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Abstract. The experiments on influence of the iron oxide cluster size on the specific magnetic moment are performed. Both free and covered clusters are investigated. The experiments are interpreted on the base of core-shell model by analogy to Weizsäcker formula in the nuclear physics. Metrological parameters for the cluster size investigation are obtained.

1. Introduction

By now, it has been firmly established by various studies that nanostructures (including nanoclusters) demonstrate a significant difference of many physical and physical–chemical properties compared to bulk materials [1,2]. For example, nanoclusters can melt at temperatures both above and below their bulk analogues [3-5]. The ionization energy, the electron affinity [1,6], the photoluminescence lifetime of semiconductor nanoclusters [1,7], etc. can not only differ from those of bulk objects but also depend strongly on the nanocluster size [2-8]. In the radiation physics field the investigations of nanoclusters have been fulfilled too [9-11].

As regards the works in the field of nanocluster magnetic physics, the situation here is considerably rich [12]; some models have been constructed and many experiments have been performed. However, the systematical analysis of experimental situation was yet not performed, but now 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 [1,2]:

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

Using of these two principles concerning the magnetism in nanophysics can be realized by means of "core-shell" idea. In present work the approach is used on the base of experiments and model construction.

Methods of magnetic nanoparticles metrological control are being developed for the usage in magnetic separation, magnetic resonance imaging, magnetic hyperthermia and other applications [13]. Our research deals with iron oxide nanoparticles synthesized by different methods. The proposed model, based on the analogy with nuclear physical Weizsäcker model [14], allows to separate contribution of surface and bulking states into the nanoparticle total magnetic moment.

2. Materials and methods of experiments

The proposed method is applied to iron oxide nanoparticles 4-22 nm synthesized by co-precipitation [15]. The samples were analyzed by X-ray diffractometer DRON2 with $CoK\alpha$ ($\lambda = 0.1789$ nm).Crystal structure was depicted and composition was controlled to avoid multiphase samples. Test results confirm the presence of one phase of the spinel structure, as well as the average particle size of 4-22 nm. Magnetic methods of diagnostics were used: SQUID and ESR [16]. Magnetic moment dependence on temperature and magnetic field was measured and ESR spectra for nanoparticles were obtained at temperatures 4.2- 380K.

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3. Results of experiments

Experimentally we obtained distribution of magnetic nanoparticles in size and determine the average size. The results are in good agreement with X-ray data and the results of transmission electron microscopy. The experimental results can be summarized as follows:

1. Specific magnetic moment of nanoclusters changes monotonically with the increase of a cluster size μ (N) (figure 1).

2. This monotonic dependence of μ (N) can be either increasing or falling for the different samples.

3. At dependencies M (H) absence of hysteresis was observed for all the magnetic nanoparticles, that indicates the absence of the coercive force and, consequently, the superparamagnetic state of nanoparticles.
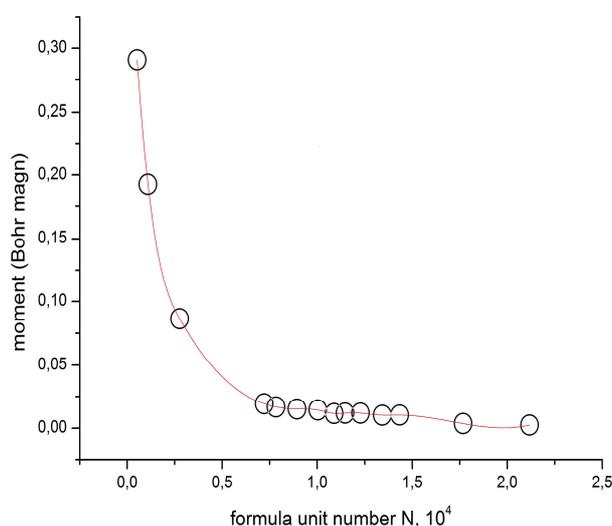

Figure 1. Magnetic moment deviation from formula unit one in iron oxide nanocluster.

