On the structural stratification of iron nanoparticles

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Abstract. It is shown that the presence of dispersion of particles with nano-sizes can lead to the appearance of a local phase transition on the surface layer of a sub-granule or a local bcc / fcc phase transition in pure Fe can occur at the intergranular boundary. In the presence of a large size factor, for example, as in Fe- (Mo, W) systems, the magnitude of the static displacements of Fe atoms located at 2–3 coordination spheres relative to the impurity atom, and simultaneously located in the surface / surface layer of the grain, when the critical value of the atomic displacement is exceeded Fe will lead to a violation of the local mechanical stability of the bcc lattice of Fe.

1. Introduction
An analysis of the results of quantum-mechanical calculations of the total energy and average magnetic moment depending on the volume of the ferromagnetic bcc phase of Fe made it possible to introduce the concepts of partial MM of Fe atoms located on different coordination spheres [1]. A statistical model was constructed taking into account the spin density anisotropy for the bcc phase of Fe- (Cr, V, Mo / W) solutions taking into account the size factor. The mechanical tensile stability was estimated for the ground state of the bcc Fe lattice in Fe-Me binary systems, which made it possible to explain the presence of an extended stability region of bcc solutions in Fe- (Cr, V) systems, limited in Fe- (Mo, W) and extremely small in Fe- (Nb, Ta, Zr) systems. It was shown theoretically and confirmed by X-ray experiments [2] that taking size factor into account leads to the appearance of static displacements of Fe atoms (from the nodes of the ideal crystal lattice) around the impurity atom and their influence on the average magnetic moment, as well as on the size of the coherent scattering regions. An analysis of the thermodynamic data $\Delta G_f$ – the Gibbs formation energy of yttrium and zirconium oxides showed that the stability of their oxides is 10–20 times higher than the stability of chromium carbides and nitrides.

To stabilize and reduce the size of the coherent scattering regions, it is advisable to strengthen the ferrite matrix with chemically compatible dispersed oxide particles. Thermodynamic calculations showed that ZrO$_2$ is chemically compatible with the bcc phase of Fe [3]. Doping of ZrO$_2$ using Y$_2$O$_3$ made it possible to lower the lower boundary of the temperature region of stability of the fluorite phase to the working temperature of ferritic steels [4]. In this regard, the study of the properties of dispersed particles of nanometer size is of scientific and practical interest. In this paper, we consider Fe nano particles and the effect of dispersion on their physical properties as a model system.

2. The model of nanoparticle
In [5], a model was proposed for Fe 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 system with different local physical properties. Suppose the coherence of the crystal lattices formed by atoms located in the
“surface” layer and atoms located in the “core” of a nanoparticle, which allows us to introduce the concepts of “surface” (quasi-two-dimensional) and bulk (three-dimensional) phases. 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. In general, both (“surface” and volume part of a nano-particle) phases of a nano-particle can contain different impurity concentrations. With increasing temperature, this ratio for different phases of a nano-particle can change. According to thermodynamic theory [6-7] heat capacity of a two-phase system has the form

\[
C_F^{\alpha+\beta}(x,T) = \alpha C_F^{\alpha}(x^\alpha) + \beta C_F^{\beta}(x^\beta) + T \left[ \alpha \left( \frac{\partial^2 G^{\alpha}}{\partial x^\alpha \partial x^\alpha} \right)_{x^\alpha} + \beta \left( \frac{\partial^2 G^{\beta}}{\partial x^\beta \partial x^\beta} \right)_{x^\beta} \right]
\]

Taking into account the “frozen” kinetics (during the actual experiment, as a rule, equilibrium is not achieved) when measuring the heat capacity in the temperature range from zero to \( T < (1-2) \theta_0 \), where \( \theta_0 \) is the Debye temperature (1) transforms into an approximate relation (2):

\[
C_F^{\alpha+\beta}(T) \approx \alpha C_F^{\alpha}(T) + \beta C_F^{\beta}(T) \quad \text{(2)}
\]

In relations (1)-(2), the \( \alpha- \) and \( \beta- \) fractions of the phases of the \( \alpha- \) and \( \beta- \) phases are the compositions of the equilibrium phases at a fixed temperature, \( G^{\alpha} \), \( G^{\beta} \), \( S^{\alpha} \), \( S^{\beta} \) - the Gibbs thermodynamic potentials of Gibbs and the entropy of the \( \alpha- \) and \( \beta- \) phases, respectively; in the bottom row of ratios (2), the fractions of the \( \alpha^{\text{vol}} \) and \( \alpha^{\text{surf}} \) phases are replaced by the fractions of the phases of the “bulk” and “surface” phases.

