Magnetism and magnetic phase transition in nanowires of diamagnetically diluted superstrong magnets $\varepsilon$-$\text{In}_x\text{Fe}_{1-x}\text{O}_3$

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Abstract. The temperature dependences of magnetization of ordered arrays of diamagnetically diluted nanoparticles of superstrong $\varepsilon$-$\text{In}_x\text{Fe}_{1-x}\text{O}_3$ magnets ($x = 0.04, 0.24$) in cooling and heating mode in the permanent magnetic fields of different strengths - strong and weak compared to the magnetic anisotropy field were measured. At temperatures of $150$ K for $x = 0.04$ and $190$ K for $x = 0.24$ a sharp drop in their magnetization is observed, practically to zero. Obtained evidence that the observed magnetic phase transition is accompanied by overturning of magnetization due to spin-reorientation transition of the first kind. The experimental results are described within the magnetodynamic and thermodynamic approaches.

1 Introduction

Iron (III) oxides exist in four basic polymorphic modifications: $\alpha$-$\text{Fe}_2\text{O}_3$ (hematite), $\gamma$-$\text{Fe}_2\text{O}_3$ (magemite), $\varepsilon$-$\text{Fe}_2\text{O}_3$ and $\beta$-$\text{Fe}_2\text{O}_3$, each with different structural, electrical and magnetic properties [1-2]. Hematite is the most stable polymorph. Metastable $\varepsilon$-$\text{Fe}_2\text{O}_3$ has attracted attention in recent years because of its enormous coercive force value up to $20$ kE at room temperature and its ability to absorb electromagnetic waves in the millimeter range [3-4]. All together this provides great potential for the applicability of $\varepsilon$-$\text{Fe}_2\text{O}_3$ for photocatalysis, gas sensors, magnetic/electrical tunable high-speed wireless communication devices and biomedical applications [5-10]. $\varepsilon$-$\text{Fe}_2\text{O}_3$ is not well suited for permanent magnet applications due to its low residual magnetization. It is expected to be used in high-density magnetic storage media requiring low residual magnetization, strong magnetic anisotropy and high coercive force so that thermal fluctuations do not lead to loss of magnetic moment orientation and loss of information [11-12]. Under conditions of strong anisotropy, the magnetic fields required to switch the magnetization direction (and hence to change the bit state of the memory cell) become unacceptably large. This marked the problem of developing a thermomagnetic way to record/erase information when the temperature of the magnetic medium crosses the compensation point or the spin reorientation temperature. Spontaneous spin reorientation...
occurs in ε-Fe$_2$O$_3$ nanoparticles at $T = 154$ K [13]. The spin reorientation temperature in ε-Fe$_2$O$_3$ nanoparticles can be raised up to room temperature by diamagnetic dilution of ε-Fe$_2$O$_3$ by introducing various impurities In, Ga, Al [14-15]. From the above, it can be concluded that studies of the magnetic phase transition parameters in ε-Fe$_2$O$_3$ are a priority for the field of modern materials science engaged in the search and creation of new materials for the element base of spintronics devices. The spin-reorientation transition in ε-Fe$_2$O$_3$ is accompanied by magnetic property anomalies. The dynamic magnetic susceptibility in the vicinity of the transition has a maximum [16], the coercive force passes through a minimum [17]. On this basis, ε-Fe$_2$O$_3$ nanoparticles near the spin-reorientation transition are attractive for use as magnetically soft and magnetostrictive materials.

The aim of the work is to establish the remagnetization mechanisms, to determine the microscopic parameters of the exchange interaction, to separate the high-temperature and low-temperature phase contributions to the total magnetization of nanoparticles, and to search for the magnetodynamic and thermodynamic regularities of the magnetic phase transition in them.