According to Langeven expression $M(H)=N\mu_{eff}(cth(\mu_{eff}H/kT)-1/(\mu_{eff}H/kT))$ the average values of effective magnetic moment of one formula unit, the effective magnetic moment of one particle, the average number of formula units in one particle were estimated as in [15-17].The dependence of the average magnetic moment' change per number of formula units in nanoparticle is obtained. In our case, it was falling.

In all presented here results samples were in the form of nanopowder. Moreover investigations of nanoparticles in liquid were carried out. Effective magnetic moment of nanoparticles didn't change sufficiently (values were estimated according to Langeven equation). Magnetic characteristics of nanoparticles on magnetite basis in the form of magnetic liquid, polymer matrix, quarts matrix were also under investigation.

The influence of nanoparticles environment and synthesis conditions on the blocking temperature for nanoparticles Tg were found. The dependence of blocking temperature of the synthesis conditions is revealed.

4. Phenomenological model

Presented experimental data can be interpreted on the basis of several different models: Heisenberg model, Ising model, Weitzecker model and quantum-chemical model. Despite the difference of these models, the basic position they are united is coexistence of different magnetic moments of surface and bulk states: μ_S^0 and μ_V^0. The simplest phenomenological model is a modification of Weitzecker model, used for analysis of specific characteristics of complex nucleus [14]. Generalizing this model on

specific magnetic moment of nanoparticles, we can write:

$$\mu(N) = (1/N) * \left\{ \sum \left(a_j * N^{\chi_j} \right) \right\}, \text{ where } j = 1, 2, \ldots \quad (1)$$

In this expression N is the number of atoms in the cluster, a_j is the phenomenological parameters (in our case μ_S^0, μ_V^0, etc.), χ_j are the rational numbers.

In the simplest case the number of surface atoms is $N^{2/3}$, and the number of volume atoms is $N - N^{2/3}$, so we obtain:

$$\mu(N) = \mu_V^0 + (\mu_S^0 - \mu_V^0) * N^{1/3}. \quad (2)$$

It is obvious that formula (2) is consistent with the qualitative conclusions of the experiments. Indeed, the theoretical dependence of $\mu(N)$ is monotone. It can be either increasing or decreasing depending on which is more: μ_S^0 or μ_V^0. In the estimations of other authors (for example [18]) analysis of isolated cobalt clusters by quantum chemical methods showed $\mu(N)$ decrease with increasing cluster size. This refers to our case when $\mu_S^0 > \mu_V^0$. Another interesting conclusion from formula (1) is that at the transition from a free native cluster to the similar one covered with passivating substance the sign of derivative $d(\mu(N))/dN$ can be changed. This is due to, for example, valence saturation in Tamm surface states and results in the following condition: $\mu_S^0 > \mu_V^0$. Thus, in this simple model, based on a modification of the Weizsäcker formula, μ_S^0 and μ_V^0 are the metrological parameters, and calculating them by measuring $\mu_{exp}(N)$, can get the size of the cluster.

$$N = [(\mu_S^0 - \mu_V^0)/(\mu_{exp} - \mu_V^0)]^3 \quad (3)$$

When the sum expression (1) is used in modified Weizsäcker formula, taking into account the third and subsequent terms of the expansion, of course complicate the expression (3). The developing model is based on assumptions, that surface states are located only in one monolayer of external cluster's atoms, but it can be easily generalized to multilayer location of "magnets" on nanoparticle surface. In this case a third phenomenological parameter appears: a/R, where a is the thickness of the surface layer, and R is the radius of the nanoparticle.

5. Conclusions

The combination of informative methods of magnetic diagnostics with phenomenological model of nanoparticles magnetic properties allows us to obtain the dependence of specific magnetic moment of nanoparticles depending on the number of its constituent magnetic formula units, as well as highlight the contributions to the magnetic moment of bulk and surface states. This approach allows us to formulate the task of metrology as finding constants in each order of Weitzecker sum expression. The work has the prospect, namely, the addition of developed phenomenology to quantum-chemical calculations. Concerning the applications these results may be applied in medicine, materials science and criminological applications [19]. Co-usage of new magnetic methods with well known methods of nanodiagnostics showed its effectiveness.

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