In [8] nano-crystalline various metals were obtained by mechanical “grinding” in an argon atmosphere, including for pure iron with an average nano-crystal size of 20 nm, and X-ray structural studies were carried out, and the temperature dependence of the heat capacity was measured in the range from zero to 300 K, and also investigated Raman spectroscopy. Neglecting the change in the coefficient of electronic heat capacity and using the Debye model for both the volume and surface components of the isobaric heat capacity, they obtained from the total heat capacity of the two phases

\[
C_T^{\alpha+\beta}(x,T) \approx \alpha C_T^{\alpha}(x^\alpha) + \beta C_T^{\beta}(x^\beta) \quad \text{(1)}
\]

Then, after measuring using electron microscopy and determining the average size of Fe nano-crystals, the authors of [8] determined the fraction of surface atoms and the Debye temperature, which well reproduced the difference between the total (measured) thermal heat capacity minus the heat capacity component related to the volume fraction atoms and calculated the Debye temperature for the “surface” phase \( \theta_D^{\text{surf}} = 301K \).

3. Discussion of the results

Taking into account that, in the high-temperature approximation, the temperature dependence of entropy in the Debye approximation has the form \( S_D(T) \approx 3R \ln(T / \theta_D) ) + 4R \), from here we obtain the difference in the vibration part of the entropy in the harmonic approximation between the “surface” and “bulk” phases

\[
S^{\text{surf}}(T) - S^{\text{vol}}(T) \approx 3R \ln(\theta_D^{\text{surf}} / \theta_D^{\text{surf}}) \simeq 1,216R, \quad T > \max(\theta_D^{\text{vol}}, \theta_D^{\text{surf}}) \quad \text{(3)}
\]
The obtained ratio exceeds the entropy of the bcc \( \Rightarrow \) fcc phase transition of pure iron by more than two times. This result demonstrates that a local phase transition can occur on the grain surface or in the inter-grain boundary.

Given the relationship between the Debye temperature and Young’s modulus

\[
\theta_D \propto (E / a)^{1/2}
\]

and neglecting the change in the lattice parameter during the transition from the “core” part of the sub-grain to the surface layer (or boundary) of the grain, we obtain the ratio of Young’s modules for the bulk and surface components of the grain

\[
\left( \frac{E_{\text{surf}}}{a_{\text{surf}}} \right) \approx \left( \frac{\theta_D}{\theta_{D_{\text{vol}}}} \right)^2 \approx \left( \frac{301}{450} \right)^2 \approx 0.45
\]

Thus, the Young's modulus for the surface part of a sub-grain or region of coherent scattering is about 2 times less in comparison with the Young's modulus for the bulk part of a sub-grain.

This result is important; taking into account the presence of a critical value of static atomic displacements in the bcc crystal lattice of pure iron of the relative equilibrium value of the lattice parameter for the ground state, the condition of local mechanical stability of the bcc lattice is lost when the bulk elastic modulus becomes zero. Using the results of quantum-mechanical calculations of the total energy of the ferromagnetic bcc phase of pure iron depending on the volume [1] in [9] the dependence of pressure on volume was obtained, which is shown in figure 1.

![Figure 1](image_url)

Figure 1. Calculation of the critical value of the volume at which the volume modulus of elasticity is \( B = \nabla P / \nabla V = 0 \), from the pressure depending on the volume, calculated by numerical differentiation of the total binding energy versus volume \( E (V) \) obtained by quantum-mechanical calculations for bcc ferromagnetic Fe [1].

