Influence of dispersity on local physical, structural, magnetic and thermodynamic properties of bcc Fe and its binary alloys

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Abstract. The model was proposed for iron nano-particles (and solid solutions based on bcc-Fe) containing a core and a surface layer coherent with each other in the form of a two-phase stratifying parts (“surface” and bulk) system with different local physical properties. Using the results of measurements of the experimental temperature dependence of the heat capacity and the application of the Debye models for both the “core”-phase and the surface layer (“surface”-phase) as two-phase heat capacity components for Fe nanoparticles, it was shown by calculations that the local elastic modulus for the surface layer is nanoparticles are approximately 2 times smaller than for the “core”-phase of the nano-particle iron. The purpose of the research is to establish the relationship between local physical properties (bulk modulus of elasticity, static displacements of iron atoms surrounding an impurity atom, magnetic moments) for the core part and the surface layer of nanoparticles. From the condition of local mechanical equilibrium it was shown that static displacements of Fe atoms around an impurity atom in various coordination spheres on the surface of nanoparticles of Fe-rich binary BCC solutions of Fe - (Cr, V, Mo, W) with nano-particles increase significantly (compared to static displacements of Fe atoms “core” of nano-particles).

1. Introduction
Based on an analysis of the results of quantum mechanical calculations of the total energy and average magnetic moment (AMM) per atom depending on the volume of bcc Fe – fig. 1, to take into account spin density anisotropy, the concepts of partial magnetic moments (PMM) of Fe atoms were introduced in [1] located in different crystallographic directions on 1÷4 coordination spheres, and their values are calculated.

2. Correlation between partial magnetic moments and static displacements of Fe atoms in bcc solutions of Fe - (Cr, V, Mo, W) systems
Within the framework of this model [1], the relationship between the partial magnetic moments and the static displacements of Fe atoms located around the impurity atom in binary bcc alloys of Fe - (Cr, V, Mo, W) systems with a dimensional factor is established. The use of the 3-sublattice model formulated in [1] made it possible to demonstrate an increase in the static displacements of Fe atoms in the bcc binary alloy matrix with an increase in the number of coordination spheres - Figs. 2 and 3.
Figure 1. Dependence of the total energy (triangles) and the average magnetic moment (circles) as a function of the atomic volume for the ferromagnetic bcc phase Fe [1]. The designations V1, V2, V3, and V4 correspond to volumes calculated from the corresponding radii of the 1st, 2nd, 3rd, and 4th coordination spheres relative to the central atom in a block constructed of eight bcc cells and containing 16 atoms.

Figure 2. Static displacements of Fe atoms located in the 1st CS (green circles), 2nd CS (red) and 3KS (blue) around the chromium atom located in the node A of the expanded cell with the atomic radius Cr R (Cr) = 1.30 Å > R (Fe) = 1.26 Å.

Figure 3. The relationship between the static displacements of Fe atoms in different coordination spheres relative to the impurity atom (Mo, W) with a large size factor located at the origin of the Cartesian coordinates.

It is shown that the size factor leads to an increase in static displacements with an increase in the number of coordination spheres, and, consequently, at different nodes (hkl) in reciprocal space, i.e. with an increase in the radii of the coordination spheres in direct space, and a decrease in the size of coherent scattering regions, which was confirmed by X-ray diffraction experiments [2] - Table 1 and Fig. 4.
Figure 4. Relative values of the crystal lattice parameters of bcc iron-based solutions measured at different nodes of the reciprocal lattice, alloys of Fe- (Cr, V, Mo) systems [2] - after their heat treatment at 750 °C for 150 hours (in double quartz ampoules - Moscow State University).

Table 1. The results of determining the linear dimensions of coherent scattering regions (CSR) of alloys of Fe- (Cr, V, Mo) systems, alloy compositions are given in at.% [2].

| The chemical composition of the alloys | 100% Fe | Fe-2Cr | Fe-4Cr | Fe-8Cr | Fe-8V | Fe-1Mo |
|--------------------------------------|---------|--------|--------|--------|-------|--------|
| L_ CSR for line (220),A              | 2600    | 880    | 750    | 740    | 1100  | 770    |
| L_ CSR for line (310) A¹             | 2000    | 750    | 520    | 510    | –     | 580    |

3. The relationship between spin density anisotropy in the bcc lattice of Fe and the size factor in Fe- (Cr, V, Mo, W) systems is the main factor in the appearance of short-range order and segregation at low-angle boundaries of coherent scattering / sub-grains

The increase in the static displacements of the matrix atoms located around the impurity atom (Cr, V, Mo, or W) is due to the presence of a size factor, which leads to the appearance of local pressures, which in turn lead to a decrease in the partial magnetic moments of the Fe atoms and the average magnetic moment of the matrix atoms. When the critical value of the static displacements of iron atoms is reached, a loss of mechanical stability occurs when the value of the bulk modulus of elasticity of the bcc lattice of the ferromagnetic phase is zero - Fig. 5 and Table 2.

