ISSN 1063-7834, Physics of the Solid State, 2006, Vol. 48, No. 1, pp. 84–87. © Pleiades Publishing, Inc., 2006.
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MAGNETISM AND FERROELECTRICITY

Change in the Critical Exponent of Magnetization in Maghemite in the Temperature Range of the Structural Phase Transition

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Received January 28, 2005

Abstract—The magnetization of maghemite and magnetite thin films is measured as a function of the temperature and orientation of the film. It is established that the temperature dependence of the spontaneous magnetization deviates from the Bloch law at low temperatures and is adequately described by the linear function $M/M_s = 2.2(1 - T/T_C)$ below the Curie temperature T_C. The linear temperature dependence of the magnetization below the Curie temperature is explained by the change in the spin of iron ions in tetrahedral positions due to local deformations of the crystal lattice.

PACS numbers: 64.60.Fr, 64.70.Kb, 75.40.Cx

DOI: 10.1134/S1063783406010173

1. INTRODUCTION

A lot of research attention has been paid to iron oxides because of their possible use in the form of thin films or multilayers for recorders in spintronics. A reduction in dimension makes it possible to modify significantly the elastic and magnetic properties of these oxides. For example, bulk maghemite (γ-Fe_2O_3) at temperatures above 560 K undergoes an irreversible transformation into hematite (α-Fe_2O_3) with a hexagonal structure. Upon introduction of divalent ion impurities in small amounts or upon deposition of maghemite or hematite onto a substrate prepared from magnesium oxide crystals, the temperature of the structural phase transition drastically increases to T = 680–780 K and the cubic phase is retained up to $T < 680$ K (according to x-ray diffraction data, photoelectron spectra, and electron microscope images [1]). Magnetite is characterized by charge-density waves propagating in the [001] direction and orbital ordering at low temperatures [2]. The charge gap between the occupied and vacant lattice sites of Fe^{2+} and Fe^{3+} in octahedral positions is equal to 0.14 eV [3].

A change in the shape of the sample along the direction of propagation of charge-density waves can lead to ejection of the electric charge onto the surface and, hence, to variations in the electrical and magnetic properties at the surface of the sample. This finding has stimulated investigations into the magnetic properties of magnetite thin films.

The structure of γ-Fe_2O_3 can be treated as consisting of three spinel lattices superimposed along the c axis. The tetrahedral and octahedral positions are occupied by trivalent iron ions. The substitution of tetravalent ruthenium for trivalent iron brings about the formation of holes at the iron ions and their selective substitution in the octahedra (according to x-ray absorption data [4]). In this case, the holes are localized in the vicinity of the substitutional impurities; consequently, the magnetic moment of the iron ions is rotated by 24° at the octahedral positions and by 33° at the tetrahedral positions. At temperatures above 600 K, the distribution of the local magnetic field at the Fe^{3+} ions, which was determined from the Mössbauer spectra, is not uniform within a region of 15 nm and, at a temperature of 700 K, involves lines characteristic of α-Fe_2O_3 [4]. The observed effects indicate a partial delocalization of the holes. This inference is qualitatively confirmed by the large dielectric losses observed in pure γ-Fe_2O_3 at these temperatures [5].

The above effects can be responsible for the unusual temperature dependence of the magnetization in the vicinity of the Curie temperature. The purpose of the present work was to determine the temperature dependence of the spontaneous magnetization in thin films of iron oxides.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

For our experiments, single-crystal thin layers (thickness, 0.1–1.0 μm) of magnetite and maghemite were epitaxially deposited using the chemical transport reaction method onto substrates prepared from magnesium oxide (MgO) crystals. Substrates in the form of thin plates were cleaved in the (100) plane of a cubic

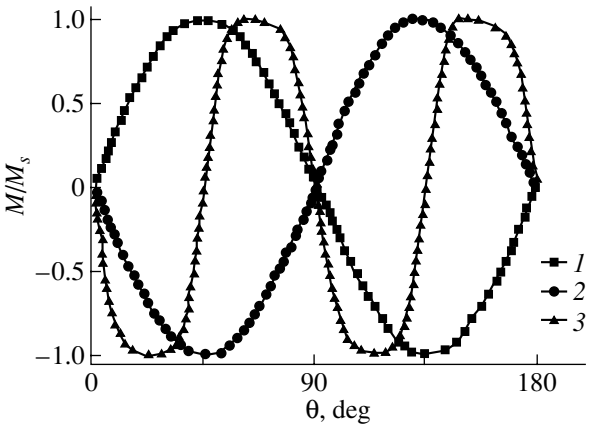

Fig. 1. Orientation dependences of the magnetization measured (*1*) along the plane of the magnetite sample, (*2*) perpendicular to the plane of the maghemite sample, and (*3*) perpendicular to the plane of the magnetite sample.

