Temperature dependence of the interphase interaction energy of core/shell nanoparticles

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Abstract. Within the framework of the Ising model, in the direct exchange interaction approximation by the “average spin” method, the constant of the interphase exchange interaction $A(T)$, which determines the exchange bias field, is estimated. It was shown that $A(T) \sim e^{-T/T_0}$, where the characteristic temperature $T_0$ is determined by the constant of the exchange interaction between the atoms of the core and the shell.

1. Introduction

The physical properties of nanoscale two-phase particles differ significantly from the properties of similar massive samples, due to the strong influence of the exchange interaction at the interface between the core and the shell. This phenomenon was discovered more than 60 years ago by W. H. Meiklejohn and C. P. Bean [1]. Size reduction down to nanometer scale may drastically change not only the mechanical properties of the material but also its electrical and magnetic properties. These changes are currently widely employed in the field of electronics [2, 3].

Numerous experimental studies have shown that the properties of nanoparticles can vary greatly depending on their composition, shape and size. In [4-7], it was shown that an increase in temperature leads to a decrease in the coercive force and exchange bias. The growth of nanoparticle size affects the magnetic properties the similar way. In [4], using the example of Fe$_3$O$_4$/FeO nanoparticles, the authors showed that the growth of the antiferromagnetic shell has the opposite effect on the characteristics of the particles. It is also worth noting the influence of the environment on the properties of the nanoparticles. For example, in [5], the effects of oxidation of Co nanoparticles as well as interparticle distance on the coercive force were studied. There, the exchange bias was not observed, since the particles were too small. It was shown that the oxidation of nanoparticles led to a sharp increase in the coercive force up to a maximum value as a result of the formation of an oxide shell. A decrease in the distance between nanoparticles led to a decrease in $H_c$ due to an increase in the strength of the dipole–dipole interaction.

The type of temperature dependence of the exchange bias field and the coercive field is determined by many factors. For example, according to the authors of the work [8], the nature of the change in $H_c$ and $H_E$ from the temperature of the NiO nanoparticles depends on the magnetic state of the surface layer. If the state of spin-glass is formed in a thin surface layer, then at temperatures below the temperature of the spin-glass transition $T_{SG}$ we have $H_c(T) \sim e^{-T/T_0}$ and $H_E(T) \sim \left(1 - \frac{T}{T_B}\right)^{\frac{1}{2}}$. $H_E(T) = 0$ at $T > T_{SG}$. The characteristic temperature $T_0$ decreases with an increase in the size of the
nanoparticle, while the blocking temperature $T_B$ increases. In addition, it was noted that the exchange bias field increases linearly with increasing nanoparticle size, and $H_c$ varies nonmonotonously, reaching a maximum at a size of 4 nm.

Authors of the work [9] associate the exponential temperature dependence of the exchange bias field with the presence of a spin-glass state.

It was shown in [10] that in the system of two-layer Co/Co$_3$O$_4$ films, $H_e \sim (1 - (T/T_0)^\alpha$, with $\alpha < 1$. The authors attribute this temperature dependence to the formation of a CoO layer at the interface.

The temperature dependence of the coercive field for systems of pure and oxidized Co nanoparticles with the formation of core/shell Co/CoO nanoparticles is given in [11]. Oxidation of the cobalt changes the character of the temperature dependence, which can be approximated using $H_c \sim (1 - (T/T_0)^\alpha$ (where $\alpha > 1$), to a dependence approximated by the exponent $H_e = e^{-T/T_0}$, which is obviously related with the occurrence of exchange interaction at the interface between Co and CoO. A similar exponential dependence can be used to approximate the temperature change in the exchange bias field in Co/CoO nanoparticle systems [12, 13, 14].

A detailed study of the temperature and size dependences of $H_e$ and $H_c$ of the core/shell Ni/NiO nanoparticles is presented in [7]. It shows that $H_e(T) = e^{-T/T_0}$. An anomalous behavior of $H_c(T)$ is also noted, which consists in the fact that at $T < T_0$ the coercive field has larger values for smaller particles. A similar size dependence of $H_c$ is also observed in Co/CoO nanoparticles [13].

Note that in [15] the exponential temperature dependence of $H_e$ was described using the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction in the ferromagnet/(antiferromagnet, spin-glass) system. The RKKY interaction was used by the authors to describe negative values of the exchange bias field. If $H_e$ does not change sign, is it necessary to use the RKKY interaction as well as the assumption of the presence of a spin-glass phase.

In this work, under the assumption of direct exchange interaction, the temperature dependence of the interphase exchange interaction constant, which determines the exchange bias $H_e$, is estimated without taking into account the possibility of spin-glass formation in a nanoparticle.

