Surface Magnetism of Ultrathin γ-Fe Films Investigated by Nonlinear Magneto-optical Kerr Effect

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By magnetization induced second harmonic generation (MSHG) the surface magnetization of fcc Fe films on Cu(100) is studied. The tetragonally distorted phase below 4 monolayers (ML) and the relaxed fcc phase above 4 ML can unambigously be distinguished by different average MSHG signals. Nearly constant asymmetry of the second harmonic intensities between 1.3 and 10 ML proves, to a good approximation, thickness independence of the surface magnetization irrespective of the phase transition at 4 ML. The nonlinear Kerr angle amounts to 4°. [S0031-9007(96)00700-4]

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Recently ultrathin fcc Fe films on Cu(100) received much interest because of their complex structural and magnetic properties [1–8]. Nonmagnetic as well as ferromagnetic and antiferromagnetic phases of fcc Fe are predicted by theory [9–11] with largely varying magnetic moments depending on the atomic volume. Experimentally, both ferromagnetism and antiferromagnetism have been observed in completely different systems as Fe films on Cu(100), Cu_3Au [12], and Cu/Au alloys [13] grown at various temperatures, in superlattices [7], or even within Fe precipitates in a Cu matrix [14]. Especially the Mössbauer spectroscopy experiments [6,7] indicate that ferromagnetic fcc Fe exists in a high spin phase while antiferromagnetic fcc Fe has only a low magnetic moment. Indeed, ferromagnetic fcc Fe is generally characterized by a higher atomic volume than the antiferromagnetic fcc Fe and is reported to occur in combination with a tetragonally distorted fcc structure, contrary to an undistorted fcc lattice in the antiferromagnetic phase. With respect to the high number of systems in which these phases have been found the two-phase behavior of fcc Fe now seems quite well established. However, it remains an open question how much the magnetic moment within each phase still depends on the precise atomic arrangement.

While thick Fe films on Cu(100) grown at room temperature exist in the thermodynamically stable bcc structure, for coverages below 11 ML (monolayers) fcc Fe films with both ferromagnetic high spin and antiferromagnetic low spin behavior are observed [6]: Below a coverage of 4 ML Fe grows epitaxially on the substrate in a tetragonally distorted fcc phase which shows characteristic buckling and shifts [3] (phase I). Linear magneto-optical Kerr effect (MOKE) confirms approximately homogeneous perpendicular magnetization in this thickness region [1], whereas spin-polarized appearance potential spectroscopy indicates a small maximum of the magnetic moment at a film thickness of 2.5 ML [8]. For the thickness range between 5 and 11 ML in the interior of the film an undistorted fcc structure exists (phase II), which has been identified as the antiferromagnetic low spin phase with a Néel temperature of ≈ 65 K. On the contrary, the first interlayer distance of the Fe film has been proved to be expanded [1,4] and hence is believed to account for the observed ferromagnetism. The sudden drop of T_c on exposure of the film to very small dosages of CO [1] or O_2 gives a further hint that the ferromagnetic order is indeed located at the surface. However, it should be stressed that none of these experiments directly measures the surface magnetization: MOKE is not intrinsically surface sensitive, and with respect to the adsorption experiments it is not known in detail how the structural and electronic properties of the interior of the Fe films including the interface to Cu are influenced. For the same reason up to now Mössbauer spectroscopy experiments could not determine the actual location of the magnetic layers, because the surface becomes heavily contaminated as a consequence of the long duration of the measurement [15]. The spin-polarized appearance potential spectroscopy experiments [8] are not exclusively surface sensitive due to the high penetration depth of the polarized electrons at the energies employed. In contrast to all cited experiments magnetization induced second harmonic generation (MSHG) is known as a technique that is intrinsically sensitive to the surface magnetization [16–18], in some cases even with submonolayer sensitivity. Therefore, in this Letter we give the first direct proof, to our knowledge, that in the thickness range between 5 and 11 ML ferromagnetic order definitely exists at the surface. We demonstrate that the surface magnetization is nearly equal in both phases, only very weakly influenced by the different reconstructions. These conclusions are drawn immediately from the thickness dependence of the asymmetry of the MSHG signals. However, it is found that the different superstructures in both phases mainly determine the absolute level of the SH yield.

The samples were prepared in an UHV system with a base pressure of 4×10^{-11} mbar. The substrate was cleaned by Ar^+ sputtering followed by short annealing at

630 °C. The Fe films were grown at 300 K at an evaporation rate of about 1 ML/min. The pressure during evaporation was below 5×10^{-10} mbar. The film thickness was determined by recording the medium energy election diffraction intensity variations and by Auger electron spectroscopy. Carbon and oxygen contaminations of the Fe film were below 2% of the main Fe Auger line.

Figure 1(a) sketches the main features of the experimental setup. The magnetization induced SHG experiments were carried out with a Ti:sapphire laser operating at a wavelength $\lambda = 769$ nm with a repetition rate of 80 MHz and a pulse width of 120 fs. p-polarized laser light was focused onto the sample under an angle of incidence of 40° resulting in a pulse intensity of about 40 $\mu J\,cm^{-2}$. The reflected fundamental light was blocked by an edge filter whereas the second harmonic light passed a polarization analyzer and was detected by a photomultiplier using the lock-in technique by chopping the incident beam.

