===== **SOLIDS** =====

Magnetic Properties of Nanoparticles of 3d Metals

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Abstract—The influence of size effects on the coercive force, magnetization, and Curie temperature in nanoparticles of 3d metals is considered. It is shown that experimental results obtained during the last two decades provide new information on peculiar magnetic properties of these particles.

INTRODUCTION

The second half of the last century was marked by the development of new fields of science, which have played a significant role in renovation of the educational, research, and industrial levels of society. The development of microelectronics, as well as information science and technologies, has become possible owing to outstanding achievements in obtaining new solid materials with peculiar physical properties.

A new trend in science known as the physics of ultradisperse media appeared in the 1960s at the intersection of metal physics and colloidal chemistry. This trend involves the study of a special class of materials in the form of macroscopic ensembles of small particles with a size ranging from 1 to 100 nm [1]. Peculiar properties of this class of materials are controlled by individual parameters of the particles and the effects of their interaction. The peculiar structure and properties of small particles are of considerable theoretical and applied interest due to their intermediate position between the structure and properties of atoms and solids. The smaller the particle size, the larger the number of specific properties exhibited by them. By the beginning of the 1990s, structural formations with a size of ≤10 nm have also been classified as small particles [2]. These particles are known as nanocrystallites, and ensembles of such particles are referred to as nanocrystalline materials.

Unique physical properties of nanoparticle associated with surface or quantum size effects have become the object of intense investigations. Special attention is paid to magnetic characteristics of nanoparticles. Considerable advances that have been made in this field in recent years are associated with the development of the methods of obtaining and stabilizing magnetic nanoparticles with simultaneous development of physical methods of certification and investigation of such particles.

When condensed media are prepared from such nanoblocks, the interaction between nanoparticles along with their individual features affects the properties of these materials, which leads to a considerable modification and even a radical change in the properties of familiar materials. Specialists predict a wide practical application of such nanocomposites in various fields of modern technology [3, 4].

COERCIVE FORCE

The interest in the influence of size effects on the coercive force of nanoparticles of 3d metals is primarily due to the fact that the value of H_C is the physical limit that determines the possibility of further expansion of the range of practical applications for magnetic nanocrystalline materials.

Transition to One-Domain State

Bulk ferromagnets in the equilibrium (demagnetized) state contain uniformly magnetized regions (domains) separated by regions with a nonuniform distribution of magnetization (domain walls). If we gradually reduce the size of the sample, at some instant its volume becomes commensurate with the equilibrium size of the domains. The main reason for the emergence of one-domain particles is that the relative surface energy of boundary layers between domains increases upon a decrease in the particle size and becomes comparable to (or even higher than) the surface energy of the sample. In this case, the one-domain state is more advantageous from the energy point of view.

A rigorous solution of this problem was obtained in [5]. The condition of uniform magnetization in a particle can be reduced to the requirement that free energy increment ΔF must be positive for any deviation from uniformity,

$$\Delta F = \Delta F_{\text{ex}} + \Delta F_a + \Delta F_d + \Delta F_H > 0,$$

where ΔF_{ex}, ΔF_a, ΔF_d, and ΔF_H are the increments of the exchange energy, magnetic anisotropy energy, mag-
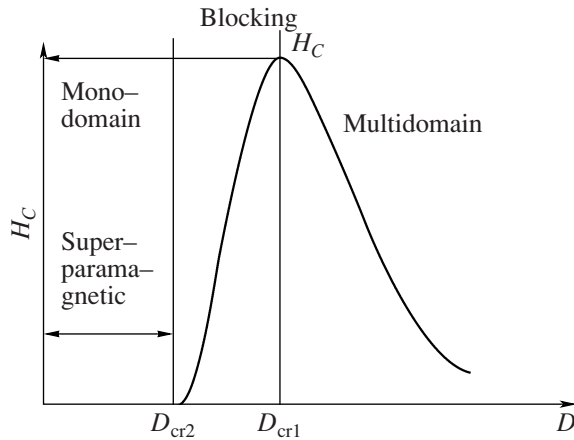
Fig. 1. Dependence of the coercive force on the particle size.

netic field energy of the particle, and Zeeman energy, respectively. In this case, the critical particle size for which the one-domain state is formed is defined as [5]

$$N_B I_S^2 R_C^2 / 6A = \ln\left(\frac{4R_C}{a}\right) - 1, \tag{1}$$

where I_S is the saturation magnetization, R_C is the critical radius, a is the lattice constant, N_B is the demagnetizing factor, and A is the exchange constant.

