Magnetization-induced second-harmonic generation in epitaxial magnetite thin films $Fe_3O_4/MgO(100)$

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(Presented on 1 November 2005; published online 20 April 2006)

The surface magnetic and structural properties of magnetite thin films have been probed by nonlinear second-harmonic generation optical method in high- (centrosymmetric, O_h) and low- (noncentrosymmetric, C_1) temperature phases. A model taking into account the cubic magnetocrystalline anisotropy and magnetic symmetry reduction due to a magnetically modified surface layer is supposed to describe the azimuth variations of the nonlinear response. The metal-isolator transition (Verwey) manifests itself in an increase of nonlinear response ($\sim 25\%$) and a decrease in magnetic contrast ($\sim 50\%$). © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2167353]

Magnetite Fe_3O_4 is a strongly correlated valence-mixed transition-metal compound. Due to electron correlation it displays many interesting phenomena, the most prominent of which is the metal-insulator transition (Verwey) at $T_V = 125$ K.[1] Promising high values of the spin polarization[2] at the Fermi-level magnetite thin films recently attract a lot of attention as potential material for spintronic applications. Therefore, surface and interfacial magnetic and structural properties of these films are of considerable interest, but remain unclear in many aspects up to now. These are the surface stoichiometry,[3] issues of surface termination and reconstruction,[4,5] the presence of magnetically "dead"[6] or modified layers, and their dependence on grown conditions. The anomalous magnetic behavior of magnetite films associated with the existence of high-density structural domains and antiphase domain boundaries[7] also attracts enhanced interest.

In this work we focus on the investigations of the surface magnetic and structural properties of magnetite thin Fe_3O_4/MgO films and their changes across the Verwey transition. For this purpose, we employed the optical method of magnetization-induced second-harmonic generation (MSHG), which is proved to be a powerful tool to study electronic and magnetic properties of surfaces and interfaces in thin films and multilayers.[8] The second-order nonlinear optical properties of magnetite have not been studied so far, whereas third-order nonlinear properties of magnetite films have been reported in Ref. 9.

Magnetite Fe_3O_4 films with a thickness of 50 nm were grown by molecular-beam epitaxy (MBE) on MgO(100) substrates maintained at 250 °C in an O_2 atmosphere of 1×10^{-7} mbar during evaporation. In situ reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) revelled $c(2\times 2)$ reconstruction of the $Fe_3O_4(100)$ surface.[10] After preparation the sample was taken out from the UHV chamber, exposed to air, and mounted onto a sample holder. The temperature dependencies of the conductivity and magnetization were measured by a two-point probe method and superconducting quantum interference device (SQUID) magnetometry, respectively. A sharp Verwey transition was observed around 118 K (see Fig. 1).

Azimuth variations of odd $\Delta I(2\omega)=I(H+)-I(H-)$ (MSHG) and even $I^e(2\omega)=[I(H+)+I(H-)]/2$ on magnetiza-

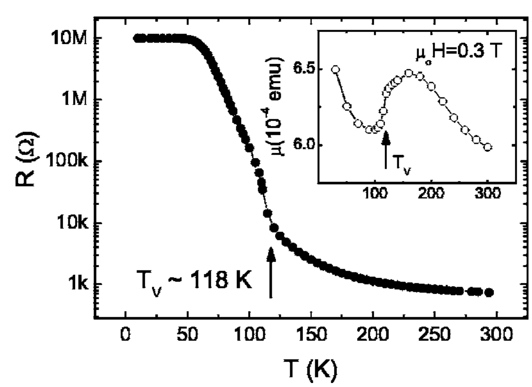

FIG. 1. Electrical resistivity vs temperature in FE_3O_4/MgO films. Inset shows temperature dependence of magnetization.

