Effect of abnormal high solubility of impurity in nanocrystals and its metrological aspects

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Abstract.
The problem of doping impurity intrusion into nanoparticles is analyzed. Thermodynamic model of the effect is developed, taking into account specific properties of nanoparticles: quantum confinement of elementary excitations and the impact of nanoparticle surface states compared with bulk ones. We obtained the size dependence of impact equilibrium solubility in nanoparticles. Magnetometric experiments, carried out on nanoparticle ensemble of iron oxide doped with gadolinium and other impurities, show lack of contradictions and good qualitative accordance between the model and the experiment.

1. Introduction
The large investigations carried out in present time in the field of nanomaterial science, have revealed a considerable quantity of the various effects [1,2] which main feature is dependence of properties of nanoscale objects from their characteristic size. In turn, one of leading places in the physical chemistry of objects of nanomaterial science [3] is the problem of the doping of nanoparticles by various impurities. This phenomenon is extremely interesting as for the understanding of features of penetration of particles in nanoobject, and it is exclusively important from the applied point of view [4]. The problem of the doping of nanoparticles in some degree have been studied from the point of view of features of penetration of impurities in nanoobjects depending on its size [5,6,7] in the experimental aspect. The theoretical analysis of penetration of impurities and defects in nanoobjects is poor [8-12]. Moreover, theoretical works have basically the modelling character and are not connected with the fundamental properties of nanoparticles. This fact does a problematics of influence of the size of nanoparticles on their alloying properties (in particular, solubility of impurities) the topical problem.

If we summarise experimental results on doping of nanoparticles then it is possible to present them in a following kind:
1. The effect of increase of impurities solubility in nanocrystals in comparison with that is observed in volume materials has been found;
2. The effect increases with the decrease of nanoparticle radius;
3. The effect that more than is less solubility in a volume material.
4. The effect of increase of impurities solubility in nanoparticle decreases with the temperature growth in comparison with the bulk material.

Considering the fundamental nature of the found effect and that circumstance, that these properties appear the general for various materials, we will analyse it from the basic thermodynamic positions.

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2. Model

With the large generality it is possible to believe, that transition to study of nanoparticles leads to necessity of the account of two new positions:

1. Quantum confinement of elementary excitations, caused by the small sizes of nanoparticles [13].
2. The total number of surface states in nanoparticle is comparable with the number of the bulk ones [1].

In the problem of nanoparticles doping as it will be shown below, both these features of nanoobjects are presented. So, really, the confinement of electron and phonon excitations leads to that the quasicontinuous spectra turn to the discrete spectra of elementary excitations. It immediately has an effect on, first, the statistical sums $Z$ describing the elementary excitation (and, also, on their thermodynamic parameters [14]). Secondly, the equilibrium constants of reactions between electrons and the charged impurity and defects will depend on the differences of energy levels of the lowest unoccupied orbital and the highest occupied one [15], i.e. from the size of nanoparticles. Furthermore, the comparable numbers of surface and bulk conditions lead to that in expressions for free energies the contributions of these states should be taken into account as comparable values. We will construct, proceeding from these positions, the simple thermodynamic model of nanoparticles doping.

We consider the following system: very large volume of a phase A (a material of the future doping impurity) with an impregnation of a nanocrystall of phase B in it having the volume $V = \frac{4}{3} \pi R^3$ and the surface $S = 4 \pi R^2$. Let the density of the phase B is $N$, the surface tension between A and B is $\sigma$, the cohesion energy of phase B is $U_B$, and the temperature of the A+B system is $T$. The free energy of A+B system before the penetration of atoms A in nanoparticle B is:

$$F_1 = F_{1A} + F_{1B} + NV \{U_B + 3kT \ln Z_B\} \quad (1)$$

Here $Z$ is the statistical sum of phonons of each atom in nanoparticle. We will calculate $Z$ in Einstein’s model, considering, however, unlike last, finiteness of the potential well, i.e. the cohesion energy, which, that is the characteristic for nanoparticle and depends on the size of nanoparticle [5] and on the concentration of the penetrated dopants [17], that is:

$$U_B = U_0(R, C) = U_0(1 - f(aS/V)) \quad (2)$$

where $a$ is the interatomic distance in nanoparticle. Indeed, as it has been shown theoretically [16] and experimentally [8], the cohesion energy is the drop-down function of $f(aS/V)$ under decrease of the nanocluster radius. In turn, the value of the cohesion energy of the alloy is the function of concentration of its components, that is $C$, that has been shown by various methods, for example, in a $\varepsilon$-dielectric formalism [17]. As a first approximation, the cohesion energy is equal $U = U_0 + CDU/dC \approx U_0 - \gamma C$.

