Magnetic properties of magnetite nanowire arrays

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Abstract. The contributions of isolated Fe^{3+} ions and the ferrimagnetic subsystem to the total magnetization of Fe_{3}O_{4} nanowires were separated. The magnetic anisotropy of nanowires was determined. The value of the magnetic anisotropy is smaller than the expected value of the shape anisotropy. The decrease in the magnetic anisotropy in nanowires can be explained by the dipole-dipole interaction between individual nanowires in the array. The Verwey transition suppression was found. A phase-inverted line corresponding to the microwave magnetoresistance was identified in the electron spin resonance spectra of nanowires.

1. Introduction

Magnetite (Fe_{3}O_{4}) is one of several iron oxides and a member of the spinel Fd3m symmetry group. The chemical formula for magnetite can also be written as FeO·Fe_{2}O_{3} with one part being wustite (FeO) and another part being hematite (Fe_{2}O_{3}). Magnetic cations Fe^{2+} (3d^{6}, S = 2) and Fe^{3+} (3d^{5}, S = 5/2) are distributed in the crystal lattice according to the following rule: eight Fe^{3+} ions are in tetrahedral positions (A-positions), while eight Fe^{2+} and eight Fe^{3+} ions are irregularly distributed in octahedral positions (B-positions). According to the Verwey theory, A and B cations form two magnetic sublattices, while conduction band electrons jump between Fe^{2+} and Fe^{3+} ions providing the exchange interaction. A competition between the exchange interactions in the negative and positive inter-sublattices results in a ferrimagnetic structure with 4 \mu_{B} per formula unit (\mu_{B} is the Bohr magneton) [1]. A high Curie temperature, T_{C} \approx 850 K, and a spin polarization of charge carriers attract interest to this material, which is promising for spintronics and other industrial applications [2, 3]. Magnetite has become an important ingredient in the formation of metallic/magnetic nanocomposites.

A discontinuous drop in conductance on cooling the sample below \( T_{V} = 100 – 120 \) K results from the metal-insulator transition in magnetite [4]. \( T_{V} \) was called the Verwey temperature and was shown to be dependent on the stoichiometry. The presence of a mixed valence in B sites motivated Verwey and many others, including Mott, to hypothesize that the electronic exchange [Fe^{2+} Fe^{3+}]_{B} \rightarrow [2Fe^{3+} + e^{-}]_{B} between ferrous and ferric ions takes place above \( T_{V} \) (the Verwey-Mott theory). A charge disorder (CD) within a B-site propagating throughout the crystal would explain the metallic nature of magnetite at \( T > T_{V} \), whereas the onset of charge ordering (CO) within a B-site below \( T_{V} \) would explain the observed metal-insulator transition.

A fundamental problem of the Verwey model is the discrepancy between predictions of the two-sublattice model and experimental data. Recently, the incorrectness of the Verwey-Mott concept has been proved irrefutably [5]. It was proposed to introduce a third magnetic sublattice formed by ordered
conduction-band electrons [6]. Nanostructured magnetite particles show changes in magnetic, electrical and other physical properties [7-9]. The reason for the size effect is not clear so far because of many factors which could simultaneously affect physical properties and the Verwey transition (changes in the electron band structure, structural disorder, surface defects and electron states, etc. [10]). Although ESR and SQUID measurements of the magnetite nanoparticles were carried out in previous works by other authors [7-9], the absence of a unified particle shape and size as well as a disoriented magnetic axis in the sample powder make it difficult to interpret magnetic properties. This problem can be avoided in aligned nanowire arrays of unified shape, size and orientation.

This work is aimed at separating the magnetic subsystem contributions to net magnetization in magnetite nanowires, and analyzing the magnetic and electro-transport properties of magnetite of mesoscale size when the nanowire diameter is comparable to or less than magnetic and electrical correlation lengths.

