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Mössbauer Spectroscopy Study of the Superparamagnetism of Ultrasmall ϵ-Fe_2O_3 Nanoparticles

Yu. V. Knyazev[a, *], **D. A. Balaev**[a], **V. L. Kirillov**[b], **O. A. Bayukov**[a], **and O. N. Mart'yanov**[b]

[a] *Kirensky Institute of Physics, Federal Research Center KSC, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

**e- mail: yuk.iph.krasn.ru*

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The superparamagnetism of an ensemble of ϵ-Fe_2O_3 nanoparticles with a mean size of 3.9 nm dispersed in a xerogel SiO_2 matrix is studied by the Mössbauer spectroscopy method. It is shown that most nanoparticles at room temperature are in the superparamagnetic (unblocked) state. As the temperature decreases, the progressive blocking of the magnetic moments of the particles occurs, which is manifested in the Mössbauer spectra as the transformation of the quadrupole doublet into a Zeeman sextet. The analysis of the relative intensity of the superparamagnetic (quadrupole doublet) and magnetically split (sextets) spectral components in the range of 4–300 K provides the particle size distribution, which is in agreement with the transmission electron microscopy data. The values of the effective magnetic anisotropy constants (K_{eff}) are determined, and the contribution of surface anisotropy (K_S) is estimated for particles of various sizes. It is shown that the quantity K_{eff} is inversely proportional to the particle size, which indicates the significant contribution of the surface to the magnetic state of the ϵ-Fe_2O_3 nanoparticles with the size of several nanometers.

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1. INTRODUCTION

A consequence of reducing the size of magnetic materials to the nanoscale is the change in their magnetic characteristics (e.g., saturation magnetization, magnetic ordering temperature, coercive force, etc.). In addition, the decrease in size is often accompanied by the appearance of superparamagnetism [1–4]. It is manifested so that the magnetic moments of atoms in a nanoparticle are in a magnetically ordered state, but the resulting magnetic moment of a single-domain particle rotates under the action of thermal fluctuations [5]. Such a state of the particle is called unblocked (or superparamagnetic). If the magnetic moment has a certain direction in the magnetic anisotropy field, the particle is in the blocked state.

Since fabrication of monodisperse samples is hardly possible, some nanoparticles in the sample can be in an unblocked state and the other (larger) nanoparticles can be in a blocked state at the same temperature according to the nanoparticle size distribution. The magnetic behavior typical of bulk magnetically ordered substances is characteristic of the blocked state of nanoparticles. The critical parameter—the particle volume V (at the given temperature) or the transition temperature T_{b} (blocking temperature for the given volume) between the blocked and unblocked states—can be obtained using the Néel–Brown relation

$$T_{\text{b}} = \frac{K_{\text{eff}}V}{\ln(\tau_0/\tau)k_{\text{B}}}. \quad (1)$$

Here, K_{eff} is the effective magnetic anisotropy constant including the volume magnetic anisotropy K_V and the surface contribution K_S to the magnetic anisotropy, k_{B} is the Boltzmann constant, τ is the relaxation time of superparamagnetic particles, and τ_0 is the characteristic time of the observation (measurement), which has a clearly defined value for each experimental method.

Since the τ value is extremely small, the fast superparamagnetic relaxation process cannot be studied by the standard static magnetic measurements, having a large characteristic time ($\tau_0 = 10^2$ s). One of the most suitable experimental techniques for studying this phenomenon is Mössbauer spectroscopy with a very short characteristic measurement time $\tau_0 = 2.5 \times 10^{-8}$ s [4], which is determined by the Larmor precession time of the iron nucleus. The Mössbauer spectrum of a nanoparticle in an unblocked state has the form of a quadrupole doublet, which is similar to the spectrum characteristic of a paramagnetic state. However, the magnetic moments of iron cations remain ordered in this case, and the resulting magnetic moment of the particle rotates under the action of thermal fluctuations. Upon lowering the temperature (or increasing the size of the particles), the magnetic moment of the particle is blocked, and the spectrum becomes the usual Zeeman sextet.