In the case of weak anisotropy $K/I_S^2 < 1$ (K is the anisotropy constant), we obtain

$$R_C = S_C \frac{A^{0.5}}{I_S}, \tag{2}$$

where S_C is a constant that varies in the interval $1.04 \leq S_C \leq 1.44$. The highest value of S_C corresponds to spherical particles and the lowest value, to cylindrical particles. We will use expression (2) for determining the value of R_C for a spherical Fe particle ($A = 10^{-6}$ erg/cm, $I_S = 1700$ emu/cm^3, and $K = 5 \times 10^5$ erg/cm^3, i.e., $K < I_S^2$), which gives $R_C \approx 84$ Å; i.e., Fe particles of diameter $D \leq 170$ Å pass to the one-domain state, which must lead to an increase in the threshold field of their magnetization reversal. Figure 1 shows the qualitative form of variation of the coercive force of magnetic particles (D_{cr1} is the critical size for which the particle passes to the one-domain state).

The increase in H_C upon a transition to D_{cr1} is associated with a change in the magnetization reversal mechanism, viz., a transition from a displacement of domain walls to a coherent rotation of the magnetic moment; for D_{cr1}, the threshold magnetization reversal field of the particle is given by

$$H_C = \frac{2K}{M_S}. $$

Transition to Superparamagnetic State

It may appear that the coercive force should not change upon a further decrease in the particle size ($D < D_{cr1}$) in the one-domain state. However, the inverse situation takes place—the value of H_C decreases and vanishes at a certain value of D_{cr2} (Fig. 1). To explain this phenomenon, let us consider the results obtained in [6], where the effects of thermal relaxation of magnetization in an ensemble of noninteracting one-domain particles with uniaxial anisotropy were investigated.

If such a system is magnetized in field H and then the field is removed, the residual magnetization will vary in accordance with the law

$$M_r = M_S \exp(-t/\tau), \tag{3}$$

where t is the time after the field removal and τ is the relaxation time of the system in thermodynamic equilibrium. The relaxation time is given by

$$\tau = f_0 \exp(-KV/k_B T), \tag{4}$$

where K is the uniaxial anisotropy constant; V is the volume of a particle; f_0 is the frequency factor, which is equal to the frequency of precession of the magnetic moment of the particle ($f_0 = 10^9$ s^{-1}); k_B is the Boltzmann constant; and T is the temperature. This exponential dependence follows from the fact that the uniaxial anisotropy energy of the particle is a function of the angle between the direction of magnetization and the easy axis. For $\tau/t \leq 1$, the system passes to the superparamagnetic state ($M_r = 0$, $H_C = 0$). In this state, an ensemble of one-domain nanoparticles behaves under the action of heat as a paramagnetic gas of molecules, the only difference being that nanoparticles remain at rest; only the orientation of their magnetic changes spontaneously, and residual magnetization $M_r = 0$ of the system is zero for $H_C = 0$.

Equation 4 can be used to determine critical volume V_{cr} of the particle, for which it passes to the superparamagnetic state at $T = $ const or temperature T_B of transition of the particle to the superparamagnetic state for $V = $ const.

Setting $\tau = 100$ s (relaxation time typical of inductive method for measuring M_r), we obtain

$$V_{cr} = \frac{25 k_B T}{K}, \tag{5}$$

$$T_B = \frac{KV}{25 k_B}. \tag{6}$$

For $H = 0$, the threshold for the transition of the system to the superparamagnetic state is $\Delta E = KV$. For $H \neq 0$, the threshold becomes lower and is given by

$$\Delta E(H) = KV \left[1 - \frac{HM_S}{2K}\right]^2. \tag{7}$$

The coercive force of the particle for $T \neq 0$ is equal to the field in which magnetization reversal threshold $\Delta E(H)$ decreases to a value for which magnetization reversal occurs due to thermal effects during experimental time t.