2. Experiment

The Fe₃O₄ nanowires with a diameter \( D \) of \((100 \pm 20) \) nm and an average distance between them \( S \) of 230 nm (figure 1) were grown inside the pores in anodized aluminum oxide (AAO) membranes as a result of decomposition of iron dodecacarbonyl in supercritical fluid CO₂ (30 min duration, 673 K temperature, 37.5 MPa pressure [11]). Structural parameters of the nanowires were determined by TEM microscopy. The temperature dependencies of magnetization, \( M \), were measured using a superconducting quantum interference device (SQUID) magnetometer (MPMX 5XL, Quantum Design) at a field strength of 0 – 1 T and \( T = 5 – 350 \) K. The magnetic field was directed along the nanowire axis. The ESR spectra were measured using a Bruker ESR spectrometer with a rectangular cavity X-band (with a frequency of the microwave field of \( \sim 9.589 \) GHz). The desired sample temperature was maintained using an ESR 900 cryostat (Oxford Instruments) allowing measurements in the 4 - 300 K temperature range.

![Figure 1. A TEM image of the magnetite aligned nanowire array in an AAO membrane.](image)

3. Experimental results and discussion

The ESR spectrum of the nanowire arrays contains four lines \( I – 4 \) at \( T = 4 \) K (figure 2).

![Figure 2. ESR spectra of the nanowires at \( T = 4 \) K (closed symbols) and 280 K (open symbols). The static magnetic field is directed along the axis of nanowires. Line numeration is given in the picture. A phase inverted line \( I \) is shown in the insert.](image)
The intensity of lines decreases with increasing temperature. Line 1 disappears at $T > 15$ K. The center of line 1 is close to zero magnetic field. The deviation of the center of line 1 from zero field is due to the residual magnetic field of the ESR spectrometer. Lines 2 and 4 disappear at $T > 90$ K and $T > 240$ K, respectively. The room-temperature ESR spectrum shows a wide line 3. Lines 3 and 4 are anisotropic, while lines 1 and 2 are isotropic.

3.1. Microwave magnetoresistance. Origin of line 1

Phase inverted ESR lines were observed at zero magnetic field in different materials: Fe/Cr/Fe epitaxial multilayers [12], La$_{0.7}$Sr$_{0.3}$MnO$_3$ films [13], synthetic forsterite [14]. Similar zero field lines can be explained by the following reasons: the resonance of singlet states of non-Kramers Fe$^{2+}$ ions [14], nonresonant electrical losses depending on the magnetic field, i.e. the magnetoresistance of the sample [12, 13]. Microwave absorption in the cavity depends on the sample resistivity. In our experiments, the line shape, its isotropy, and the absence of a field hysteresis of the spectrum allow us to suppose a non-resonant origin of line 1. The phase of the non-resonant line depends on the MR sign corresponding to a negative MR in our experiments (figure 2). The negative MR was observed in the magnetite single crystals at low temperatures in the DC (Direct Current) condition by other authors [1]. The MR of magnetite was explained in the terms of the model assuming the decrease in the t$_{2g}$ orbitals overlapping in the cation-anion pairs under a magnetic field [1]. These changes lead to the partial delocalization of electrons and a negative MR corresponding to the interference of hopping electrons [1]. The model of hopping electrons is applicable to heavily doped disordered semiconductors with electron localization [1]. Polycrystalline magnetite nanowires with a random distribution of Fe$^{2+}$ and Fe$^{3+}$ ions in B-sites are similar to disordered compounds. The exchange interaction is an additional reason for the localization of charge carriers in magnetite.