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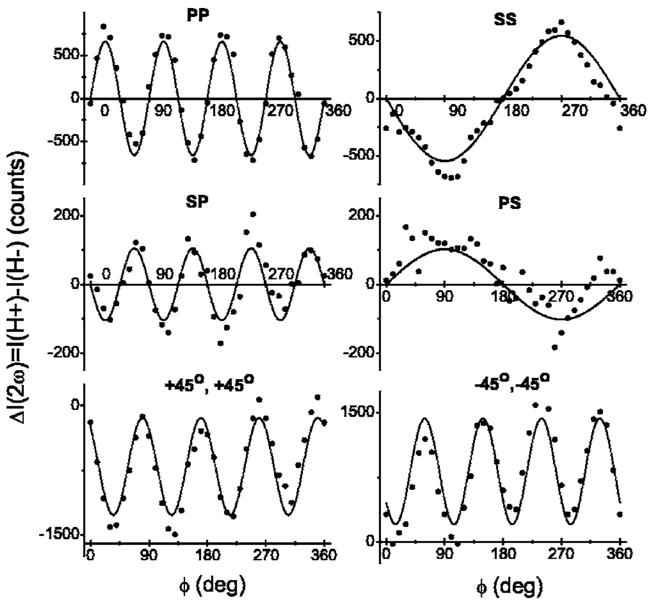

FIG. 2. Azimuthal variations of magnetically induced SHG for different polarization combinations of input (ω) and output (2ω) light in Fe_3O_4/MgO(100) films.

tion contributions to the second-harmonic generation (SHG) signal were studied in the reflection geometry for a nearly normal ($\theta \sim 5°$) incidence of light using a Ti:sapphire femtosecond laser in the spectral region of the charge transfer ($Fe^{2+} \rightarrow Fe^{3+}$) (Ref. 11) transitions for different combination of incoming (E=1.55 eV) and outgoing (E=3.1 eV) light. The light was focused into a spot of about 300 μm and the incidence light power was about 30 mW. The reflected SH was received by a photomultiplier and measured by a photon counting technique. The rotational anisotropy measurements were carried out at 300 K by rotating the sample around the normal of the film plane $\mathbf{Z}$. Magnetic fields H up to 0.3 T were applied in the film plane $\mathbf{H} \perp \mathbf{Z}$ and in the plane of light incidence $\mathbf{H} \| \mathbf{X}$ (longitudinal geometry). Temperature studies of SHG were performed within an optical cryostat.

The azimuthal variations of the MSHG signal ΔI for different combinations of input (ω) and output (2ω) polarizations of the light are compiled in Fig. 2. Taking into account the large value of the absorption coefficient at $2\omega(\sim 2\times 10^5\ \mathrm{cm}^{-1})$,[12] as well as the fact that the coverage with a thin (2 nm) protective layer of MgO essentially weakens the MSHG signal, we consider the nonlinear response to arise from the surface only. For *pp* and *sp* configurations ΔI is proportional to $\sim \sin 4\phi$, where ϕ is the angle between the magnetic field $\mathbf{H}$ and the [100] direction of the film. In contrast to that in *ps* and *ss* configurations ΔI is described by first-harmonic $\sin \phi$. The amplitudes of ΔI for *pp* and *sp* and also for *ps* and *ss* configurations differ in sign.

The magnitude of the magnetic contrast defined as $\rho = \Delta I / I^e$ is remarkable and reaches its maximal value about 80% for *ss* configuration. In intermediate configurations (45°,45°) and (−45°,−45°), ΔI is described by a combination of a constant and a fourth-harmonic term $\sim \sin 4(\phi \pm \delta)$. The sign of both constant term and phase shift (δ) in these configurations is different.

Because Fe_3O_4 is centrosymmetric at T=294 K bulk electric dipole contribution to SHG is forbidden and the symmetry breaking at the surface and high-order mechanisms reflecting quadrupole or magnetic dipole symmetries act as sources of SHG. For the (100) face the surface nonmagnetic contribution to SHG is described by a polar tensor χ_{ijk} of rank 3, taking for the symmetry class C_{4v} the nonzero components $\chi_{xzx}=\chi_{yzy}$ and $\chi_{zxx}=\chi_{zyy}$, χ_{zzz}. A magnetically induced contribution in longitudinal geometry is described by a tensor χ^m_{ijk}, which contains ten nonvanishing elements, whereby five of them are even and five odd under magnetization reversal. For $\mathbf{M}\|\mathbf{X}$ the elements odd in magnetization are χ^m_{yxx}, χ^m_{yyy}, χ^m_{yzz}, χ^m_{zyz}, and χ^m_{xxy}, but for $\mathbf{M}\|\mathbf{Y}$ these are χ^m_{xxx}, χ^m_{xyy}, χ^m_{xzz}, χ^m_{zxz}, and χ^m_{yxy}. The elements even in magnetization sum up with the surface nonmagnetic ones, causing the last ones to become independent. Using the general expression,[13] which relates the components of light at frequency 2ω in reflection and components of fundamental beam, we have for SHG intensities