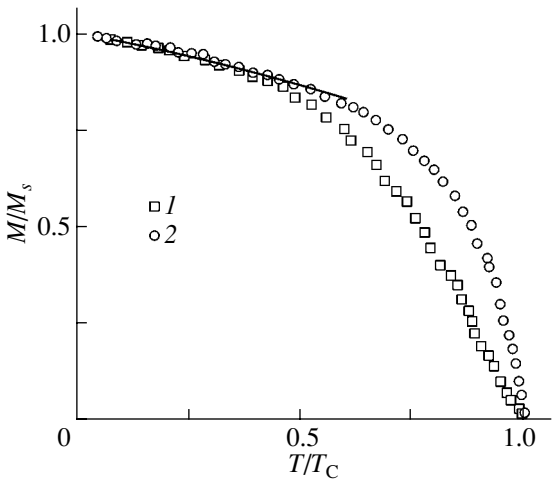

Fig. 2. Dependences of the spontaneous magnetization normalized to the saturation magnetization at room temperature M/M_s on the normalized temperature T/T_C for (*1*) maghemite and (*2*) magnetite. The solid line shows the approximation of the experimental data by the power function $M/M_s = 1 - 0.3(T/T_C)^{1.2}$.

single crystal with a unit cell parameter of 4.21 Å. It should be noted that epitaxial deposition is characterized by oriented growth of a crystal on a crystalline substrate [6]; consequently, single-crystal layers of magnetite and maghemite grow in the (100) plane. The lattice parameters of the samples were determined using x-ray diffraction and turned out to be 8.37 Å for magnetite and 8.35 Å for maghemite.

The anisotropic properties of the samples were examined on a magnetometer in a horizontal magnetic field with a strength of 1–7 kOe for two orientations of the sample (horizontal and vertical orientations of the sample plane). In the former case, we revealed two easy magnetization axes along the [110] crystallographic directions (Fig. 1, curve *3*). In the latter case, the magnetization was aligned parallel to the plane of the magnetite sample (Fig. 1, curve *1*) and perpendicular to the plane of the maghemite sample (Fig. 1, curve *2*).

3. RESULTS AND DISCUSSION

Figure 2 shows the dependences of the spontaneous magnetization (normalized to the saturation magnetization at room temperature) on the temperature normalized to the Curie temperature, which is equal to 685 K for maghemite and 860 K for magnetite. It should be noted that the behavior of the temperature dependences of the spontaneous magnetization, as well as the Curie temperature for the maghemite sample, remains unchanged after several heating–cooling cycles. The experimental data for the magnetite sample are approximated well by the power function $M/M_s = 1.5\sqrt{\tau}$ (where $\tau = 1 - T/T_C < 0.1$) and fall in the range of critical exponents β obtained in the mean-field approximation. For the maghemite sample, the normalized magnetization is adequately described by the linear function $M/M_s = 2.2(1 - T/T_C)$ in the temperature range $600 < T < 685$ K, as can be seen in Fig. 3.

Maghemite has a ferrimagnetic structure with ferromagnetic ordering of ions in octahedral and tetrahedral positions. The sublattices are coupled through antiferromagnetic exchange. As follows from the Mössbauer spectra and structural data, the tetrahedral environment of the iron ions is distorted to the greatest extent upon the phase transition $\gamma\text{-}Fe_2O_3 \longrightarrow \alpha\text{-}Fe_2O_3$. Possibly, the $1e_g4t_{2g}$ term with spin $S = 3/2$ is admixed to the $2e_g3t_{2g}$ ground term of Fe^{3+} ions with spin $S = 5/2$. The difference between the energies of these terms is comparable