Thus, Mössbauer spectroscopy makes it possible to observe the dynamics of superparamagnetism in a number of systems, including various polymorphs of Fe_2O_3 iron oxide [1–3, 6, 7]. For example, the authors of [3] observed the decrease in the superparamagnetic contribution (quadrupole doublet) to the Mössbauer spectrum of hematite at room temperature with the increase in the size of nanoparticles from 5 to 19 nm.

Recently, much attention has been paid to the study of the magnetic structure and properties of systems based on ϵ-Fe_2O_3 oxide, which shows very interesting magnetic properties: a high coercive force (up to 20 kOe at room temperature), electromagnetic radiation absorption in the millimeter wavelength range [6], a high magnetic ordering temperature (500 K for the magnetically hard phase [8–10] and ~850 K for the transition from the magnetically soft phase to the paramagnetic state [11, 12]). This opens up the prospect of applying ϵ-Fe_2O_3 oxide in microelectronics. This iron oxide polymorph exists only in the form of nanoparticles with a diameter of no more than 30 nm or nanowires up to 70 nm in length; with an increase in their size, they are sharply transformed from the ϵ-Fe_2O_3 phase to the α-Fe_2O_3 phase [13–16]. It was shown that the crystal structure of ϵ-Fe_2O_3, unlike other forms of iron oxide, has four nonequivalent iron positions, one of which has a tetrahedral environment. These positions are distinguished well using Mössbauer spectroscopy and, in the case of large particles, are usually described by four Zeeman sextets of equal spectral weight, two of which have very close Mössbauer parameters [8, 10].

Previously, Mössbauer spectroscopy studies were performed on ϵ-Fe_2O_3 samples with the size of more than 10 nm, and the magnetic behavior of nanoparticles involved a trivial order–disorder transition at high temperature [10, 17]. The superparamagnetic behavior on ϵ-Fe_2O_3 samples was observed later in [9, 11]. However, the superparamagnetic state could not be studied in such systems because of a very large dispersion of the nanoparticles. In this regard, a careful study of the superparamagnetism of ϵ-Fe_2O_3 nanoparticles is of fundamental novelty and importance.

Recently, we proposed an original method for the synthesis of ϵ-Fe_2O_3 nanoparticles in a silicate matrix, at which the size characteristics of particles were determined by the pores of the xerogel matrix [18]. In this work, we used the Mössbauer effect technique in a wide temperature range of 4–300 K to study the superparamagnetism of ultrafine ϵ-Fe_2O_3 particles enclosed in a xerogel matrix.

2. SAMPLES AND METHODS

The method for the synthesis of the 5 wt % ϵ-Fe_2O_3 sample in silicon dioxide xerogel is described in detail in [18]. According to the X-ray diffraction data, all observed diffraction peaks belong to the ϵ-Fe_2O_3 structure. The particle size distribution was determined from high-resolution transmission electron microscopy (HRTEM) images obtained on a JEOL JEM 2010 microscope at an accelerating voltage of 200 kV. The interplanar distances measured by HRTEM are consistent with the X-ray diffraction parameters of ϵ-Fe_2O_3 [13]. The Mössbauer spectra of the studied ϵ-Fe_2O_3 samples were recorded on an MS-1104Em spectrometer (Research Institute of Physics, Southern Federal University, Rostov-on-Don, Russia) in the transmission geometry with a Co^{57}(Rh) radioactive source in the temperature range of 4–300 K using a CFSG-311-MESS cryostat with a sample in the exchange gas (Cryotrade Ltd.). The interpretation of the spectra was carried out by varying the entire set of hyperfine parameters using the least squares method in the linear approximation.

3. RESULTS

The histogram of the size distribution of ϵ-Fe_2O_3 nanoparticles is shown in Fig. 1. According to the HRTEM results, the mean size of particles is 3.9 nm. The rather narrow distribution makes it possible to consider this sample as a model sample for studying the superparamagnetism of ϵ-Fe_2O_3 oxide using the Mössbauer spectroscopy method.