In approach of a finite potential well, for the individual Einstein’s oscillator we have:

$$\ln Z_B = \ln \sum_{n} \exp\left[-(n+1/2)\hbar\omega/kT\right] = \{(1-\delta^n)/(1-\delta)\}, \text{ where } \delta = \exp\{-\hbar\omega_B/kT\}. \quad (3)$$

Here summation is made on $n$, changing from $n=0$ up to $m=U_B/\hbar\omega_B - \frac{1}{2} = \frac{U_B}{\hbar\omega_B}$, where $m$ is the maximum number of phonons located in the potential well, which is equal to the cohesion energy, and $\omega_B$ is the frequency of Einstein’s phonon. Then $\ln Z_B \approx -\hbar\omega_B/kT - \ln m$.

Now we write the free energy of A+B system after the end of the doping process, assuming, that a part of A atoms has replaced a part of B atoms, and taking into account, that the changes in the large system A are negligibly small ($F_{2A} \approx F_{1A}$).

$$F_2 = F_{1A} + NV(1-C)\{U_B + 3kT \ln Z_B\} + NV(CU_{A/B} + 3kT \ln Z_{A/B}) + NVCKTnC + (\sigma + C\sigma/dC)S \quad (4)$$

Here A/B indexes mean the A atoms, penetrated in B, the derivative $d\sigma/dC = -\beta$ means the “speed”
of change of surface tension under transition of A atoms in B (see [9]). The change of free energy under doping is equal:

$$F_2 - F_1 = NVC(U_{A/B} - U_B) + 3NVC \left\{ \ln(Z_B/Z_{A/B}) \right\} + C(d\sigma/dC)S + NVkTClnC.$$  \quad (5)

Equilibrium value $C$ corresponds to the solution of equation:

$$d(F_2 - F_1)/dC = 0$$  \quad (6)

If $\Delta U(C,S/V) = U_{A/B} - U_B = \Delta U_0 \{1 - f(aS/V)\}(1 - \gamma C)$, then the solution of the equation (6) leads to the transcendental equation relative unknown concentration $C$:

$$C = A_0 \exp\{2\gamma C/kT\};$$  \quad (7)

Here $A_0 = [U_0^B/U_{A/B}]^3 [\omega_{A/B}/\omega_B]^3 \exp\{-[\Delta U_0/k(1 - f(aS/V) - 1)] + \beta S/NkTV\}$; $U_0^B$, $U_{A/B}^0$ are the cohesion energies of atoms B and A in the phase B (that is A/B), in a hypothetical case of a bulk phase of C.

The equation (7) is convenient for solving graphically (figure 1). However, for small $\gamma$ the simple analytical solution takes place:

$$C = (A_0)/(1 - A_0 2\gamma/kT).$$  \quad (8)

It is evident, that the concentration $C$ sharply depends on the nanoparticle radius, equal $3(S/V)^{-1}$, and super exponentially increases at decrease of the nanoparticle size. This dependence is much stronger, than found in [9]. It is obvious, that at $\gamma > 0$ and $\beta > 0$ all properties 1-4 of Introductions are satisfied, that speaks about a rationality of the suggested model. Note, that at $\gamma = 0$ our results (8) also are not reduced to [9] since in our model the finiteness of cohesion energy and its dependence on the nanoparticle size are considered.

![Figure 1](image)

**Figure 1.** The graphic solution of the equation (7); $\gamma_2 > \gamma_1$.

3. Discussion

The experimental check of effect of increase of solubility of a doping impurity in nanoparticle at reduction of its size represents a not trivial problem. Apparently, the magnetic nanometrology [18] methods can play a special role here. In this connection we performed the experimental research of magnetic parameters of the iron oxide nanoparticles $\text{Fe}_3\text{O}_4$ doped as by gadolinium, as by other
impurities. The magnetic properties were measured on SQUID magnetometer and on the vibratory magnetometer. Were investigated the electron paramagnetic resonance (EPR) spectra of these nanoparticles. The standard technology of chemical co-deposition at pH 10 - 12 has been used for synthesis of the gadolinium-replaced ferrite. The size of Fe\(_{1-x}\)Gd\(_{x}\)O\(_4\) nanoparticles was≈10 nm and has been supervised by TEM. The Curie temperature of these nanoparticles is enough high, and the specific magnetisation decreases with the increase of gadolinium content (table 1, figure 2). It is established, that the Gd doping influences on the Curie temperature weakly. It would seem, for the increase of nanoparticles magnetisation it is necessary to partially replace Fe\(^{3+}\) by ions with the big magnetic moment, for example, by Gd\(^{3+}\). However, the result was opposite (see table 1). The growth of gadolinium percentage reduced considerable (by two order) the magnetic moment of nanoparticles (figure 2).