2. Model

To assess the influence of the interface between core and shell of nanoparticles on their magnetic properties, along with various types of interaction energies, the interfacial exchange interaction energy is considered [16]:

$$E_{ex} = -\frac{2A_{in}}{d} \cos(\theta^{(1)} - \theta^{(2)}) s$$

(1)

where $A_{in}$ is the interfacial exchange interaction constant, $s$ and $d$ are the surface area and width of the interface respectively, and $\theta^{(1)}$ and $\theta^{(2)}$ are the angles determining the orientation of the magnetic moments of the core and shell.

We consider the interface between core and shell as a set of a monolayer of the shell and a monolayer of the core, with averaged values of the magnetic moments of atoms in the layers of $\mu_1(T)$ and $\mu_2(T)$. For simplicity, we assume that the concentration of magnetic atoms $n$ in the layers is the same. Then, the energy of the interphase exchange interaction can be estimated as follows:

$$E_{ex} = -\alpha \mu_1 \mu_2 nsd \cos(\theta^{(1)} - \theta^{(2)}) s$$

(2)

where $\alpha$ is a temperature independent constant which has the dimension of a volume. Comparing (2) with (1) we have:
where $A = \alpha \mu_1 \mu_2 n d^2 / 2$. To estimate $m_1(T)$ and $m_2(T)$, we use the random interaction field method [17].

According to [18], the distribution function of random interaction fields $H$ on an atom in the monolayer $n = 1, 2$ is determined as follows:

$$W_n(H) = \int \delta \left( H - \left[ \sum_k h(r_k, m_k) \right] \right) \prod_k F_k(m_k) \delta(r_k - r_{0k}) \, dr_k \, dm_k$$

where $\delta(x-x_0)$ the Dirac delta function, $h = h(r, m)$ is the field created by atoms with magnetic moments $m$ located at points with coordinates $r$ on $n$-th atom, $r_{0k}$ are the coordinates of lattice sites, $F_k(m_k)$ is the distribution function of the magnetic moments on the atom in the $n$-th monolayer, which in the approximation of the Ising model for a ferromagnet can be represented as:

$$F_k(m_k) = [\alpha_k \delta(\theta_k) + \beta_k \delta(\theta_k - \pi)] \delta(m_k - m_0)$$

Here $\theta$ is the angle between $m$ and the Oz axis, $m_0$ is the magnetic moment of the $k$-th atom, and $\alpha_k$ and $\beta_k = 1 - \alpha_k$ are the relative probabilities of orientations of the magnetic moment of the atom along ($\theta_k = 0$) and against ($\theta_k = \pi$) the Oz axis, respectively. They can be defined as the average thermodynamic values of the vector $m_k / m_0$:

$$\alpha_k = \frac{\exp \left( \frac{m_0 H}{k_B T} \right)}{\exp \left( \frac{m_0 H}{k_B T} \right) + \exp \left( -\frac{m_0 H}{k_B T} \right)}$$

$$\beta_k = \frac{\exp \left( -\frac{m_0 H}{k_B T} \right)}{\exp \left( \frac{m_0 H}{k_B T} \right) + \exp \left( -\frac{m_0 H}{k_B T} \right)}$$

where $k_B$ is the Boltzmann constant and $T$ is the temperature.

We assume that the atoms are nearest neighbours. Then, the field of exchange interaction between atoms is $h = J \, m \, \cos \theta_k$, where $J = 0$ if the atoms do not belong to the nearest neighbours and $J$ is the constant of exchange interaction. In this approximation, we can construct the characteristic distribution function of the interaction fields:

$$A_n(H) = \left[ W_n(H) \exp(i \rho H) \right] \prod_{\{mk\}} \left[ \{\alpha_k \exp(i \rho J_{mk} m_0) + \beta_k \exp(-i \rho J_{mk} m_0) \} \right]$$

Here the summation is carried out over the nearest neighbours to the atom in the monolayer with the number $n$.

Thus, the distribution function of the interaction fields can be represented as follows:

$$W_n(H) = \prod_{\{mk\}} \left[ \{\alpha_k \exp(i \rho J_{mk} m_0) + \beta_k \exp(-i \rho J_{mk} m_0) \} \right] \exp(-i \rho H)$$

In the "average spin" approximation [18], the average thermodynamic values $\alpha_k$ and $\beta_k$ in expression (6) are replaced by the values $<\alpha_k>$ and $<\beta_k>$, which are averaged using the interaction field distribution function $W_n(H)$. Having determined the relative average magnetic moment $\mu_n$ as the difference between $<\alpha_n>$ and $<\beta_n>$: $\mu_n = <\alpha_n> - <\beta_n>$ and expressing $<\alpha_n>$ and $<\beta_n>$ in $\mu_n$
\[ \langle \alpha_i \rangle = \frac{1 + \mu_\alpha}{2}, \quad \langle \beta_i \rangle = \frac{1 - \mu_\alpha}{2}, \]  