The Mössbauer spectra of the sample are shown in Fig. 2. They are superpositions of a magnetically split component (Zeeman sextets) and a quadrupole doublet. A part of the spectrum with a magnetically split

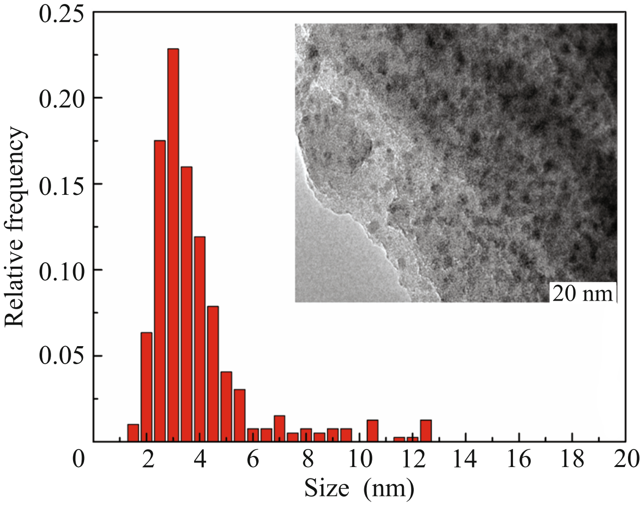

Fig. 1. (Color online) Particle size distribution obtained from the electron microscopy data.

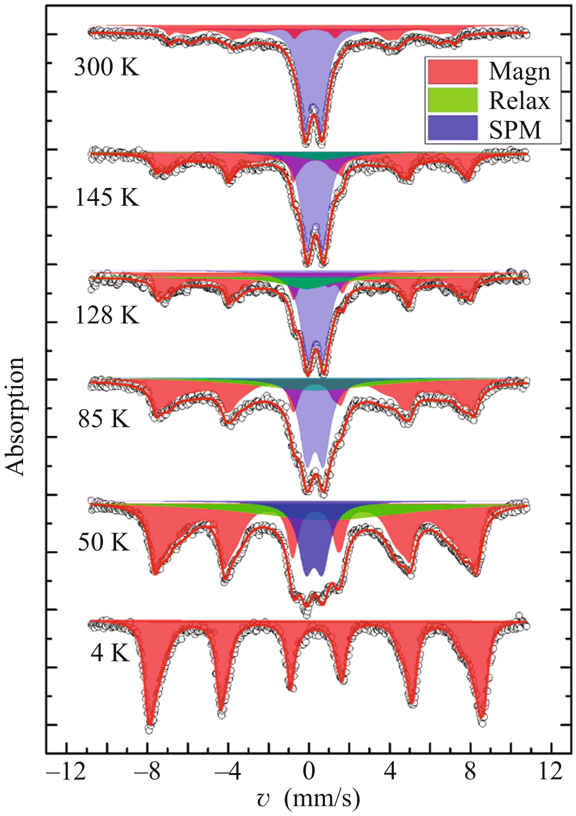

Fig. 2. (Color online) Temperature evolution of the Mössbauer spectra. The solid line shows the result of the interpretation of the spectra. Corresponding components are shaded in color.

hyperfine structure describes particles in the blocked state, and a quadrupole doublet corresponds to particles in the superparamagnetic state, i.e., with the unblocked magnetic moment at the given temperature [9, 18].

Table 1. Relative population A (with an accuracy of 0.03) of the magnetically split and superparamagnetic components in the sample at temperatures of 4–300 K: (Magn) magnetically ordered (blocked) particles, (SPM) particles in the superparamagnetic state, and (Relax) particles for which $\tau = \tau_0$

T, K	Component	$A \pm 0.03$	T, K	Component	$A \pm 0.03$
4	Magn	0.94	128	Magn	0.53
	SPM	0.06		SPM	0.34
				relax	0.13
50	Magn	0.58	145	Magn	0.51
	SPM	0.16		SPM	0.40
	Relax	0.26		relax	0.09
82	Magn	0.47	300	Magn	0.40
	SPM	0.26		SPM	0.60
	Relax	0.28			

The observed temperature evolution of the Mössbauer spectra is due to the size distribution of nanoparticles [2], as well as to superparamagnetic relaxation [19, 20], since it was previously shown that the transition temperature to the magnetically ordered state of nanoparticles with the ϵ-Fe_2O_3 structure is much higher than room temperature and nanoparticles exhibit a superparamagnetic behavior [9, 18].