Table 1. Magnetic parameters of Fe\([\text{Gd}_{x}\text{Fe}_{2-x}]\)O\(_4\) nanoparticles

| x   | \(T_{\text{Curie}}\), K | \(M_s\), emu/g | \(N=M_s/\mu_{\text{Fe}_3\text{O}_4}\) |
|-----|-------------------------|----------------|---------------------------------|
| 0.1 | 738                     | 29.1           | 7.657*10\(^{20}\)              |
| 0.16| 873                     | 27.1           | 7.124*10\(^{20}\)              |
| 0.71| 893                     | 19.0           | 4.998*10\(^{20}\)              |
| 0.97| 891                     | 15.1           | 3.211*10\(^{20}\)              |
| 1   | 724                     | 14.68          | 3.862*10\(^{20}\)              |
| 1.12| 833                     | 12.94          | 3.404*10\(^{20}\)              |
| 1.9 | 626                     | 1.36           | 3.590*10\(^{19}\)              |

Note, that in view of the big difference of the ionic radiuses of trivalent gadolinium ions and of iron ions (for example, for Gd\(^{3+}\) ionic radius in spinel is 1.15 Å, and for Fe\(^{3+}\) it is 0.67 Å) gadolinium in a volume variant cannot penetrate into a spinel matrix [12]. It follows from the data of the roentgen-phase analysis, that in system \((1-x)\text{Fe}_2\text{O}_3 + x\text{Gd}_2\text{O}_3\) the hard solutions [19] are not formed. At the same time, under doping of nanoparticles as it has been shown preliminary by us [5], the situation is opposite. Indeed, on the base of measurement of magnetic characteristics of nanoparticles system of “iron oxide with the impurity of gadolinium” it is possible to show, that gadolinium replaces the ions of iron and it transits in Gd\(^{3+}\) state [5,20]. It is obvious for the system of Fe3O\(_4\) with gadolinium, that \(\gamma<0\) and \(\beta<0\). Thus, it is evident, that gadolinium became a very good test for model, satisfying to points 1 and 3 (see Introduction).

![Figure 2](image-url) The magnetic field dependence of the specific magnetic moment for iron oxide nanoparticles doped by gadolinium. X is the Gd content.
It is possible to explain the paradoxical result presented in a figure 2 as follows. The basic contribution to formation of the total magnetic moment of the nanoparticles ensemble gives one-domain small nanoparticles. The curves of magnetisation presented in figure 2 have superparamagnetic character, that is the contribution to formation of the magnetic moment of the nanoparticles ensemble gives small one-domain particles with radius, smaller than $R \sim 5$ nanometer. This fact, that the gadolinium solution "worsens" the magnetic properties, i.e. reduces the full magnetic moment of ensemble, confirms, that the basic adolinium solution occurs in small nanoparticles. As to the microscopic mechanism of "damage" of one-domain small particles, that, probably, here can play a role the "facilitated" mechanism of formation of dislocations, vacancies and other defects in small and ultrasmall nanoparticles under reduction of the characteristic sizes of nanoobjects, found in [8, 21, 22].

As to the possible mechanism of the "facilitated" formation of dislocations in small particles it is possible to note the following. The large difference of radiuses of $Fe^{3+}$ ions, replaced by $Gd^{3+}$, causes the critical tension [20]. In the case of large difference of the sizes of the doping impurity and the replaced nanocrystall atoms, the realization of other mechanism of the reduction of free energy of nanocrystall+impurity system is hypothetically possible in principle, i.e. the spontaneous formation of misfit dislocation with the core of an impurity atom. The similar phenomenon is known in the heteroepitaxy physics, namely formation of the van der Merve dislocation [22]. The dislocations in small particles of radius $R \sim 5$ nanometers possess considerably smaller elastic energy according to the formula [23]: $U_{ebot} \sim Gb^2\ln(R/a^*)$, where $G$ is the elastic module of shift, $b$ is the Burgers vector of the misfit dislocation, $a^*$ is the size of the impurity atom. As the linear size $R$ of nanocrystall is much less than the linear size $L$ of bulk samples, the energy of formation of the misfit dislocation in nanocrystall is much more small, than in a bulk crystal. Hence, the process of dopant penetration in the nanocrystall becomes possible, whereas in the bulk material it is impossible. The same mechanism, apparently, is more significant and for the impregnation of the doping impurity in nanocrystall in the form of ultrasmall cluster. Note, that the presented microscopic mechanism of abnormal of the impurity penetration in nanocrystall has not been discussed till now. In case of penetration of magnetic, fluorescent, plasmon etc. labels in the nanocrystall, their concentration and measured amount refer to one nanoparticle are directly connected according to the formula (1) with the size $R$ of the nanoparticle and therefore can serve as a reference point for determination of the metrological parameters of nanoparticle.

4. Conclusions
In present work is constructed the model of dependence of the effect of increase of solubility of the doping impurity in nanocrystall from the nanoparticle size, i.e. from the amount of atoms penetrating into it. The comparison of experiment with the theory allows to receive the parametres essential for the diagnostics of nanocrystalls: "speeds" of decrease of cohesion energy from the nanocrystall size and "speeds" of reduction of surface tension coefficient at the change of concentration of the penetrating impurity. These two characteristics are essentially important in a problem of metrology of the nanocrystalls doping process. The given approach is actual, because multipurpose nanoparticle are used in nanodiagnostics, in medicine, in criminalistics and many other things areas.

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