From the condition that the equilibrium pressure is equal to zero, the value of the equilibrium volume follows, as the root of equation (6)

\[
P(V) = -\left( \frac{\partial E_{\text{tot}}}{\partial V} \right) = 0 \quad \Rightarrow V_0,
\]

from which follows value \( V_0 = 77.072 \pm 0.514 \text{ a.u.}^3 \).
An analysis of the constructed dependence of the total pressure on the volume—figure 1 demonstrates the presence of a local extremum. This extreme corresponds to the condition that the isothermal bulk modulus of elasticity for the ground state vanish (T = 0K),

$$B_r = \frac{\partial P}{\partial \ln V} = 0$$  \hfill (7)

The root of equation (7) gives the value of volume at the point of extremum of the dependence $P(V)$, namely, the critical value of volume $V_{crit} = 123.149 \pm 2.019 \, \text{a.u.}^3$. The ratio of the critical value of volume to the equilibrium value of volume gives us a value of 1.5978, hence the critical value of the relative linear change in the local parameter of the bcc lattice is 16.9%.

Let us consider the effect of these results as applied to alloys based on bcc Fe in Fe-(Cr, Mo, W, V) systems. Given the different values of the static displacements of iron atoms located in different coordination spheres around the impurity atom [1], including their experimental confirmation on the melted and heat-treated alloys Fe-Cr, Fe-V, Fe-Mo [2] and take into account the local mechanical equilibrium between the “core” part of the grain and the surface layer of grain coherent with it. We find that the ratio of the static displacements of Fe atoms is equal to the reciprocal of the ratio (5). In other words, the magnitude of the static displacements of Fe atoms located in the 2- and 3 (relative to the impurity atom) coordination spheres and located in the surface layer of grain will be approximately 2 times greater than the magnitude of the static displacements of Fe atoms located on similar coordination spheres, but located in “core” part of the grain. The table shows the results of calculations of the linear dimensional factor for the bulk and surface parts of grains in the bcc solution of the Fe-X binary system (X = Cr, V, Mo, W) in comparison with the critical displacement value for bcc pure iron.

Table 1. Calculations of the linear dimensional factor for the bulk and surface parts of grain in the bcc solution of the Fe-X binary system (X = Cr, V, Mo, W) in comparison with the critical displacement value for bcc pure iron.

| The Fe-X system | Fe-Cr | Fe-V | Fe-Mo | Fe-W |
|-----------------|-------|------|-------|------|
| a(X),Å          | 2.886 | 3.04 | 3.147 | 3.155|
| $\epsilon_{lin}^{surf}(111) \times 100\%$ | 0.698 | 6.07 | 9.8   | 10.08|
| $\epsilon_{lin}^{surf}(111) \times 100\%$ | 1.55  | 13.49| 21.79 | 22.41|
| $\epsilon_{surf}/\epsilon_{crit}$ | 0.0917| 0.798| 1.289 | 1.326|

*) $\epsilon_{lin}^{surf} (111) = \{(a(X) - a(bcc - Fe)) / a(bcc - Fe), a(bcc - Fe) = 2.866Å [10]$

In the presence of a large size factor, for example, as in Fe-(Mo, W) systems, the magnitude of the static displacements of Fe atoms located in 2-3 coordination spheres relative to the impurity atom and simultaneously located in the surface / subsurface layer of grain, when the critical displacement is exceeded atoms Fe (calculated in [9] from the analysis of quantum-mechanical calculations for bcc Fe depending on the volume) will lead to a violation of the local mechanical stability of the bcc Fe lattice.

Of course, the above estimates relate to the ground state and are made without taking into account the effect of temperature on the change in the dimensional factor. For example, given that the linear coefficients of thermal expansion of bcc iron and chromium differ from each other by about two times [11], the size factor in binary solutions at 1000 K becomes equal to zero. However, for other binary systems Fe-X, X=Mo, W, Nb, .., in which the size factor for the ground state is an order of magnitude higher than the size factor in the iron-chromium system, the conclusion obtained in this work will be valid about the loss of mechanical stability of bcc iron on the grain surface and leads to the formation of intermetallic phases with a different crystal structure, for example tetragonal Laves phases with structure C14.
Acknowledgments
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