3.2. Electron paramagnetic resonance of Fe$^{3+}$ ions. Origin of lines 2 and 4

Lines 2 and 4 have the $g$-factors $g \approx 4.3$ and $g \approx 2.0$, respectively. These lines correspond to the resonance of an individual Fe$^{3+}$ ion and were observed in many iron-containing compounds [15]. The isotropic line 2 corresponds to $M_S = +1/2 \leftrightarrow M_S = -1/2$ transitions in individual Fe$^{3+}$ ions in the strong crystalline field of rhombic symmetry with a wide range of parameters [16]. These transitions can be described by the spin-Hamiltonian

$$\hat{H} = g \mu_B HS + D[S^2 - 1/3S(S+1)] + E[S_x^2 - S_y^2],$$

where $g \mu_B HS$ is the Zeeman term, and $D$ and $E$ are the parameters of the axial and rhombic crystalline fields [17]. The isotropic signal at $g = 30/7$ ($g \approx 4.28$ is close to the value observed in our work) corresponds to $D/E = 1/3$ in agreement with theoretical predictions in [17]. The anisotropic line 4 corresponds to $M_S = -1/2 \leftrightarrow M_S = +1/2$ transitions of Fe$^{3+}$ ions in the octahedral crystal field [18]. The approximation of the angular dependence of the $g$-factor of line 4 (figure 3) by a standard formula

$$g^2 = g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta$$

results in the axial symmetry parameters $g_\parallel = 2.018$ and $g_\perp = 2.011$. The sum of integral intensities of lines 2 and 4 obtained by double integration of the ESR spectra is proportional to the magnetic susceptibility of Fe$^{3+}$ ions. The temperature dependence of Fe$^{3+}$ ions follows the Curie law (figure 4(a)). In contrast to lines 2 and 4, the temperature dependence of the integral intensity of line 3 is not monotonous and shows the maximum at a temperature of about 200 K. This fact indicates another origin of line 4.

3.3. Ferrimagnetic resonance. Origin of line 3

The calculations of a spin number by double integration of line 3, and the comparison of this value with that obtained for the reference sample showed that the number of iron ions exceeds the value estimated for non-interacting spins. This fact verifies the ferromagnetic resonance corresponding to line 3. The width $\Delta H$ and the shape of line 3 obey the distribution of anisotropy fields of nanowires of
different diameters. The angular dependence of the effective g-factor of line 3 \( (g = h\nu/\mu_B H_{\text{res}}) \) can be approximated by the equation:

\[
(h\nu/\mu_B g)^2 = [H_{\text{res}} \cos(\theta - \theta_a) + H_a \cos^2(\theta)][H_{\text{res}} \cos(\theta - \theta_a) + H_a \cos(2\theta)],
\]

where \( H_a \) is the anisotropy field, and \( \theta_a \) is the angle between the anisotropy field and the direction of the nanowire axis [19]. As a result of this approximation, the values \( H_a = 175 \) Oe and \( \theta_a = 0 \) were obtained, i.e. the axis of easy magnetization is directed along the axis of the nanowire at \( T = 15 \) K. The equation \( H_a = 2K/M_S \) allows us to estimate the anisotropy constant \( K_{\text{ESR}} = 3.9 \times 10^4 \) erg/cm\(^3\) using the value of saturation magnetization equal to \( M_S = 400 \) emu/cm\(^3\) [11]. This value of the anisotropy constant \( K_{\text{ESR}} \) obtained from high-frequency experiments will be compared below with \( K_{\text{SQUID}} \) obtained in the static magnetic field in a SQUID magnetometer.

The temperature dependencies of the magnetic moment of nanowire arrays, obtained by a SQUID magnetometer are shown in figure 4(b). These temperature dependencies contain two contributions: of the ferrimagnetic system with a blocking temperature \( T_B \approx 200 \) K and of the paramagnetic system of Fe\(^{3+}\) ions, observed at \( T < 25 \) K. This fact is in a good agreement with the above discussed magnetic contributions distinguished by the ESR method. At \( T > 25 \) K, one should discuss the ferromagnetic behavior without a negligibly small paramagnetic admixture. The temperature point of divergence of the temperature dependencies of the sample cooled in zero magnetic field (ZFC) and cooled in a magnetic field (FC conditions) gives the blocking temperature \( T_B \approx 200 \) K (figure 4(a)).

