in Table 1.

<table>
<thead>
<tr>
<th>( \rho_i = R_i/a )</th>
<th>( &lt;m_i(\rho_i)&gt; ), ( \mu_B/\text{atom} )</th>
<th>( n_i(\rho_i) )</th>
<th>( V_i )</th>
<th>( \ln[V_i(\rho_i)] )</th>
<th>( \Gamma_m(\rho_i) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_i = 0.865 )</td>
<td>1.7</td>
<td>8</td>
<td>49,8799</td>
<td>3,9096</td>
<td>0.694</td>
</tr>
<tr>
<td>( \rho_i = 1 )</td>
<td>2.2</td>
<td>3</td>
<td>76,7951</td>
<td>4,341</td>
<td>0.71</td>
</tr>
<tr>
<td>( \rho_i = 1.41 )</td>
<td>3.15</td>
<td>3+1=4</td>
<td>217,209</td>
<td>5.381</td>
<td>0.14</td>
</tr>
<tr>
<td>( \rho_i = 1.73 )</td>
<td>3.25</td>
<td>1</td>
<td>399,039</td>
<td>5.989</td>
<td>0.052</td>
</tr>
</tbody>
</table>

**Table 1**

The values of the partial magnetic moments of the Fe atoms located in different coordination spheres, the number of atoms \( n_i(\rho_i) \), the atomic volumes corresponding to different radii of the coordination spheres \( V_i(\rho_i) \), the values of \( \ln[V_i(\rho_i)] \), the values of the magnetic components of the Grüneisen parameter \( \Gamma_m(\rho_i) \) equal to the logarithmic derivative in volume from the logarithms of the partial magnetic moments atoms located on different coordination spheres for the bcc lattice of pure Fe

**Influence of the dimensional factor on magnetism and structural properties of the bcc-phases of the Fe- (Cr, V, Mo, W) systems**

An expanded cell containing 8 bcc cells or 16 atoms in Fig. 5 is considered.

For the ground state of binary alloys Fe- (PM = paramagnetic metal) in (5), the internal mixing energy functional for the expanded cell is constructed.
The dimension factor was taken into account self-consistently by expanding the energies of pair interactions between the atoms of the components located at different CSs in powers of the atomic displacements relative to the nodes of the ideal lattice.

A system of state equations is obtained for ferromagnetic bcc alloys for binary systems in the 1\(\frac{1}{3}\) CS approximation. It is shown that when one atom of an impurity is introduced into an extended cell, the spin density anisotropy in the bcc lattice of pure Fe is responsible for the occurrence of short-range order in bcc-FM alloys rich in Fe in Fe- (Cr, V, Mo, W) systems (5). The magnetic component of the Gibbs free energy functional was described within the framework of the empirical formalism of Inden-Hillert-Jarl (ICD) [8-9], which is widely used for the calculation of phase diagrams within the framework of the CALPHAD method [10].

The magnetic component of the Gibbs energy for the FM bcc phase, Fe, according to [8-10], depending on the mean magnetic moment \(<m>\) and temperature related to the Curie temperature \(\tau = T/T_{C}\), has the form

\[
G_{\text{mag}}(T, <m>) = RT \left\{ \ln [1 + <m>] \right\} g(\tau),
\]

where

\[
g(\tau) = \begin{cases} 
1 - \left[ \frac{79\tau^{-1}}{140p} + \frac{474}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right] / D, \quad \tau \leq 1, \\
\left[ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right] / D, \quad \tau > 1, \quad D = \frac{518}{1125} + \frac{11692}{15975} \left( \frac{1}{p} - 1 \right).
\end{cases}
\]

\(p = 0.40\) or \(D = 1.55828482\) for bcc phase (9).

At \(T = 0\) K, a difference is obtained from (1) between the Gibbs energies between the FM and the paramagnetic phases of the Fe

\[
G_{\text{mag}}(T \to 0, <m>) = R \left\{ \ln [1 + <m>] \right\} \lim_{T \to 0} \left[ T \cdot g(\tau) \right] = -R \left\{ \ln <m> + 1 \right\} \frac{79T_{C}}{140pD},
\]

in particular for the bcc phase of ferromagnetic pure iron we have

\[
G_{\text{mag}}^{\text{Fe}}(T \to 0, <m>) = -R \ln [2.2 + 1] \frac{79 \cdot 1043}{140 \cdot 0.4 \cdot 1.55828482} = -9.131 \text{ kJ/mol}.
\]
The relation (7) is valid (within the framework of the IHJ formalism) for describing the magnetic component of the Gibbs energy for a pure component and for alloys, knowing from the experiment the Curie temperature and the MMM per atom.