In the general case, the magnetic energy of nanoparticles includes not only the anisotropy energy but also the energy of the dipole–dipole interparticle interactions [11]. However, in view of a very low concentration of ϵ-Fe_2O_3 in the bulk of the xerogel matrix (5 wt %), we can ignore these interactions and consider the blocking of particles at the decrease in the temperature as an individual characteristic of each nanoparticle of a certain size only under the effect of the magnetic anisotropy, which is taken into account by Eq. (1).

The fractions of the magnetically split (Magn) and superparamagnetic (SPM) components of the spectra is given in Table 1. We note that superparamagnetism leads to the appearance of the relaxation component (relax) in the spectra when $\tau \approx \tau_0$. This component of the spectrum was approximated by a wide single line, and its relative fraction in the spectrum is also given in Table 1. According to these data, the quadrupole doublet at 300 K has a spectral weight of 60%. According to these results and electron microscopy data, 60% (of the total volume) of ϵ-Fe_2O_3 nanoparticles have a diameter of less than 4 nm. These particles in the sample are in the unblocked state. The fraction of such particles, according to the Mössbauer spectra of ϵ-Fe_2O_3, decreases with decreasing temperature, which is caused by the blocking of the magnetic moment of particles of a certain size at the corresponding temperature.

It was found previously that spherical magnetite particles ($K_{\text{eff}} = 7.5 \times 10^5$ erg/cm^3 [1]) with diameter of less than 8 nm exhibit a superparamagnetic behavior at $T = 300$ K (in the absence of an external magnetic field), whereas the critical diameter of hematite nanoparticles under the same conditions is about 14 nm [4]. Thus, among all known iron oxide polymorphs, ϵ-Fe_2O_3 has the smallest critical particle diameter, which indicates a very strong magnetic anisotropy. To estimate its value, we calculated the effective anisotropy constant as a function of the particle size using Eq. (1). In the calculations, the data on the particle size distribution (Fig. 1) were used, and the characteristic time τ was determined by the formula [21]

$$\tau = \frac{a\rho N_{\text{A}} h}{M K_{\text{eff}}}, \tag{2}$$

where $a = 2$ is the geometrical factor of spin rotation in the superparamagnetic state, $\rho = 5$ g/cm^3 is the den-

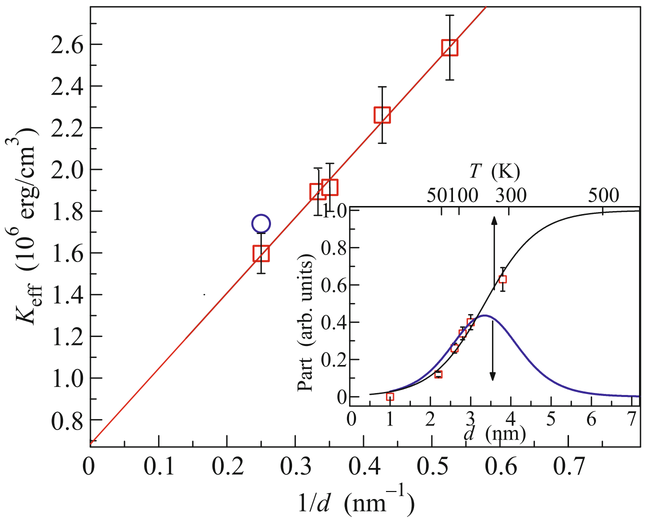

Fig. 3. (Color online) Effective anisotropy constant versus the inverse particle diameter. The squares are the calculation results according to the Mössbauer spectroscopy data; the circles are based on the magnetic measurement data. The inset shows the temperature dependence of the (black solid line) calculated and (squares) measured fractions of the superparamagnetic component in the spectra. The blue line shows the particle size distribution.