Equations (5)–(7) lead to

$$H_C = H_{C_0}\left[1 - \left(\frac{V_{cr}}{V}\right)^{1/2}\right] = H_{C_0}\left[1 - \left(\frac{D_{cr}}{D}\right)^{3/2}\right], \quad (8)$$

$$H_C = H_{C_0}\left[1 - \left(\frac{T}{T_B}\right)^{1/2}\right], \quad (9)$$

where H_{C_0} is the coercive force of the particle at $T = 0$.

Equation (8) shows that when the particle size approaches D_{cr}, the value of H_C substantially decreases. This dependence can be used for obtaining nanocrystalline materials with a low coercive force. This gives rise to the problem of determining the value of D_{cr} for nanoparticles of 3d metals. Using the parameters for bulk materials, Bean and Livingston [6] obtained $D_{cr2} \approx 200$ Å for α-Fe particles at $T = 300$ K.

Figure 2 shows the experimental dependences of the coercive force on the particle size, which were obtained in [7] for powders of Fe, Co, and some ferrites.

The value of H_C first increases upon a decrease in the particle size, attains its maximum value for $D \approx 200$ Å, and then decreases. Since the transition to one-domain and superparamagnetic states of 3d metals at $T = 300$ K occurs for approximately the same particle size ($D_{cr1} \approx 170$ Å and $D_{cr2} \approx 200$ Å for Fe), measurements on the Fe and Co powders were carried out at $T = 76$ K to separate these processes. At this temperature, $D_{cr2} \approx 50$ Å for Fe particles.

Thus, we can conclude that for nanoparticle size $D_{cr2} < D < D_{cr1}$ (blocked state; see Fig. 1), the $H_C = f(D)$ dependence is determined by the effect of thermal fluctuations on the magnetic anisotropy, and the coercive force is zero for $D = D_{cr2}$.

Violation of Homogeneity of the Structure

The above data on the effect of the size of magnetic particles on their coercive force were obtained in the 1950s–1960s. A new impetus in the research in this field of physics of magnetic phenomena was associated with advances in the development of new methods for obtaining nanoparticles of 3d metals with $D < 100$ Å with a stringent control of their structure and size dispersion [8, 9].

Numerous experiments demonstrated that the structure of particles changes together with their size, which leads to the formation of a "core–shell" system. The central part of such a "sheathed" particle is occupied by a 3d metal, while the circumference is filled with its oxides, carbides, etc.

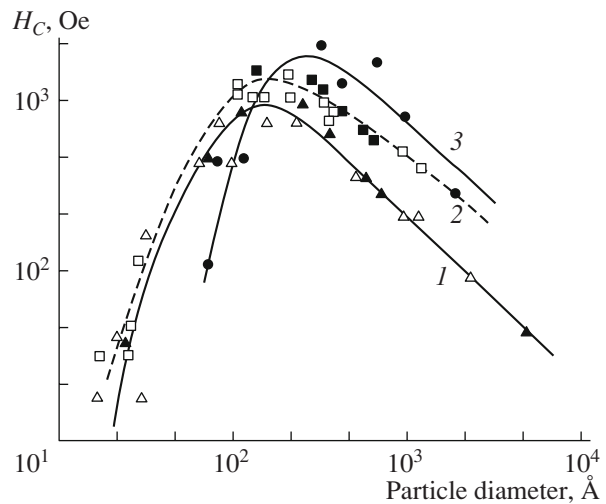Naturally, the finer the particle, the greater the relative volume occupied by the circumference. As a result,

Fig. 2. Dependence of coercive force H_C on the mean size of particles for powders of Fe (*1*), Co (*2*) (at 76 K), and some ferrites (curve *3* corresponds to CoO · Fe$_2$O$_3$ [7]).

the magnetic properties of nanoparticles (in particular, magnetic anisotropy) change considerably.