(9)

it is easy to obtain a system of N self-consistent equations with N unknowns, which determines the relationship between the average magnetic moment of the \( n \)-th atom and the average magnetic moments of the atoms of the neighbours:

\[ \mu_n = \int \tanh \left( \frac{m_n H}{k_B T} \right) W_n(H; \alpha_n \to \frac{1 + \mu_\alpha}{2}, \beta_n \to \frac{1 + \mu_\alpha}{2} \right) dH \]  

(10)

According to (8), the distribution functions of random interaction fields in monolayers are:

\[
W_n(H) = \frac{1}{2^z z_n z_t} \sum_{k=0}^{z_n} \sum_{l=0}^{z_t} C_m^k C_m^l (1 + m_\alpha) (1 - m_\alpha) (1 + m_\beta) (1 - m_\beta) \cdot \\
\delta(H - [(2k - z_n)m_n J_{1,2} + (2l - z_t)m_n J_{2,2}]) \tag{11.1}
\]

\[
W_z(H) = \frac{1}{2^z z_n z_t} \sum_{k=0}^{z_n} \sum_{l=0}^{z_t} C_m^k C_m^l (1 + m_\alpha) (1 - m_\alpha) (1 + m_\beta) (1 - m_\beta) \cdot \\
\delta(H - [(2k - z_n)m_n J_{1,2} + (2l - z_t)m_n J_{2,2}]) \tag{11.2}
\]

In relations (11.1) and (11.2), \( C_m^k \) is the binomial coefficient, \( z_{n,t} \) and \( J_{n,t} \) are the numbers of the nearest neighbours and constants of the exchange interaction between atoms in the layer with the number \( n = 1, 2, z_{12} = z_{21} \) is the number of nearest neighbours to the first (second) atom located in the second (first) layer, \( J_{1,2} (J_{2,1}) \) is the exchange coupling constant between atoms in neighbouring monolayers.

Using (10), (11.1) and (11.2), it is easy to obtain a system of equations that determine the average values of magnetic moments in each interface monolayer:

\[
m_1 = \int \tanh \left( \frac{m_1 H}{k_B T} \right) W_1(H) dH = \sum_{k=0}^{z_n} \sum_{l=0}^{z_t} C_m^k C_m^l (1 + m_\alpha) (1 - m_\alpha) (1 + m_\beta) (1 - m_\beta) \cdot \\
\times \tanh \left( \frac{2k - z_n + (2l - z_t)i_{12}}{t} \right) \tag{12.1}
\]

\[
m_2 = \int \tanh \left( \frac{m_2 H}{k_B T} \right) W_2(H) dH = \sum_{k=0}^{z_n} \sum_{l=0}^{z_t} C_m^k C_m^l (1 + m_\alpha) (1 - m_\alpha) (1 + m_\beta) (1 - m_\beta) \cdot \\
\times \tanh \left( \frac{2k - z_n + (2l - z_t)i_{12}}{t} \right) \tag{12.2}
\]

Where \( i_{12} = J_{2,1}/J_{1,1}, i_{12} = J_{2,2}/J_{1,1}, i_{21} = J_{2,1}/J_{1,1} \) and \( t = k_BT/J_{1,1} \) is the relative temperature.

3. Results

We assume that the first layer of the interface belongs to a ferromagnetic metal (for example, Ni, Co, Fe), and the second - to the sublattice of an antiferromagnetic.

In case of Ni/NiO nanoparticles, the number of nearest neighbours in nickel is \( z_1 = 4 \), and \( z_{12} = z_{21} = 1 \). The nickel oxide lattice has a monoclinic syngony with two periods \( a = 2.95 \text{ Å} \) and \( c = 7.23 \text{ Å} \), and if the long side of the lattice with a period \( c = 7.23 \text{ Å} \) is located in the adjacent layer, then \( z_2 = 2 \).

To estimate \( i_2 \), we use the value of the exchange energy in the NiO sublattice of \( J_2 = 16k_B \text{ erg} \) and \( J_1 = J_{Ni \sim 200k_B \text{ erg}} \) [19]. Thus, \( i_2 = 0.08 \), and \( i_{12} = i_{21} \) will be considered as a variable parameter.