2 Methodology and materials of the experiment

ε-In$_{0.04}$Fe$_{1.96}$O$_3$ nanoparticles (Fig. 1a) of spherical shape with an average diameter of 25 nm and ε-In$_{0.24}$Fe$_{1.76}$O$_3$ (Fig. 1b) of nonspherical shape with length 80 nm and diameter 35 nm were fabricated by using two methods, inverse micelle synthesis and sol-gel method [14-15]. The nanoparticles were grown in a reverse micelle solution containing iron and indium nitrates. Nanoparticles were characterized by mass spectrometry, transmission electron microscopy, and X-ray diffraction [14-15]. The nanoparticles have an orthorhombic crystal structure with four non-equivalent cation positions of Fe$^{3+}$ ions (Fig. 1c). However, one of them has a tetrahedral environment, and the other three have an octahedral environment. Indium ions are substitution impurities and are embedded in the octahedral positions of iron ions.
The temperature dependences of the magnetic moment of nanoparticles were measured in the cooling and heating mode using a vibrating magnetometer of the multifunctional measuring cryomagnetic unit CFMS by Cryogenic Ltd, UK in various constant magnetic fields of strength $H = 0.5 - 50$ kOe in the temperature range.

3 The results of experiments and discussion

3.1 $\varepsilon$-In$_{0.24}$Fe$_{1.76}$O$_3$ nanowires. Magnetodynamic approach
Fig. 2. Temperature dependence of magnetization $M$ of $\varepsilon$-In$_{0.24}$Fe$_{1.76}$O$_3$ nanowires measured in a magnetic field of strength 1 kOe in the cooling mode. The solid line shows the approximation. The dashed line shows the Bloch 3/2 dependence when $\varepsilon = 0$. The dotted line shows the dependence of the angle difference $\phi - \theta$. The inset shows the way the angles $\phi$ and $\theta$ are counted.

At temperatures below $T_C = 414$ K [14] the nanowires are in a magnetically ordered state as evidenced by the magnetic hysteresis loops on the dependence of $M(H)$ with coercivity $H_C = 6$ kOe at $T = 300$ K [18, 19]. At high temperatures $T = 190 - 300$ K an increase in magnetization with decreasing temperature is observed (Fig. 2). In the vicinity of 190 K there is a sharp decrease in magnetization to nearly zero, which remains almost constant with further decreases in temperature. Observed in the vicinity of 190 K magnetic phase transition, accompanied by a sharp decrease in magnetization, also leads to "collapse" of the hysteresis loop on the dependence of $M(H)$, so that at a temperature of $T = 100$ K coercive force takes the value of $H_C = 200$ Oe, i.e., dramatically decreases [18, 19].

In the absence of an external magnetic field in a magnetically ordered crystal with magnetic anisotropy of the "light axis" type, the magnetization vector is directed along the light magnetization axis. Applying a magnetic field at some angle $\phi$ to the light axis causes the magnetization vector to rotate by an angle $\theta$ (see inset in Fig. 2). The magnetization of the sample measured in the magnetometer is the projection of the magnetization vector on the magnetic field direction:

$$M = M_S \cos(\phi - \theta),$$

where $M_S$ is the magnetization of saturation. In magnetically ordered crystals, the temperature dependence of magnetization is described by the Bloch 3/2 formula [5]:

$$M_S(T) = M_S(0) \left(1 - BT^{3/2}\right),$$

where $M_S(0)$ is the magnetization of saturation at $T = 0$ K, $B$ is the spin-wave parameter. The Bloch function 3/2 (2) increases with decreasing temperature, so the sharp decrease in magnetization to nearly zero in the vicinity of 190 K can be due to the multiplier containing a cosine in the expression (1). The angle $\theta$ is a function of the magnetic field and does not depend on temperature. Therefore, the only explanation for the sharp decrease in nanowire magnetization is a change in the angle $\phi$, signifying the rotation of the light magnetization axis (spin-reorientation transition). To describe the dependence of $\phi(T)$, we chose a Heaviside-type step function:
\[ \phi = \frac{\phi_0}{1 + \exp(kT - b)} \]

The solid line in Fig. 2 shows the approximation of the dependence \( M(T) \) by the system of equations (1-3). From the approximation, the parameters \( MS(0) = 11 \, \text{emu/g}, B = 7-10^{-5} \, \text{K}^{-3/2} \) were determined. In Fig. 2, the dashed-dashed line shows the Bloch 3/2 dependence when \( \phi \neq 0 \). The dotted line shows the dependence of the angle difference \( \phi - \theta \), where \( \phi(T) \) is described by expression (2) with parameters \( \phi_0 = 154^\circ, k = 0.3 \, \text{K}^{-1}, b = 51 \).