The table contains the data demonstrating the dependence of K on the size of the "core" of Fe nanoparticles obtained by vacuum deposition in argon atmosphere [8]. The value of K was determined from the law describing the approach towards saturation. The thickness of the "shell" for these particles varies from 12 to 22 Å.

It can be seen from the table that effective anisotropy in nanoparticles exceeds the value of K for bulk α-Fe by almost an order of magnitude, its value increasing upon a decrease in the particle diameter. Naturally, the change in anisotropy of nanoparticles must affect the dependence $H_C = f(D)$. Figure 3 shows the dependence of the coercive force on the diameter of the core of a Fe nanoparticle [8].

The total diameter of a nanoparticle, including its shell, varies from 60 to 180 Å. It can be seen from Fig. 3 that the coercive force at $T = 300$ K decreases to zero for particles with $D \sim 50$–60 Å; i.e., the value of this quantity is much smaller than the value of $D_{cr2} = 200$ Å obtained in [6]. The difference lies in the fact that the parameters of bulk α-Fe were used for calculating the values of D_{cr2}.

Dependence of K on the size of the "core" of Fe nanoparticles obtained by vacuum deposition in argon atmosphere

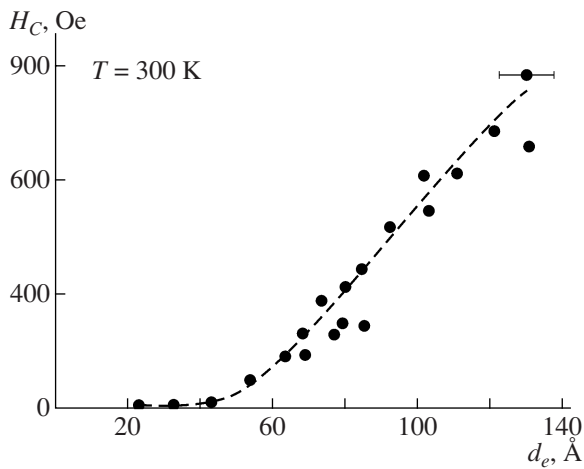| D cores, Å	K, erg/cm^3
33	4.9×10^6
44	3.7×10^6
84	2.5×10^6
121	2.1×10^6

H_C, Oe

Fig. 3. Dependence of the coercive force on the core diameter of a shell α-Fe nanoparticle [8].

Thus, the analysis of the influence of size effects on the coercive force of nanoparticles of 3d metals shows that nanocrystalline materials with a large value of H_C can be obtained not only via a transition from the multidomain to one-domain state, but also using the effects of structural rearrangement of nanoparticles. As a result, for Fe nanoparticles with a diameter of 180 Å, the value of $H_C \sim 1000$ Oe was obtained at $T = 300$ K [10]. This approach is undoubtedly of practical importance for preparing magnetically hard materials; however, the factor responsible for the enhancement of the effective magnetic anisotropy in nanoparticles must be determined in this case. It is necessary to find out whether this enhancement is associated with the interaction of the core and the shell or with the structural rearrangement of surface layers of nanoparticles without a change in their chemical composition [9, 10].

CURIE TEMPERATURE AND MAGNETIZATION

Until the 1980s, the effect of the size of particles on their physical properties was basically studied using only one approach, viz., transition from a bulk body to an atom. It was shown that in particles with spontaneous magnetization, a change in the magnetic moment as compared to bulk analogs is observed [11]. This was attributed to the fact that the magnetic state of particles of a certain size cannot be homogeneous and that such particles exhibit "twisting" of the magnetic moment [12].

The minimal particle size for which ferromagnetism disappears was estimated in [7]. Proceeding from the Heisenberg uncertainty relation $\Delta p \approx \hbar/D_0$ (Δp is the indeterminacy in the momentum of an electron freely moving in the bulk of a particle having a linear size D_0 and $\hbar$ is the Planck constant), we can state that electron energy $\Delta\varepsilon_0$ associated with a limited size of the particle is

$$\Delta\varepsilon_0 \approx \frac{(\Delta p)^2}{2m_e} \approx \frac{\hbar^2}{3m_e D_0^2},$$

where m_e is the electron mass. Equating $\Delta\varepsilon_0$ to exchange energy $A \approx k_B T_C$, where T_C is the Curie temperature, we can determine the critical size of a ferromagnetic particle, for which magnetic ordering disappears even for $T = 0$. For 3d metals with $T_C = 500–1000$ K, this size is $D_0 \leq 10$Å.