When the impurity atom is located in the center of the expanded cell, the presence of a dimensional factor (DF) leads to the appearance of static displacements (SD) of Fe atoms located in different CS (Fig. 5, 6).

Fig. 5. Static displacements of Fe atoms located in the first CS (green circles), 2nd CS (red) and 3CS (blue) around the chromium atom located in the node A of the enlarged cell. R (Cr) = 1.30 A > R (Fe) = 1.26 A.

This situation will lead to a decrease in the MMM according to the relationship

\[
<m>^V = \frac{n_{Fe}^V (\rho_1 + \epsilon_{111}) + n_{Fe}^V (\rho_2 + \epsilon_{100}) + n_{Fe}^V (\rho_3 + \epsilon_{110})}{16} + \frac{n_{Fe}^V (\rho_4 + 4\epsilon_{111})}{16} \left( \mu_B / \text{atomFe} \right) .
\]  

In formula (9), the superscript V indicates that this refers to atoms in the expanded cell inside the volume.

So, the presence of a size factor leads to the appearance of static displacements of matrix atoms in the grain body, which will lead to the creation of local pressures, leading to a decrease in the values of both the partial magnetic moments and the average magnetic moment of the matrix atoms.
Fig. 6. The relationship between the static displacements of Fe atoms in different CS relative to the impurity atom (Mo, W) with a large dimensional factor located at the origin.

Thus, the emerging gradient of the magnetic components of Gibbs energies between local chemical compounds in the center of the grain and the grain boundary is the energy stimulus for the transfer of partially impurity atoms to the grain boundary. This displacement of the impurity atoms on the grain boundary will partially "quench" the static displacements of the atoms, carrying out the relaxation of the local elastic fields caused by the presence of a size factor in binary systems.

It was experimentally established in (16) that at the grain boundaries in austenitic steels HP304 + Si (analogue of stainless steel X18H10T) irradiated with 2 MeV protons with a dose equal to 5 dpa at a temperature of 360°C, the local chemical composition over nickel increased to about 75±80 at. %. In comparison with the average chemical composition of about 11.6 at.%, and the local composition for Si increased to 20 at.% In comparison with the composition of the matrix equal to 2.05 at.% Si.

At the grain boundary, the local Fe concentration falls from 70 at. % (at a distance of 10 nm from the boundary) to zero, and chromium - from 19 at. % up to 2-3 at.%. 
The influence of the dimensional factor on the magnitude of the coherent scattering blocks in the binary alloys of the Fe- (Cr, V, Mo) systems

In order to test the theoretical model [5], experimental X-ray studies were performed to construct the concentration dependences of the parameters of crystal lattices measured for different crystallographic indices for bcc alloys [2] and the sizes of the coherent scattering regions (CXR) for annealed at 700 °C for 150 hours of alloys of Fe- (Cr, V, Mo) systems.

Alloys were prepared in the IMET RAS from Armco - iron, chromium, vanadium and molybdenum. The smelting was carried out in an arc furnace with a copper hearth in an argon atmosphere, turning the ingots several times.

The mass of the ingots was about 30-35 g. The alloys were heat treated at 750 °C in double quartz ampoules for 150 hours. Details of the preparation of alloys for X-ray studies are described in [11].

The linear dimensions of the coherent scattering regions (CSR) of Fe- (Cr, V, Mo) systems alloys are determined. The effect of surface hardening on the broadening of the diffraction lines for the reciprocal lattice sites {(110), (200), (211) and (220)} of Fe-8 at. % Cr is investigated. The results are shown in Table 2 and in Fig. 7.