In the theory of spin waves, the parameter \( B \) included in the Bloch 3/2 formula (2) is related to the spin-wave stiffness coefficient \( D \) by the expression \[ B = 2.612 \frac{\mu_B}{M_S(0)} \left( \frac{k_B}{4\pi D} \right)^{3/2} \]

where \( g = 2 \) is the \( g \)-factor of Fe3+ ions, \( S = 5/2 \) is the spin of Fe3+ ions, \( k_B \) is the Boltzmann constant, \( \mu_B \) is the Bohr magneton. The known values of \( B \) and \( MS(0) \) determined from the approximation of the dependence of \( M(T) \) (Fig. 2) allowed us to estimate the value of spin-wave stiffness \( D = 355 \, \text{meV} \cdot \text{Å}^2 \) (3 -10^9 \, \text{Oe} \cdot \text{cm}^2). The values of spin-wave parameter \( B \) and spin-wave stiffness \( D \) are close to the corresponding values in similar materials: in \( \gamma \)-Fe2O3 nanoparticles \( B = 2.8 \cdot 10^{-5} \, \text{K}^{-3/2}, D = 440 \, \text{meV} \cdot \text{Å}^2 \) [21]; in Fe nanoparticles \( B = 4.8 \cdot 10^{-5} \, \text{K}^{-3/2} \) [22], in Fe3O4 nanoparticles \( B = 3.5 \cdot 10^{-5} \, \text{K}^{-3/2}, D = 320 \, \text{meV} \cdot \text{Å}^2 \) [23].

The spin-wave stiffness coefficient \( D \) is related to the exchange integral \( J \) by the expression \[ J = \frac{Dg\mu_B}{2Sr^2_S} \]

where \( r_s \) is the average distance between Fe3+ ions. Evaluation of the exchange integral by formula (5) gives the value \( J = 9.7 \, \text{cm}^{-1} \). On the other hand, the exchange integral can be estimated in the Weiss molecular field approximation by equating the average energy of the exchange interaction with the energy of thermal fluctuations [20]:

\[ k_B T_C = \frac{2J(S+1)}{3} \]

where \( J \) is the exchange integral calculated by formula (5). The value of the exchange integral \( J = 8.2 \, \text{cm}^{-1} \) turned out to be close to the value determined by formula (5) and close to the theoretical estimates \( J = 3.9 – 5.4 \, \text{cm}^{-1} \) obtained in [14].

3.2 \( \varepsilon \)-In0.04Fe1.96O3 nanowires. Thermodynamic approach
Domain walls usually serve as the germs of the new phase, since they always contain areas in which the direction of magnetization coincides with that in the new phase.

Fig. 3. Temperature dependences of magnetization of $\varepsilon$-In0.04Fe1.96O3 nanoparticles measured during cooling (blue symbols) and heating (red symbols). The solid vertical line indicates the spin reorientation transition temperature $T_{SR} = 150$ K. Dotted vertical lines indicate temperatures $T_1$ and $T_2$, corresponding to the metastable state of coexistence of both phases. The arrows indicate the directions of temperature change. The insets schematically show the directions of magnetization of each of the iron sublattices relative to the crystallographic axes in each of the phases.