**Figure 3.** The orientation dependencies of the g-factors of line 3 (open symbols) and line 4 (closed symbols) at 15 K. The approximation of the orientation dependences is shown by solid lines. The scheme of the AAO membrane and rotation of nanowires in the resonant cavity is shown in the insert.

**Figure 4.** (a) The temperature dependences of magnetic susceptibilities corresponding to the sum of integral intensities of lines 2, 4 (open symbols) and 3 (closed symbols). The solid line is the approximation by the Curie law. (b) The temperature dependences of the magnetic moment of the nanowire array cooled down in zero magnetic field ZFC (closed symbols) and in a 10 kOe magnetic field FC (open symbols). The magnetic field was directed along the nanowire axis. The approximation of the temperature dependences by a semi-analytical model is shown by solid lines.
In ZFC conditions, the magnetic moments of nanowires are directed along the easy magnetization axis as well as in the opposite direction equiprobably. The magnetic anisotropy fixes the magnetic moment aligned antiparallel to the magnetic field resulting in a zero net magnetic moment at $T \approx 25$ K. Heating the sample up to $T > 25$ K unfreezes the thermally activated reorientation of the magnetic moments along the magnetic field, resulting in an increase in $M$ (figure 4(b)). In FC conditions, a magnetic field of 10 kOe aligns the magnetic moments of nanowires along the magnetic field, resulting in a constant magnetic moment in the temperature range $25 < T < 200$ K (figure 4(b)).

The FC and ZFC temperature dependencies of the magnetic moment were approximated by a semi-analytical model [20] to determine the magnetic anisotropy (FC) (figure 4(b)). A satisfactory approximation of the $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ curves was attained by the following expressions [45]:

$$M_{\text{ZFC}}(T) = N \int_0^\infty \frac{M_s^2 H}{3k_{\text{SQUID}} V} e^{-\nu(T)\delta(T)} \left[ + \frac{K_{\text{SQUID}} V}{k_B T} \left( 1 - e^{-\nu(T)\delta(T)} \right) \right] f(D) dD + \frac{C}{T},$$

$$M_{\text{FC}}(T) = N \int_0^\infty \left( \frac{M_s^2 H}{3k_{\text{SQUID}} V} e^{-\nu(T)\delta(T)} + \frac{M_s^2 H}{3k_B T} \left( 1 - e^{-\nu(T)\delta(T)} \right) \right) f(D) dD + \frac{C}{T},$$

where $N$ is the number of nanowires, $\nu$ is the frequency of the thermally activated reorientation of magnetic moments, $\delta$ is the temperature elevation rate, $M_s$ is the saturation magnetic moment, $H$ is the magnetic field strength, $K_{\text{SQUID}}$ is the anisotropy constant, $V$ is the nanowire volume, $k_B$ is the Boltzmann constant, $f(D)$ is the normal distribution of nanowire diameters $D$, and $C/T$ is the term of the paramagnetic Fe$^{3+}$ contribution following the Curie law. The anisotropy constant $K_{\text{SQUID}} = 1.2 \cdot 10^4$ erg/cm$^3$ was extracted. This value is of the same order of value as determined from the angular dependence of the ferromagnetic resonance.

The shape anisotropy of nanowires can be estimated by the following equation: $H_a = 2\pi M_s = 2.5$ kOe. This $H_a$ value is higher than $H_a = 175$ Oe, determined from FMR experiments. A possible explanation of this fact is the dipole-dipole magnetic interaction between nanowires. The dipole-dipole interaction depends on the filling factor $w = \pi D^2/2S^2$ resulting in the anisotropy field $H_a = 2\pi M_s(1-3w)$ [19] ($S$ is the average distance between nanowires). The normal distribution of nanowire diameters provides the anisotropy field determined by the expression:

$$H_a^{\text{tot}} = \int_0^\infty H_a(D) f(D) dD,$$

where $f(D)$ is the function of the normal distribution of nanowire diameters $D$. If one assumes a saturation magnetization of 400 emu/cm$^3$ as it was determined in [11], the anisotropy field $H_a^{\text{tot}} = 270$ Oe will be obtained. This value is in good agreement with $H_a = 175$ Oe obtained in our FMR experiments. The width of line 3 $\Delta H \sim \Delta H_s \sim 1800$ Oe is close to the experimental value $\Delta H \sim 1600$ Oe.