Thus, the main conclusions on the effect of the size of nanoparticles on their magnetic properties drawn on the basis of this approach can be formulated as follows: a decrease in the particle size leads to a decrease in the effective magnetic moment, and ferromagnetism of the particles of 3d metals disappears when $D \leq 10$ Å.

At the beginning of the 1980s, another approach to analysis of this problem (i.e., a transition from an atom to a bulk sample) was proposed. The object of investigation was particles whose size is determined by the number of atoms contained in them. It was found that particles containing tens or hundreds of atoms form a new phase of the substance, which differs from solids, liquids, and gases. Such particles were called clusters or microclusters [13].

Many properties of clusters are determined by the fact that they mainly consist of surface atoms. In a densely packed cluster consisting of 20 atoms, only one atom is in the bulk, while for clusters consisting of 100 atoms, not more than 20 atoms are in the bulk. The most stable and, hence, equilibrium clusters are those consisting of certain numbers of atoms known as magic numbers. The defectiveness of the surface of clusters with magic numbers of atoms is minimal, while for remaining atoms it may be significant [2]. To correctly interpret the properties of clusters, we must take into account the fact that clusters lose their metallic properties upon a decrease in their size (i.e., the type of the chemical bond in a cluster depends on its size).

Let us consider the magnetic properties of clusters of 3d metals (saturation magnetization and Curie temperature) in greater detail. The magnetic moments of Fe clusters containing 24–700 atoms (N) were studied in [14]. Clusters with $25 < N < 130$ possessed a magnetic moment of $3\mu_B$ at $T = 300$ K; for clusters with number of atoms $N = 500$, the magnetic moment is approximately equal to the magnetization of bulk α-Fe. Experiments with Co clusters ($N = 20–200$ atoms) revealed that these particles possess a magnetic moment exceeding the magnetic moment of bulk Co even at $T = 300$ K [15].

These results contradict the data obtained using the first approach. An attempt at eliminating this contradiction was made by Kimura [16]. He considered the magnetic moment of a one-domain Fe particle or a cluster containing N atoms in Bohr magnetons per atom using averaging over the entire volume of the particle. He proceeded from the assumption that the magnetic moment of the cluster, which is comparable with the
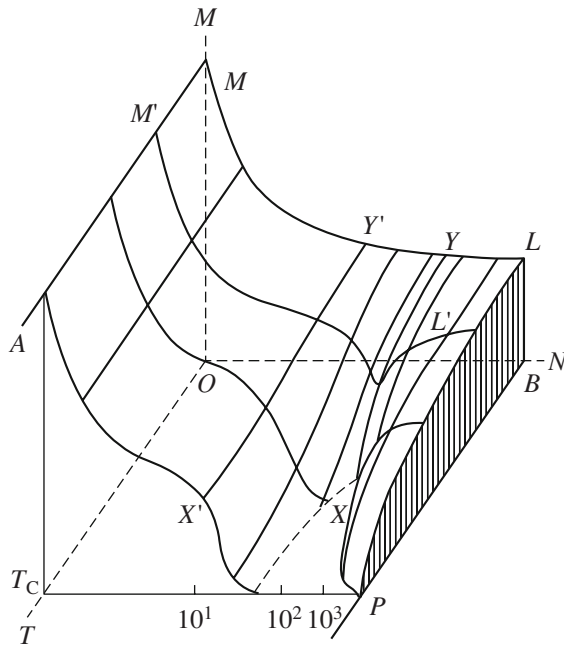
Fig. 4. Phase diagram for Fe clusters [16].

magnetic moment of a bulk solid, is in a thermodynamic equilibrium state, which has an infinitely long lifetime and is independent of the field. When the size of the particle is decreased to a level of several atoms, all spins of the particle are in the ground (high-spin) state. The high-spin state of a molecule and the ferromagnetic state of a particle are equivalent except for the fact that an energy gap between the ground and excited states exists for the molecule. This difference is manifested in the temperature dependence of magnetic properties.