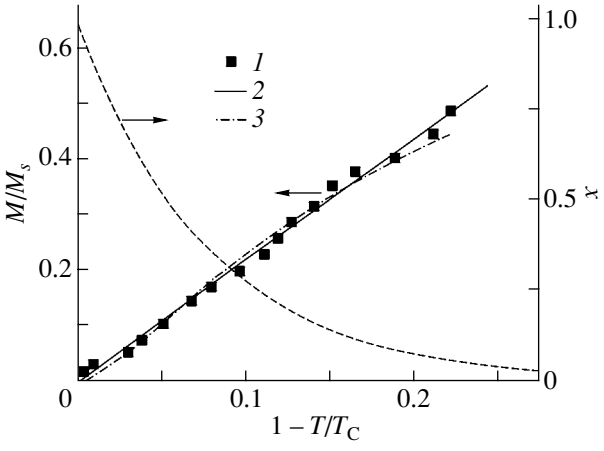

Fig. 3. Dependences of the magnetization of the maghemite sample on the normalized temperature $\tau = 1 - T/T_C$ below the Curie temperature according to (*1*) the experimental data, (*2*) the linear approximation $M/M_s = 2.2\tau$, and (*3*) the nonlinear approximation $M/M_s = (1 - 0.6x)\sqrt{\tau}$. Concentrations of iron ions with spin $S = 3/2$ are plotted along the right ordinate axis.

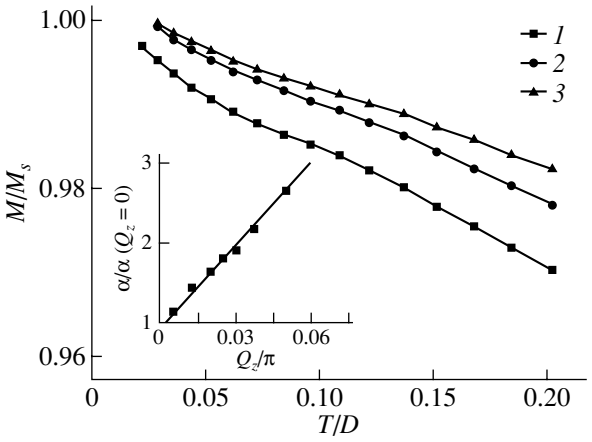

Fig. 4. Calculated dependences of the magnetization on the temperature normalized to the spin-wave stiffness constant with the long-wavelength magnon cutoff Q_z/π = (*1*) 0.007, (*2*) 0.020, and (*3*) 0.038. The inset shows the linear dependence $\alpha/\alpha(Q_z = 0) = 1 + 35Q_z/\pi$ for the exponent in the power function $M/M_s = 1 - A(T/D)^{\alpha}$, where D is the spin-wave stiffness constant.

to the energy gap in the electronic excitation spectrum, which is equal to 2.04 eV for the cubic structure [5]. Local distortions of the structure can give rise to fluctuations of the Coulomb potential and lead to the generation of localized states at the bottom of the upper Hubbard band t_{2g}. The formation of the $1e_g4t_{2g}$ term also favors the emergence of uniaxial anisotropy due to the spin–orbit interaction. For example, the observed perpendicular crystalline magnetic anisotropy considerably exceeds the shape anisotropy of maghemite single-crystal thin layers. For the same reason, the experimentally observed formation of the easy magnetization axis perpendicular to the plane of the layer occurs in magnetite samples upon oxidation of magnetite to maghemite, which is accompanied by tetragonal distortion of the cubic lattice of the magnetite [7]. From analyzing the orientation dependence of the remanent magnetization on the direction of the external magnetic field, we obtained the critical strength of the magnetic field H_c = 5.3 kOe for the magnetization vector lying in the plane of the sample. This is in qualitative agreement with the results obtained from studying nanoparticles, according to which the magnitude of the coercive field increases by a factor of 1.5 as compared to that in the bulk samples [8].