The results of determining the linear dimensions of the coherent scattering regions (CSR) of the alloys of the Fe- (Cr, V, Mo) systems, the composition of the alloys are given in at%.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>100%Fe</th>
<th>Fe-2Cr</th>
<th>Fe-4Cr</th>
<th>Fe-8Cr</th>
<th>Fe-8V</th>
<th>Fe-1Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_ CSR _ for line(220)A</td>
<td>2600</td>
<td>880</td>
<td>750</td>
<td>740</td>
<td>1100</td>
<td>770</td>
</tr>
<tr>
<td>L_ CSR _ for line (310) A</td>
<td>2000</td>
<td>750</td>
<td>520</td>
<td>510</td>
<td>–</td>
<td>580</td>
</tr>
</tbody>
</table>
Fig. 7. Relative values of the parameters of crystal lattices of BCC solutions measured at different sites of the reciprocal lattice, alloys of the Fe- (Cr, V, Mo) systems (11) - after heat treatment at 750 C for during 150 hours (in double quartz ampoules-MSU).

The linear dimensions of the coherent scattering regions (CSR) of alloys of Fe- (Cr, V, Mo) systems are determined. The effect of surface hardening on the broadening of the diffraction lines for the reciprocal lattice sites \{(110), (200), (211) and (220)\} of Fe-8 at. % Cr. The results are shown in the table and in Fig. 7.

Thus, an analysis of the results of x-ray studies on the size of CSR showed that:

1) the linear dimension of the CSR decreases upon alloying, in comparison with the pure iron,

2) the linear dimension of the CSR decreases with increasing concentration of the alloying component (Fe-Cr system alloys)

3) the linear dimension of the CSR decreases with the growth of the size factor, for example, doping with 1 at.% Mo leads to the same SDs size as 8 at.% Cr.
The relationship between the anisotropy of the spin density in the bcc lattice of Fe and the size factor in the Fe- (Cr, V, Mo, W) systems as the main factor for the onset of short-range order and segregations at the small-angular boundaries of coherent scattering / sub-grains

We estimate the value of the SMM in the case when the expanded cell is dissected by a plane of the (110) type passing through the central atom of the impurity, and leaves in the form of a grain boundary, considered as a fragment of a single crystal, on the surface of the grain boundary.

In this case, the number of Fe atoms located on different CSs relative to the impurity atom decreases by 2 atoms in the 1st, 2nd and 4th CS and by 5 in the 3CS. It is reasonable to assume that the Fe atoms located on the remaining 1÷4 CS are displaced together with the impurity atom into the space of the interface itself, extinguishing the field of local stresses.

Then the MMM of the grain boundary is equal to

$$<m>_S^{\mu} = \frac{6m_{Fe}^{S}(\rho_1) + 2m_{Fe}^{S}(\rho_2) + (1+7/4)m_{Fe}^{S}(\rho_3) + (6/8)m_{Fe}^{S}(\rho_4)}{6 + 2 + (1+7/4) + (6/8)} = 2.235(\mu_B / \text{atomFe}) \quad (10)$$

When calculating the MMM for the extended cell, using (10), the PMM of Fe-Table 1 atoms were used. The results of calculations using formulas (7), (9) - (10) for the differences in the magnetic components of Gibbs energies for the ground state between bulk and surface expanded cells are given in Table 3 (see also Fig. 8).

Application of thermodynamics of two-phase systems for nano materials

According to the thermodynamic theory of two-phase systems (13-14), the temperature dependence of the heat capacity is described below by the following relation

$$C_p^{\mu+\beta}(x,T) = \alpha C_p^{\mu}(x^\mu) + \beta C_p^{\beta}(x^\beta) + T\left\{\alpha \left[\frac{\partial S_\alpha^{\mu}}{\partial x} - \frac{\partial S_\alpha^{\mu+\beta}}{\partial x}\right] \frac{\partial x_\alpha^{\mu}}{\partial T} + \beta \left[\frac{\partial S_\beta^{\beta}}{\partial x} - \frac{\partial S_\alpha^{\mu+\beta}}{\partial x}\right] \frac{\partial x_\beta^{\beta}}{\partial T}\right\} =$$

$$= \alpha \left[\frac{C_p^{\mu}(x^\mu)}{\partial T}\right]^2 \left\{\frac{\partial^2 G_\alpha^{\mu}}{\partial x^2}\right\} + C_p^{\beta}(x^\beta) + T\left\{\frac{\partial x_\beta^{\beta}}{\partial T}\right\}^2 \left\{\frac{\partial^2 G_\beta^{\beta}}{\partial x^2}\right\} \quad (11).$$
Fig. 8. The expanded cell is dissected by a plane of the (110) type passing through the central impurity atom, emerging at the boundary of the coherent scattering block (sub-grains). A plane of the type (110) "cuts out" the different atoms (marked in arrows by the arrows) located at different 1 ÷ 4 CS in the bcc lattice of pure Fe (2 in 1, 2 and 4CSs, and 5 atoms in 3CSs) (6).