Due to an increase in the static displacements of iron atoms located around the impurity atom, with an increase in the number (and hence the radius) of the coordination sphere, upon reaching a critical size of the static displacements, the mechanical stability of the bcc lattice of the matrix is locally lost, thereby limiting the size of the coherent scattering region or sub-grains. Obviously, in the space of the small-angle boundary of the coherent scattering region (CSR) (or sub-grain), partial (or complete) relaxation of the static displacements of Fe atoms located in 1-3 coordination spheres relative to the impurity atom closely located in the vicinity of the small angular border. This relaxation partially or completely reduces the local pressure values, which leads to an increase in the partial magnetic moments of iron atoms in comparison with the local magnetic moments of atoms inside the CSR (or sub-grain) of the matrix. Due to the presence of local gradients of the magnetic moments of atoms located in the vicinity of the CSR (or sub-grain), in comparison with the values of the partial magnetic...
magnetically moments located around the impurity atoms in the body (core) of the grain, a gradient of the Gibbs energy $\Delta G_{\text{mag}}(T=0K)$ – see table 3.

![Figure 5](image_url)

**Figure 5.** Calculation of the critical value of the volume at which the volume modulus of elasticity is $B = -\frac{V\partial P}{\partial V} = 0$ from the pressure depending on the volume by the calculated numerical differentiation of the dependence of the total binding energy on the volume $E(V)$ - Fig. 1 obtained by quantum mechanical calculations for the bcc ferromagnetic Fe, and the equilibrium value of the average magnetic moment.

### Table 2. Equilibrium and critical values of volumes for the ferromagnetic bcc phase of Fe.

|                      | Minimum value | Maximum value | Absolute inaccuracy | Relative inaccuracy, % |
|----------------------|---------------|---------------|---------------------|------------------------|
| $V_{\text{equal (at.u.)}}$ | 76,55759      | 77,5868       | 1,02921             | 1,33                   |
| $V_{\text{crit (at.u.)}}$ | 121,130425    | 125,16811     | 4,037685            | 3,23                   |
| $V_{\text{crit}}/V_{\text{equal}}$ | 1,5822        | 1,6133        | 0,0311              | 1,96                   |
| $\varepsilon_{\text{lin. cr. mech.}}$ | 0,1652        | 0,1728        | 0,0076              | 4,06                   |

### Table 3. The difference in the energies of the magnetic components for the ground state between the average magnetic moments for the grain center of alloys of the composition of 6.25 at.% Binary systems of Fe-(Cr, V, Mo, W) and the type surface (110) for pure Fe, depending on size factor - the static displacement of $\varepsilon(111)$ atoms located in 1CS.

|                      | Fe-Cr | Fe-V | Fe-Mo | Fe-W |
|----------------------|-------|------|-------|------|
| $\varepsilon(111)^*100\%$ | 0,3384 | 0,7577 | 4,89847 | 5,21248 |
| $<m>_{V}$, $\mu_B$ | 2,0406 | 1,9292 | 1,8417 | 1,816 |
| $<m>_{V}$/$<m>_{\text{Surf Fe}}$ | 0,913 | 0,863 | 0,824 | 0,813 |
| $\Delta G_{\text{mag}}(T=0K)$, KJ/mol. | -0,486 | -0,779 | -1,017 | -1,088 |

The presence of a gradient of the magnetic part of the Gibbs energy $G_{\text{mag}}$ leads to the movement of impurity atoms on the boundary of the sub-grain into the space between the CSRs (sub-grains), which contributes to the occurrence of segregation at grain boundaries [3] during the operation of ferritic steel at elevated temperatures $\approx (0.5-0.6)T_{\text{melt}}$. The presence of small segregations, for example, Laves phases, at the boundaries of sub-grains, due to the exploitation of the material under load, leads to coagulation (coarsening) of segregations. This circumstance, in turn, leads to an increase in the local volume occupied by the inter-angle boundary between grains and, as a consequence, to an increase in the total surface area of the interface. Due to the fact that the diffusion rate along the grain boundaries significantly exceeds the diffusion rate over the grain body, this leads to both an increase in grain size and to inter-granular slippage, which leads to increased creep of ferritic steel.

To prevent the grain size growth process, it is advisable to introduce reinforcing nanoparticles: 1) which have a large Gibbs energy of formation in a wide temperature range, 2) that must be chemically
compatible with the ferrite matrix, 3) in addition, the crystal lattice of nano-particles must be coherent with the crystal lattice with a ferrite matrix, which will allow “closing” the boundary between the grain of the matrix and the nano-dispersed particle.