sity of ϵ-Fe_2O_3 [9], N_A is the Avogadro number, h is Planck's constant, and $M = 160$ g/mol is the molecular weight of the oxide. The condition $\tau \geq 1/\nu_L = 2.5 \times 10^{-8}$ s is fulfilled for particles in the superparamagnetic state. Here, $\nu_L = 4 \times 10^7$ Hz is the Larmor frequency for iron nuclei [21]. Including the surface contribution through the surface anisotropy constant K_S, the effective magnetic anisotropy constant is given by the expression [1, 9, 22]

$$K_{\text{eff}} = K_V + \frac{6K_S}{d}. \qquad (3)$$

Thus, it is expected that the dependence of the effective anisotropy constant on $\frac{1}{d}$ will be linear. The results with allowance for the experimental error are shown in Fig. 3 (squares with error bars). The effective magnetic anisotropy constant increases with decreasing particle diameter, and the dependence $K_{\text{eff}}\left(\frac{1}{d}\right)$ is linear in accordance with Eq. (3). The circle in Fig. 3 is the effective anisotropy constant obtained from the static magnetic measurements ($T_b = 30$ K, $\langle d \rangle \approx 4$ nm, $\tau = 10^2$ s). It is seen that the quantity K_{eff} is in good agreement with the analysis of Mössbauer spectroscopy data for the sample under study.

The dependence obtained makes it possible to estimate the contribution of the volume (K_V) and surface anisotropy (K_S) to the total anisotropy energy. According to the Mössbauer spectroscopy data, these values are $K_V = 6.8 \times 10^5$ erg/cm^3 and $K_S = 0.06$ erg/cm^2. The volume contribution to the anisotropy energy is much less than that for large particles (according to the magnetic measurements for $d = 25$ nm, $K_V = 5 \times 10^6$ erg/cm^3) [6]. In this case, the value $K_S = 0.06$ erg/cm^2 corresponds to the previous magnetic measurements for ϵ-Fe_2O_3 particles with a mean diameter of 6 nm [9]. However, the relative contribution of surface anisotropy increases with decreasing particle size; as a result, $K_{\text{eff}} = 1.75 \times 10^6$ erg/cm^3 in the sample under study at $d = 4$ nm, while $K_{\text{eff}} = 1.4 \times 10^6$ erg/cm^3 at $d = 6$ nm [9]. Thus, it is obvious that the effect of surface anisotropy on the magnetic behavior of ϵ-Fe_2O_3 increases.

Using the Mössbauer spectroscopy data, we obtained the size distribution of nanoparticles in the sample. To this end, we used the fractions of the superparamagnetic and magnetically split components of the spectra at the corresponding temperature. It was shown in [21] that this distribution can be described using the probability integral of a random variable x (in our case, the diameter of the nanoparticles), which has the form

$$\Phi(x) = \frac{2}{\sqrt{2\pi}} \int_{s=1}^{4^N} e^{\frac{-x^2}{2}} dt. \qquad (4)$$

The probability integral is shown graphically in the inset of Fig. 3 and it shows that 50% of all particles are in the magnetic state at 223 K, which corresponds to $K_{\text{eff}} = 1.7 \times 10^6$ erg/cm^3 in accordance with the calculated dependence $K_{\text{eff}}\left(\frac{1}{d}\right)$ (Fig. 3). This temperature corresponds to the maximum of the calculated distribution. According to Eq. (1), the calculated mean diameter of particles is $d = 3.4$ nm, which is close to the HRTEM value (Fig. 1).

4. CONCLUSIONS

To summarize, we have measured the Mössbauer spectra of an ensemble of ϵ-Fe_2O_3 nanoparticles in a xerogel matrix in the temperature range of 4–300 K. The Mössbauer spectra at 300 K have demonstrated that a large fraction of nanoparticles exhibits a superparamagnetic behavior at room temperature. At the same time, this fraction decreases with decreasing temperature, which is caused by different blocking temperatures for nanoparticles of different sizes in the ensemble. The calculated effective anisotropy constants from the experimental spectra are in agreement with the results previously obtained from magnetization measurements for ϵ-Fe_2O_3 nanoparticles in a silica gel matrix. The resulting dependence $K_{\text{eff}}\left(\frac{1}{d}\right)$ is inversely proportional to the size of nanoparticles, which indicates a large contribution from surface anisotropy. The size distribution of nanoparticles calculated from the fractions of the superparamagnetic and magnetic components in the spectra in the range of 4–300 K is in agreement with the transmission electron microscopy results.

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