At present, the observed magnetic phase transition from a high-temperature phase (HTP) with a high magnetization value to a low-temperature phase (LTP) with a low magnetization value has been described using different approaches and approximations [11, 13, 17]. The key one among them is the magnetodynamic approach discussed above, according to which the observed magnetic phase transition is a spin reorientation transition. This transition is characterized by the fact that, when the temperature changes, the orientation of magnetization with respect to the crystallographic axes (the axes of light magnetization) changes. In the general case, there are three possible phases. Two collinear phases with $\theta = 0, \pi$, $K_1 \geq 0$ (BTF) and $\theta = \pi/2, 3\pi/2, K_1 + 2K_2 \leq 0$ (LTP) with light axis and light plane type anisotropy, respectively [25]. And the angular phase with $\sin^2 \theta = -K_1/2K_2$, $K_1 < 0$ and $K_1 + 2K_2 \geq 0$ anisotropies of the light axis magnetization cone type [25]. Here $\theta$ is the angle specifying the orientation of the magnetization vector in the crystal, $K_1$ and $K_2$ are the first and second magnetic anisotropy constants. If $K_1$ changes sign and $K_2 > 0$ as the temperature changes, both collinear and angular phases can exist in the crystal. Spin reorientation occurs as two phase transitions of the second kind. When $K_2 < 0$, the angular phase is unstable, and the temperature regions of existence of the collinear phases overlap (Fig. 4).
Fig. 4. Schematic of the phase diagram of $\varepsilon$-In$_{0.04}$Fe$_{1.96}$O$_3$ nanoparticles in coordinates ($\theta$, $T$). The areas with sloping shading correspond to each of the phases (LT and HT). The vertical lines indicate the temperatures $T_1$ and $T_2$, corresponding to the metastable coexistence state of both phases. The cross-hatching corresponds to this region. The overlapping boundaries of the regions of phase coexistence at temperatures $T_1$ and $T_2$ are given by the expressions $K_1(T_2) = 0$ and $K_1(T_1) + 2K_2 = 0$ (see boxes).

Spin reorientation occurs as a single phase transition of the first kind. The change in the sign of the anisotropy constants of $\varepsilon$-Fe$_2$O$_3$ with temperature change is attributed to the competition of the single-ion and dipole-dipole anisotropy contributions, which have a different temperature dependence [13].

Another fundamental approach is the thermodynamic approach, which will be discussed below. For this purpose, we will use the model of Slichter and Drickamer [26], usually used to describe the thermodynamics of the transition from the low-spin to the high-spin state of transition metal ions at spin crossing. In Slichter and Drickamer's work, the Gibbs energy is written in the form [26]:

$$G = (1 - \gamma)G_{LT} + \gamma G_{HT} - T S_{mix} + g f$$

Here $G_{LT}$ and $G_{HT}$ – are the Gibbs potentials of HTP and LTP, respectively; $\gamma$ is the reduced quantity of HTP; $T$ is temperature; $S_{mix} = -k_B [\gamma \ln \gamma + (1 - \gamma) \ln (1 - \gamma)]$ is configuration entropy ($k_B$ is Boltzmann constant); $g f$ is interaction energy ($G$ is interaction parameter). The equation of phase equilibrium is obtained by equating the Gibbs energy derivative over the parameter $\gamma$ to zero:

$$\frac{dG}{d\gamma} = -G_{LT} + G_{HT} + \Gamma (1 - 2\gamma) - k_B T \ln \left( \frac{1 - \gamma}{\gamma} \right) = 0$$

or

$$\Delta H - T \Delta S + \Gamma (1 - 2\gamma) - k_B T \ln \left( \frac{1 - \gamma}{\gamma} \right) = 0$$

where $\Delta H$ and $\Delta S$ are enthalpy and entropy changes during the magnetic phase transition.