$$I^{\pm}_{pp} = A(|\alpha_{s1}|^2 + |\chi^m_{xxx}|^2 M_y^2 \pm 2|\alpha_{s1}||\chi^m_{xxx}|\cos\Delta_1 M_y),$$

$$I^{\pm}_{ps} = A|\chi^m_{yxx}|^2 M_x^2,$$

$$I^{\pm}_{sp} = A(|\alpha_{s2}|^2 + |\chi^m_{xyy}|^2 M_y^2 \pm 2|\alpha_{s2}||\chi^m_{xyy}|\cos\Delta_2 M_y),$$

$$I^{\pm}_{ss} = A|\chi^m_{yyy}|^2 M_x^2,$$

$$I^{\pm}_{45,45} = A(|\alpha_{s1}|^2/2 \pm |\alpha_{s1}||\alpha_{m1}|\cos\Delta_3 M_x \pm |\alpha_{s1}||\alpha_{m2}|\cos\Delta_4 M_y),$$

$$I^{\pm}_{-45,-45} = A(|\alpha_{s1}|^2/2 \mp |\alpha_{s1}||\alpha_{m1}|\cos\Delta_3 M_x \pm |\alpha_{s1}||\alpha_{m2}|\cos\Delta_4 M_y),$$

where A is coefficient proportional to I^2_ω, $\alpha_{s1}=\Theta[(\chi_{xzx}+\chi_{yyz})/n+N(\chi_{zxx}+\chi_{zyy})/2]$, $\alpha_{s2}=N\Theta\chi_{zyy}$, N and n are refraction indices at 2ω and ω correspondingly, $\alpha_{m1}=[\chi^m_{xxy}+(\chi^m_{yxx}+\chi^m_{yyy})/2]$, $\alpha_{m2}=[\chi^m_{yxy}+(\chi^m_{xxx}+\chi^m_{xyy})/2]$, $\cos\Delta_{(1-4)}$ accounts for the relative phases of complex tensor elements, and the signs + or − correspond to the positive or negative direction of magnetic field. It follows from equations above that in *pp* and *sp* configurations ΔI is related to the magnetization component M_y, which is perpendicular to the applied magnetic field $\mathbf{H}$. The azimuthal variation of M_y is expressed by $M_y = \beta \sin 4\phi$. The existence of this component follows from the cubic magnetic anisotropy of magnetite and correlates with torque measurements of Fe_3O_4(100) thin films.[14] The parameter β depends on the magnetic anisotropy constants K_1 and K_2 and magnetic field as $1/H$. In configurations (45°,45°) and (−45°,−45°) the component $M_y = \beta \sin 4\phi$ provides an azimuthal variation of $\Delta I \sim \sin 4\phi$ of the same amplitude, but without any phase shift (δ=0). The component M_x in these configurations gives rise to a constant term of opposite sign in accordance with the experiment. For explanation of the nonzero value of δ we should take into account also an azimuthal variation of the component M_x in the form $M_x = M_x^0 + \xi \sin^2 2\phi$, where M_x^0 is the average magnetization for the magnetic field $\mathbf{H}$ along the [100] direction. The presence of such a variation of M_x can be attributed also to the cubic magnetic anisotropy of Fe_3O_4. The magnetization process for a magnetic field along the middle [110] and hard [100] directions is characterized by different magnetic susceptibilities. Therefore, the magnetization value differs for the same magnetic field **H** applied along the [110] and [100] directions. It should be noted that in contrast to the bulk magnetite thin films reach saturation only in very high magnetic fields—much larger than $H=0.3$ T used in this experiment.