The results obtained in [16] are presented in Fig. 4, which shows the phase diagram for a Fe cluster. The ordinate (0–M) shows the magnetic moment in Bohr magnetons. Point L corresponds to the magnetization of α-Fe at $T = 0$. Abscissas (0–T) and (0–N) reflect the temperature and size of particles (N is the number of atoms). The L–M curve shows the variation of the magnetic moment upon a transition from the bulk sample (point B) to an atom (point M) at $T = 0$ (i.e., we observe an increase in the magnetic moment upon a decrease in N). This result, as well as the results obtained in [15, 16], contradicts the conclusions of [7]. This contradiction can be attributed to the fact that the change in the electron structure of nanoparticles was disregarded in [7], which led to an increase in the exchange interaction parameter. An interesting singularity is observed on the $M(N)$ dependence at temperatures on the order of hundred kelvins (curve L'–M'). The minimum on this curve is associated with a decrease in the role of the magnetic dipole interaction. According to [12], a critical radius exists, such that twisting of the magnetic moment takes place (a small component twisted along the surface is

superimposed on the uniform magnetization) when the radius slightly exceeds the critical value, while for radii smaller than the critical value, magnetization must be uniform.

The diagram in Fig. 4 reflects another peculiar magnetic property of nanoparticles. Although their magnetic moment at $T = 0$ is larger than for bulk Fe, it may become smaller than M_S of α-Fe at $T > 0$ (Y–X curve); i.e., the magnetization of nanoparticles exhibits a stronger temperature dependence. For clusters containing from tens to hundreds of atoms, M_S can even be zero at $T = 500$–600 K. However, the P–X and W–X curves do not mark the true boundary of a transition from the ferromagnetic to the paramagnetic state, but rather denote a smooth transition from the high-spin (ferromagnetic) to the low-spin (antiferromagnetic) state. The true paramagnetic state for such clusters can be attained at higher temperatures.

At the same time, the magnetic moment of clusters with $N \leq 10$ remains practically unchanged in the temperature range from zero to T_C (curves Y'–X'). All these data indicate that it is difficult to mark a sharp boundary between the properties of clusters and a solid.

CONCLUSIONS

Analysis of physical properties of nanoparticles has become an interdisciplinary problem lying on the intersection of many fields of science. In this connection, some contradictions in terminology are encountered. For example, a nanoparticle was defined in [2] as "a small particle having a size of <100 Å and a number of surface atoms differing from the number of bulk atoms by an order of magnitude or even less," while the definition given in [17] is as follows: "a metallic nanoparticle is a spherical object located in a medium of light particles and consisting of 10–10^3 atoms, which has a diameter of 1–10 nm and a ratio of the number of surface atoms to the number of atoms in the bulk equal to or greater than unity ($N_S/N_V \geq 1$)." The former definition was given by a physicist and the latter by a chemist. The basic difference in these definition of the concept of nanoparticle is that that the medium is the latter definition plays the leading role; i.e., the chemist believes that the size properties of nanoparticles are not independent parameters of the object under investigation, but are controlled by its interaction with the surrounding medium.

Indeed, in view of the large number of surface atoms, nanoparticles exhibit a high chemical activity, which complicates the analysis of their properties. However, a detailed description of the properties of nanocrystalline materials in the form of an ensemble of nanoparticles embedded into a discrete medium requires a clear-cut separation of peculiar properties of nanoparticle from the effects of their interaction with the medium. The methods ensuring the solution of this problem have already been developed [14, 15].

At the same time, the interdisciplinary nature of the problem being solved forces the specialist in one field of science to be engaged in allied fields. The Nobel laureate Richard Feynman wrote in 1959 that as soon as soon as physicists develop devices capable of operating with individual atoms, many traditional synthesis methods will be replaced by "atomic assembling." The most interesting thing is that physicists can indeed learn how to synthesize any substance proceeding from its chemical formula [18].

Thus, on the route of studying size effects, physicists anticipate new discoveries and the possibilities for a further development of nanotechnologies.

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