The emergence of the uniaxial anisotropy leads to a change in the low-temperature behavior of the magnetization. The approximation of the experimental data by the power function $1 - M/M_s = A(T/T_C)^{\alpha}$, which is shown by the solid line in Fig. 2, leads to the exponent $\alpha = 1.2$. This value is inconsistent with the Bloch law for all thin films of magnetite and maghemite. All the above changes can be caused by the long-wavelength spin excitation cutoff as the thickness of the film decreases. The average number of magnons n was calculated taking into account the cutoff of the long-wavelength momentum on the z axis ($Q_z \neq 0$) in the low-temperature range $k_BT \ll D$ (where D is the spin-wave stiffness constant) according to the relationship

$$n = \int_0^{\pi} dk_x \int_0^{\pi} dk_y \int_{Q_z}^{\pi} dk_z \frac{1}{e^{D(k_x^2 + k_y^2 + k_z^2)/k_BT} - 1}.$$

It turned out that the average number of magnons n decreases with an increase in the momentum Q_z. The calculated temperature dependences of the normalized magnetization $M/M_s(T)$ are shown in Fig. 4. The approximation of the experimental data by the power function leads to the linearly increasing exponent $\alpha/\alpha(Q_z = 0) \approx 1 + 35Q_z/\pi$ (see inset to Fig. 4). In our case, the thickness of the films varies in the range $120a < L < 1000a$ (where a is the lattice constant) and, correspondingly, the wave vector changes in the range $0.002 < Q_z/\pi < 0.017$, which should result in a significant increase in the exponent. However, as follows from the experimental data, the exponent should decrease. This can be associated with the change in the electronic structure at the surface of the films, which, in turn, can initiate non-Heisenberg exchange.

The model accounting for the change in the spin of iron ions in tetrahedral positions offers a satisfactory explanation for the linear dependence of the magnetization $M/M_s(T)$ on the temperature normalized to the Curie temperature for maghemite. In particular, the spontaneous magnetic moment for maghemite with a spinel structure containing Fe^{3+} ions (S = 5/2) in octahedral positions with the weighting factor y_B = 1/4 and those in tetrahedral positions with the weighting factor y_A = 3/4 is determined to be $M_s(x) = y_A[5/2(1 - x) + x3/2] - y_B5/2$, where x is the concentration of iron ions with spin S = 3/2 in the tetrahedral positions (it is a function of temperature). In our calculations, we used the following expression for the temperature dependence of the magnetization, which was obtained from the expansion of the free energy into a power series of the order parameter: $M/M_s(x = 0) = (1 - 0.6x)(1 - T/T_C)^{0.5}$, where $M_s(x = 0) = 2.5\mu_B$. Among the three (power, logarithmic, and exponential) functions used in our calculations, the best agreement with the experimental results (Fig. 3) was achieved using the function $x(\tau) = \exp(-13\tau)$, which is plotted by the dashed line in Fig. 3.

4. CONCLUSIONS

Thus, it was demonstrated that the linear temperature dependence of the magnetization of maghemite below the Curie temperature is adequately described in the framework of a model accounting for the change in the spin of iron ions in tetrahedral positions due to strong local deformations that, at $T > T_C$, bring about the transformation of the crystal structure. The low-temperature behavior of the magnetization of iron

oxide films deviates from the Bloch law and cannot be explained within the model of the long-wavelength magnon excitation cutoff associated with the size effects.

REFERENCES

1. M. Aronniemi, J. Lahtinen, and P. Hamtojarvi, Surf. Interface Anal. **36** (8), 1004 (2003).
2. I. Leonov, A. N. Yaresko, V. N. Antonov, M. A. Korotin, and V. I. Anisimov, Phys. Rev. Lett. **93** (14), 146 404 (2004).
3. S. K. Park, T. Ishikawa, and Y. Tokura, Phys. Rev. B: Condens. Matter **58** (7), 3717 (1998).
4. O. Helgason, J. M. Greneche, F. J. Berry, and F. Mosselmans, J. Phys.: Condens. Matter **15** (17), 2907 (2003).
5. Y. Suzuki, Annu. Rev. Mater. Res. **31**, 265 (2001).
6. *Crystal Growth: Theory and Techniques*, Ed. by C. H. L. Goodman (Plenum, London, 1974; Mir, Moscow, 1977), Vol. 1.
7. L. I. Rabkin, S. A. Soskin, and B. Sh. Epshteĭn, *Ferrites: Production, Properties, and Plant Technology* (Énergiya, Moscow, 1968), p. 145 [in Russian].
8. X. Batlle and A. Labarta, J. Phys. D: Appl. Phys. **35** (17), R15 (2002).

Translated by V. Artyukhov