Solving equation (8), assuming that $G \to 0$, we can write an equation describing the dependence of $\gamma$ on $T$:

$$\gamma = \frac{1}{1 + \exp \left[ \frac{\Delta H (1 - \gamma)}{T} \right]}$$

or

$$\gamma = \frac{1}{1 + \exp \left[ \frac{\Delta H / \Delta S}{T_1} (1 - \gamma) \right]}$$

where $\frac{\Delta H}{\Delta S}$.
The temperature dependence of magnetization $M(T)$ is determined by the contributions of the HTP and LTP magnetizations:

$$M(T) = (1 - \gamma)M + \gamma M_{HT},$$

where $M_{LT}$ and $M_{HT}$ – magnetizations of HTP and LTP, respectively. The $M_{LT}$ and $M_{HT}$ values in the narrow temperature range of the magnetic phase transition can be assumed constant.

Fig. 5 shows fragments of the temperature dependences of the magnetization of $\varepsilon$-In$_{0.04}$Fe$_{1.96}$O$_3$ nanoparticles in the vicinity of the temperature hysteresis, measured in different magnetic fields.

The solid lines in Fig. 5 show the approximation using expression (10). From the approximation, the values of $M_{LT}$ and $M_{HT}$, magnetizations, enthalpy and entropy, as well as other thermodynamic characteristics of the discussed spin-reorientation transition registered in different magnetic fields were determined (Table 1).

**Table 1.** Thermodynamic characteristics of spin-reorientation phase transition in $\varepsilon$-In$_{0.04}$Fe$_{1.96}$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Magnetic Field (kOe)</th>
<th>$T_{1/2}^\downarrow$, K</th>
<th>$T_{1/2}^\uparrow$, K</th>
<th>$\Delta T$, K</th>
<th>$\Delta H$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>107.1</td>
<td>112.7</td>
<td>5.6</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>103.4</td>
<td>110.2</td>
<td>6.8</td>
<td>13.9</td>
</tr>
<tr>
<td>10</td>
<td>95.1</td>
<td>103.5</td>
<td>8.4</td>
<td>17.5</td>
</tr>
</tbody>
</table>

Fig. 6 shows an example of the temperature dependence of $\gamma$ established from the approximation.
Fig. 6. Phase diagram of $\varepsilon$-In$_{0.04}$Fe$_{1.96}$O$_3$ nanoparticles in coordinates ($\gamma$, $T$). The arrows indicate the directions of temperature change. The vertical dashed lines indicate the temperatures $T_{1/2}^{\downarrow}$ and $T_{1/2}^{\uparrow}$, at which $\gamma = 0.5$ (marked by the horizontal dashed line) corresponds to the LT and HT equilibrium. The difference $T_{1/2}^{\uparrow} - T_{1/2}^{\downarrow}$ is the width of the spin reorientation temperature hysteresis $\Delta T$. It follows from Table 1 that under the influence of the magnetic field of strength $H$ there is a linear shift of reorientation temperatures $\Delta T(H) \sim H$ (Fig. 7), in agreement with theoretical notions [25].

**Fig. 7.** Field dependence of the spin reorientation temperature shift $\Delta T$. The solid line shows the approximation by a linear function $\Delta T(H)$. The solid line shows the

4 Conclusions

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LT

$\gamma = 0.5$

$T_{1/2}^{\downarrow}$

$T_{1/2}^{\uparrow}$

$\Delta T$

$\gamma$, arb. unita

$T$, K

HT

$\Delta T$, K

$H$, kOe

$\Delta T$, K

$H$, kOe

5.5 6.0 6.5 7.0 7.5 8.0 8.5

0 2 4 6 8 10

5.5 6.0 6.5 7.0 7.5 8.0 8.5

$\Delta T$, K

$H$, kOe
5 Acknowledgements

References

Note: The references are not fully visible in the image, but they seem to include various scientific articles and conference proceedings.
Magnetoelectric coupling in $\varepsilon$-Fe$_2$O$_3$ nanowires

Large coercivity and low reorientation transition temperature in $\varepsilon$-Fe$_2$O$_3$ nanoparticles

$\varepsilon$-Fe$_2$O$_3$ nanoparticles Journal of Applied Physics 98(4)

Magnetic properties of $\gamma$-Fe$_2$O$_3$

Ultrafine Fe particles in Fe-SiO$_2$


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