The temperature dependencies of the integral intensity of FMR line 3 (figure 4(a)), as well as the magnetic moment of the nanowire array, do not contain any specific features at $T \sim 120$ K (figure 4(b)), where the Verwey transition was observed in the bulk sample [1]. Similar results were obtained for nanoballs [21]. The absence of any specific features at $T \sim 120$ K in nanostructured magnetite can be explained by the suppression of the Verwey transition by size effects or stoichiometry change due to oxygen vacancies or antiphase borders.

4. Summary

The lines corresponding to the paramagnetic resonance of individual Fe$^{3+}$ ions and the ferrimagnetic resonance, as well as a phase-inverted line corresponding to the magnetoresistance, were identified in the ESR spectra of the magnetite nanowire array. The absence of any specific features in the
temperature dependence of the magnetic moment at $T \sim 120$ K is a prerequisite for comparing bulk and nanowire properties. The magnetic anisotropy of nanowires was experimentally measured and theoretically proved.

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**References**

[1] Belov K L 1993 *Phys. Usp.* **36**(5) 380
[2] Prinz G A 1998 *Science* **282** 1660
[3] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chutichkanova A Y and Treger D M 1998 *Science* **294** 1488
[4] Piekarz P, Parlimski K and Oleś A M 2007 *Phys. Rev. Lett.* **97** 156402
[5] Margulies D, Parker F, Spada F, Goldman R, Li J, Sinclair R and Berkowitz A 1996 *Phys. Rev. B* **53** 9175
[6] Ziese M and Blythe H J 2000 *J. Phys.: Condens. Matter.* **12** 13
[7] Eerenstein W, Palstra T, Hibma T and Celotto S 2002 *Phys. Rev. B* **66** 201101
[8] Ramos A V, Moussy J B, Guittet M J, Bataille A M, Gautier-Soyer M, Viret M, Gatel C, Bayle-Guillemaud P and Snoeck E 2006 *J. Appl. Phys.* **100** 103902
[9] Kim W, Kawaguchi K, Koshizaki N, Sohma M and Matsumoto T 2003 *J. Appl. Phys.* **93** 8032.
[10] Eerenstein W, Palstra T, Saxena S and Hibma T 2002 *Phys. Rev. Lett.* **88** 247204
[11] Kazakova O, Daly B and Holmes J D 2006 *Phys. Rev. B* **74** 184413
[12] Krebs J J, Lubitz P, Chaiken A and Prinz G A 1991 *J. Appl. Phys.* **69** 4795
[13] Golosovsky M, Monod M, Muduli P K, Budhani R C, Mechlin L and Per P 2007 *Phys. Rev. B* **76** 184414
[14] Tarasov V F 1998 *JETP Letters* **68** 394
[15] Singhal A, Achary S N, Manjanna J, Jayakumar O D, Kadam R M and Tyagi A K 2009 *J. Phys. Chem. C* **113** 3600
[16] Aad E A and Aboukais A 2000 *Catal. Today* **56** 371
[17] Evmiridis N P 1986 *Inorg. Chem.* **25** 4362
[18] Buzare J Y, Silly G, Klein J, Scholz G, Stösser R and Nofz M 2002 *J. Phys.: Condens. Matter* **14** 10331
[19] Ramos C A, Vassalo-Brigneti E and Vazquez M 2004 *Physica B* **354** 195
[20] Tamion A, Hillenkamp M, Tourmus F, Bonet E and Dupuis V 2009 *Appl. Phys. Lett.* **95** 062503
[21] Goya G F, Berquo T S, Fonseca F C and Morales M P 2003 *J. Appl. Phys.* **94** 3520