To fulfill the 1st and 2nd conditions, the most suitable are nano-particles of the fluorite phase of zirconium dioxide, proposed in [4]. Considering that the fluorite phase of ZrO2 is stable in the temperature range of 2653–2715°C, and ferritic steels must be operated in the working temperature range of 650–700°C, therefore, the fluorite phase of zirconium dioxide was stabilized in [5] by doping with 18 mol. % Y2O3.

4. The effect of particle dispersion on the local physical, structural, magnetic and thermodynamic properties of bcc Fe and its binary alloys

With a significant dispersion of the matrix grains, the number of “surface” atoms can be comparable with the number of atoms located in the “core” nanoparticles. Assuming the conjugation of crystal lattices formed both by atoms located in the “surface” layer of nano-particles and by atoms located in the “core” nano-particles, this allows us to introduce the concepts of surface (quasi-two-dimensional) and bulk (three-dimensional) phases, treating their occurrence as a separation of the common phase.

In [6], a model was proposed for iron nanoparticles (and solid solutions based on bcc Fe) containing a core and a surface layer coherent with each other in the form of a two-phase stratified system with various local physical properties. It is logical to assume the conjugation of crystal lattices formed by atoms located in the “surface” layer and atoms located in the “core” nanoparticles. This allows us to introduce the concepts of “surface” (quasi-two-dimensional) and bulk (three-dimensional) phases, treating their occurrence as a stratification of the common phase. The purpose of the research is to establish the relationship between local physical properties (bulk modulus of elasticity, static displacements of iron atoms surrounding the impurity atom, magnetic moments of iron atoms located in different coordination spheres relative to the impurity atom) for the “core” component and the surface layer of the nano-particles. Such an interpretation makes it possible to use the ratio obtained in the framework of thermodynamics for the specific heat of a two-phase (“surface” and volume) system, taking into account the “frozen” kinetics (during the actual experiment, as a rule, equilibrium is not achieved) when measuring the specific heat in the temperature range from zero to $T<\left(1+2\theta_0\right)$, where $\theta_0$ is the Debye temperature. In the general case, both (the “surface” and bulk part of the nano-particle) phases of the nano-particle can contain different impurity concentrations. With increasing temperature, this ratio for different phases of a nano-particle can change.

Using the results of measuring the experimental temperature dependence of specific heat [7] and using Debye models for both the “core” phase and the surface layer (“surface” phase) as two-phase heat capacity components for Fe nanoparticles obtained by grinding in the atmosphere argon up to 20 nm, calculations in [7] showed different Debye temperatures of 450 K (for the “core” part of nano-particles) and 300 K for the surface layer of nano-particles. Taking into account the relationship between the Debye temperature and the elastic modulus in [6], it was shown that the local elastic modulus for the surface layer — phases of nano-particles of the body-centered cubic phase of pure iron is about 2 times less than for the “core” phase of a pure iron nano-particle. From the condition of local mechanical equilibrium of the “core” phase and the “surface layer” (surface phase) in [6] it was shown that the static displacements of Fe atoms around the impurity atom in different coordination spheres on the surface of nanoparticles of Fe-rich binary bcc solutions Fe - (Cr, V, Mo, W) with nano-particles increase significantly (compared with the “core” component of nano-particles).

Thus, it is possible to establish the relationship between the Debye temperature ($\theta_0$) of the bulk isothermal elastic modulus ($B_{11}(V)$) and the static displacements of atoms (bulk $\varepsilon_c$ and linear in different crystallographic directions $\varepsilon_{111}(V)$, $\varepsilon_{110}(V)$, $\varepsilon_{100}(V)$ as for “core” - phase on the one hand, and the physical and structural properties of $\theta_0$, $B_{11}(V)$, $\varepsilon_{111}(V)$, $\varepsilon_{110}(V)$, $\varepsilon_{100}(V)$ of the “surface” phase, as well as of the “core” fraction — hohl and surface phases of nanoparticles. The obtained results of different Debye temperatures for the core component and the surface layer of 20 nm of pure bcc Fe nano-
particles at elevated temperatures above Debye temperatures lead to a difference in vibrational entropies (in the harmonic approximation) of these phases
\[ S_{D}^{\text{Surf}} - S_{D}^{V} \approx 3R \ln \left( \frac{\theta_{D}^{V}}{\theta_{D}^{\text{Surf}}} \right) = 1.216R, \quad T > \text{max}(\theta_{D}^{V}, \theta_{D}^{\text{Surf}}). \]

The obtained equation demonstrates the significant influence of the “surface” contribution on its relative stabilization in comparison with the “core” component of the nanoparticles.

Taking into account the interrelation between the static displacements of Fe atoms located in the environment of impurity atoms and the partial magnetic moments of Fe obtained in [1], the interrelation between the average magnetic moments of the “surface” and “core” phases of nanoparticles is obtained.

The described approach opens up the possibility of creating stable nano-composite materials under the condition of coherence of the crystal lattice of the matrix with nano-particles.

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