In *ss* and *ps* configurations the azimuthal variations of components M_x and M_y should not lead to any magnetic contrast. The $\Delta I \sim \sin\phi$ experimentally observed in these configurations can be explained on the basis of set of equations above by accounting for additional magnetization $\mathbf{M}_1$ (or antiferromagnetic moment) directed perpendicular to [100], which is strongly pinned and cannot be switched by an external field. Such pinning could take place at the antiphase boundaries. In this case the components M_{1x} and M_{1y} vary upon rotation of the film as $M_{1x}=M_1 \sin\phi$ and $M_{1y}=M_1 \cos\phi$. The interference of magnetic SHG signals induced by magnetizations **M** and magnetization $\mathbf{M}_1$ gives rise to the appearance of $\Delta I \sim \sin\phi$. In *pp* and *sp* configurations the magnetization $\mathbf{M}_1$ does not contribute to ΔI. Another source of the first harmonic in ΔI may be related to the presence of surface areas with a symmetry lower than C_2. In this case, the nonmagnetic contribution to SHG from these areas can involve terms proportional to $\sin\phi$. The interference of magnetic SHG induced by the susceptibility χ^m_{yyy} in *ss* configuration and χ^m_{yxx} in the *ps* configuration with a low-symmetry nonmagnetic contribution also results in $\Delta I \sim \sin\phi$.

To study the structural and magnetic changes across the Verwey transition we have measured the temperature dependences of the ρ and I^e (Fig. 3). The measurements have been performed in *ss* polarization configuration for a fixed sample azimuth close to the maximum of magnetic contrast at $\phi=90°$. The Verwey transition manifests itself in an increase of the $I^e \sim 25\%$. This increase is accompanied by a $\sim 50\%$ decrease of ρ. On the first sight, one may expect a stronger increase of the I^e, since the Verwey transition is known to be a transition from a high-temperature centrosymmetric (O_h) to a low-temperature triclinic (C_1) (Ref. 15) phase, where a strong contribution from the bulk should be expected. However, taking into account very small changes in angles and bondings giving rise to a distortion of only 0.2° along the (110) axis, this result seems to be plausible. The $\sim 50\%$ drop of the magnetic contrast observed is much bigger than the drop of the magnetization moment observed in SQUID measurements (Fig. 1). This fact can be explained by the difference of dc and magneto-optical susceptibilities.

We have studied the second-order nonlinear response of magnetite thin films in high (centrosymmetric) and low (non-centrosymmetric) phases in an external magnetic field. We found that the azimuthal dependences of odd and even on magnetization contributions to SHG cannot be described by the simple picture of an isotropic layer corresponding to a (100) cubic surface. We propose a model taking into account the cubic magnetocrystalline anisotropy and the presence of magnetically or structurally modified surface layers. This model allows us to satisfactorily describe the experimental results. The modification at the surface could be due to a certain type of surface termination or a coexistence of different magnetic iron-oxide phases appearing due to ambient air exposure.

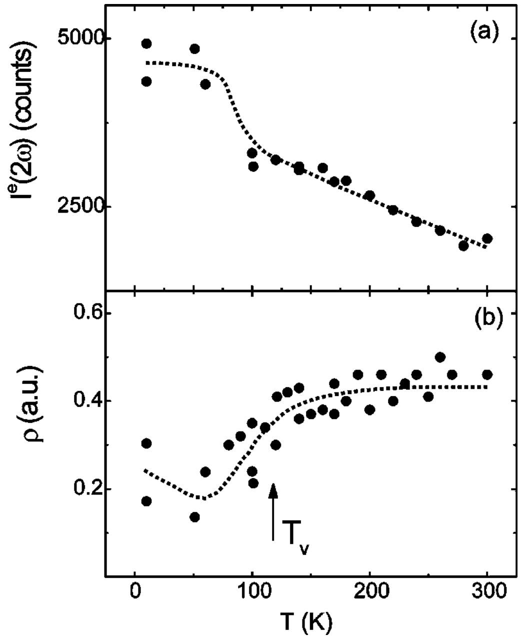

FIG. 3. Even on magnetization contribution to SHG (a) and magnetic contrast (b) vs temperature in *ss* configuration. Dashed line is a guide for the eyes.

The authors would like to thank U. F. Hillebrecht for fruitful discussions and help. This work for one of the authors (B.B.K.) was supported by the Russian Foundation for Basic Research (Grant No. 05-02-16451-a).

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