Table 3

<table>
<thead>
<tr>
<th></th>
<th>Fe-Cr</th>
<th>Fe-V</th>
<th>Fe-Mo</th>
<th>Fe-W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon(111)\ast 100%$</td>
<td>0.3384</td>
<td>0.7577</td>
<td>4.89847</td>
<td>5.21248</td>
</tr>
<tr>
<td>$&lt;m&gt;V, \mu_B$</td>
<td>2.0406</td>
<td>1.9292</td>
<td>1.8417</td>
<td>1.816</td>
</tr>
<tr>
<td>$&lt;m&gt;V/&lt;m&gt;^{Surf}_{Fe}$</td>
<td>0.913</td>
<td>0.863</td>
<td>0.824</td>
<td>0.813</td>
</tr>
<tr>
<td>$\Delta G_{mag} (T = 0K), kJ/mol$</td>
<td>-0.486</td>
<td>-0.779</td>
<td>-1.017</td>
<td>-1.088</td>
</tr>
</tbody>
</table>

In the bottom line, the ratios (11) $\alpha$ and $\beta$ are the fractions of the $\alpha$- and $\beta$- phases, respectively.

In the temperature range from zero to the Debye temperature, in the course of the actual experiment, to measure the temperature dependence of the heat capacity for nanomaterials, as a rule, equilibrium is not attained during the measurement.

Therefore, there remains a simplified version for the temperature dependence of the heat capacity of two-phase systems for nanomaterials.
\[ C_{p}^{\text{vol+surf}}(T < \theta_D) \approx \alpha_{\text{vol}}^{\text{vol}} C_{p}^{\text{vol}}(T) + \alpha_{\text{surf}}^{\text{surf}} C_{p}^{\text{surf}}(T). \] (12)

In the ratio (12) and \( \alpha_{\text{vol}} \) and \( \alpha_{\text{surf}} \) - the fractions of "cores" of the sub-grains and the "surface" constituents of the sub-grains; and the temperature dependences of the heat capacities of the "cores" of the sub-grains and the "surface" constituents of the sub-grains. In work (15), nanocrystalline different metals were obtained, including for pure iron with an average size of nanocrystals of 20 nm and conducted X-ray studies, measurements of the temperature dependence of the heat capacity in the interval from zero to 300 K, and also studied Raman spectroscopy.

Reflecting the change in the electronic heat capacity and using the Debye models for both the bulk and surface components of the heat capacity, they obtained the volume component of the heat capacity from the total heat capacity of a two-phase (volume and surface) using the Debye temperature for bulk samples.

And after measuring by means of electron microscopy, determining the average size of Fe nanocrystals, we determined the fraction of surface atoms and the Debye temperature, which reproduced well the difference between the total (measured) thermal heat capacity after subtracting from it the heat capacity component related to the fraction of "bulk" atoms authors (15) assessment the ‘surface” Debye temperature \( \theta_{D}^{\text{surf}} = 301 K \).

**The assessments of the "surface" Young's modulus**

Taking into account the interrelation between the Debye temperature and the Young's modulus

\[ \theta_D \propto \left( \frac{E}{a} \right)^{1/2}, \] (13)

and neglecting the change in the lattice parameter (a) in equation (13) upon transition from the "core" sub-grain, we obtain the ratio of Young's moduli for the bulk and surface components of the Young's modules of the “volume” and “surface” components

\[ \left( \frac{E_{\text{surf}}}{\alpha_{\text{surf}}} \right) \left( \frac{E_{\text{vol}}}{\alpha_{\text{vol}}} \right) \left( \frac{\theta_{D}^{\text{surf}}}{\theta_{D}^{\text{vol}}} \right) \approx \left( \frac{301}{450} \right)^2 \approx 0,45 . \]
Thus, the Young's modulus for the surface component of the sub-grain or sub-grain is about half that in comparison with the Young's modulus for the volume component of the sub-grain.

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**References**
5. Udovskii A. Three-Sub-lattice Model that Takes into account the spin density anisotropy, short-range order, and dimensioned factor for the binary Fe–Cr(V, Mo) systems. Russian Metallurgy (Metally) 2011, (9) 889–909.
10. Dinsdale A.T. SGTE DATA FOR PURE