The temperature dependences of the relative mean moments \( m_1(T) \), \( m_2(T) \) and the relative interfacial interaction constant \( A_{int}(T)/A \) are calculated using relations (2) - (4) for different values of...
the interfacial exchange interaction energy $J_{12} = J_i^{12}$ and presented in figures 1 and 2. The dependence $A_{\text{in}}(T)$ is approximated by the exponent for $i_{12} = 0.005$:

$$A_{\text{in}}(T) = A \exp \left(-\frac{t}{t_0}\right) = A \exp \left(-\frac{T}{T_0}\right)$$

(13)

The characteristic temperature $T_0 = (J_{11}/k_B) t_0$ expressed through the approximation parameter $t_0$ is determined by the energy of the interphase exchange interaction $J_{12} = J_i^{12}$. Expressing the energy of the exchange interaction of nickel atoms $J_{11} = J_{Ni}$ through the relative Curie temperature $t_c = k_BT_c/J_{11}$, we have: $t_0 = t_c T_0/T_c$. To determine the characteristic temperature, we use the results of [7] where it was experimentally shown that the temperature dependence of the exchange bias field of the hysteresis loop of Ni/NiO nanoparticles is described by the exponent: $H_E(T) \sim \exp(-T/T_0)$, where $T_0 = 9.1$ K. Assuming that $H_E(T) \sim A_{\text{in}}(T)$ we assume $T_0 = 9.1$ K. Using the value calculated by using equations (4) $t_c = 3.05$, the experimental values $T_0$ and assuming that the Curie temperature of nickel depends on size of nanoparticles [19] $T_c(a) = 627(1-(\xi_0/a)^{1/3})$, $\xi_0 = 0.67$ nm, $\nu = 0.7$, we can estimate the size dependence of the parameter $t_0$ for nanoparticles studied in [7] (see table 1).

![Figure 1.](image1.png)  ![Figure 2.](image2.png)

**Figure 1.** Dependence of the relative mean moments $m_1(T)$, $m_2(T)$ on the relative temperature $t = k_BT_c/J_{Ni}$ and the relative energy of the exchange interaction between the atoms of the interface $i_{12} = J_i^{12}/J_{Ni}$. The red line is $m_2(T)$ with $i_{12} = 0.005$, the yellow line with $i_{12} = 0.05$, and the green line with $i_{12} = 0.25$. The blue line is $m_1(T)$ with $i_{12} = 0.005; 0.05; 0.25$.

**Figure 2.** Dependence of the relative interfacial coupling constant $A_{\text{in}}(T)/A$ on the relative temperature $t = k_BT_c/J_{Ni}$. The curve marked by dots is constructed using relations (2) - (4) with $i_{12} = 0.005$, the solid line is approximated by the exponent $A_{\text{in}}(T)/A \sim \exp(-t/t_0)$.

**Table 1.** The approximation parameter $t_0$, the exchange interaction energy $J_{Ni}$ and the energy of the interphase exchange interaction $J_{12}$ for Ni/NiO nanoparticles.

| Nanoparticle size $a$ (nm) | Approximation parameter $t_0$ | Exchange interaction energy $J_{Ni}$ $(10^{-14}$ erg$)$ | Energy of the interphase exchange interaction $J_{12}$ $(10^{-16}$ erg$)$ |
|---------------------------|-----------------------------|----------------------------------------------------------|----------------------------------------------------------|
| 9                         | 0.0454                      | 2.77                                                     | 0.886                                                    |
| 11                        | 0.0451                      | 2.79                                                     | 0.891                                                    |
| 23                        | 0.0446                      | 2.82                                                     | 0.902                                                    |

To estimate the exchange interaction energy of nickel, we use the expression for the reduced Curie temperature $t_c = k_BT_c/J_{11} = 3.05$: $J_{11} = J_{Ni} = k_BT_c/3.05$ (see table. 1). The calculation carried out using
the relations (4) showed that the $t_0$ and $i_{i2} = 3.1 \times 10^{-3}$ values presented in the table correspond to certain values of the interfacial exchange interaction energy $J_{i2}$.

The energy values $J_{Ni}$ and $J_{i2}$ presented in table 1 agree with the results of the experiments $J_{Ni\text{exp}} = 2.7 \times 10^{-14}$ erg (see, for example, [20]) and $J_{i2\text{exp}} = 0.06a_{Ni}^2 \approx 0.8 \times 10^{-16}$ erg [7].

4. Conclusion

Modeling of the temperature dependence of the interphase exchange interaction constant $A(T)$, carried out in the framework of the “average spin” theory, showed that with increasing temperature the constant $A(T)$ decreases exponentially: $A(T) = A \exp(-T/T_0)$. The characteristic temperature $T_0$ is determined by the constant of the exchange interaction between the atoms of the core and the shell $J_{i2}$. Estimates show that for Ni/NiO nanoparticles, the exchange interaction constant between nickel and its oxide is $J_{i2} = 0.9 \times 10^{-16}$ erg, which is consistent with the experimental results [7].

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