Bulk dipole SHG is forbidden in centrosymmetric media and possible bulk quadrupole and interface dipole contributions can be neglected for reasons discussed below. Thus, at the Fe surface a nonlinear polarization $P_i(2\omega) = \chi_{ijk} E_j(\omega) E_k(\omega)$ is induced by the incident laser field $\mathbf{E}(\omega)$ which generates the SH light. From symmetry considerations [19] one finds three independent tensor elements ($\chi_{xxz} = \chi_{yyz} = \chi_{xzx} = \chi_{yzy}$, $\chi_{zxx} = \chi_{zyy}$, and χ_{zzz}), which are even with respect to reversal of the magnetization and one ($\chi_{xyz} = \chi_{xzy} = -\chi_{yzx} = -\chi_{yxz}$) which is odd. Therefore, for p-polarized incident light the p-component of $\mathbf{P}(2\omega)$ and hence the corresponding SH field component is entirely determined by even tensor elements, while the s-component depends only on the odd tensor element: $\mathbf{E}(2\omega, \pm M) = [E_p(2\omega), \pm E_s(2\omega) e^{i\varphi}]$, with $E_s(2\omega)$ and $E_p(2\omega)$ the magnitudes and φ the relative phase between p component and the s component of the outgoing SH field.

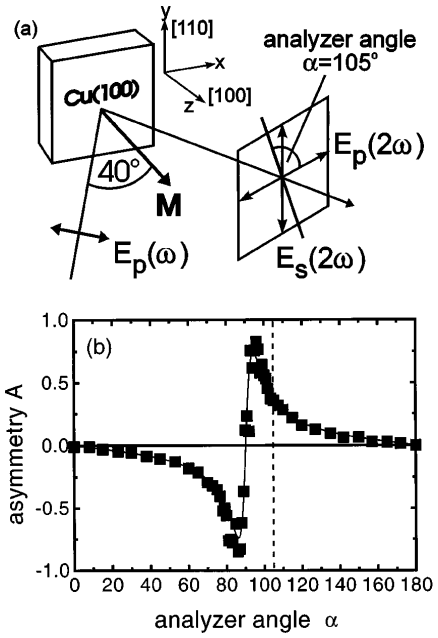

FIG. 1. (a) Experimental setup. (b) Asymmetry A as a function of the analyzer angle α for a 7 monolayer Fe film on Cu(100) for p-polarized incident light. $\alpha = 0$ corresponds to p-polarized outgoing second harmonic light. Solid line: fit according to Eq. (1). The vertical dashed line indicates the analyzer angle at which the thickness dependence of the surface magnetization was measured.

After having passed the analyzer set at angle α with respect to the plane of incidence the resulting SH intensity is measured for both magnetization directions:

$$I(2\omega, \alpha, \pm M) \propto |E_p(2\omega)\cos\alpha \pm E_s(2\omega) e^{i\varphi} \sin\alpha|^2.$$

Defining an asymmetry $A(\alpha) = [I(2\omega, \alpha, +M) - I(2\omega, \alpha, -M)]/[I(2\omega, \alpha, +M) + I(2\omega, \alpha, -M)]$ it is easily calculated that

$$A(\alpha) = 2\Phi_K \tan\alpha [1 + (\Phi_K \tan\alpha)^2]^{-1} \cos\varphi\,, \quad (1)$$

with $\Phi_K = E_s(2\omega)/E_p(2\omega)$ the magnitude of the nonlinear complex Kerr angle. Because Φ_K is given by the magnitude of the ratio between the odd tensor element and a linear combination of the even tensor elements, it is a direct measure of the surface magnetization.

Figure 1(b) shows the asymmetry as a function of the analyzer angle α for a 7 ML Fe film on Cu(100). Using Eq. (1) a nonlinear Kerr angle $\Phi_K = 4° \pm 0.5°$ is derived. The corresponding ellipticity $\Phi'' = \Phi_K \sin\varphi = 2.5°$ exceeds the linear MOKE ellipticity by nearly 2 orders of magnitude. In this respect, our results agree very well with the large Kerr angles found for other systems [17,20].

The thickness dependence of the surface magnetization was investigated at a constant analyzer angle $\alpha = 105°$ as indicated by the dashed line in Fig. 1(b). At this angle a good signal-to-noise ratio is achieved and the term $\Phi_K \tan\alpha$ in Eq. (1) is small. Therefore, Eq. (1) can be simplified to $A(\alpha) = 2\tan\alpha\,\Phi_K \cos\varphi$, which is directly proportional to the nonlinear Kerr angle Φ_K. As shown by the two representative examples in Fig. 2 the films always show square shape (nonlinear) Kerr hysteresis curves indicating good magnetic order. The hysteresis

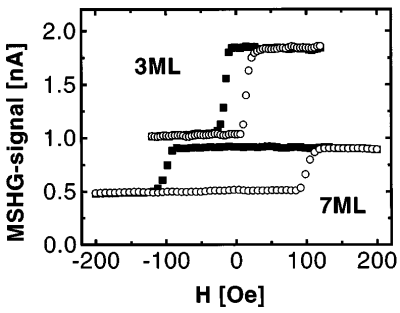

FIG. 2. Magnetization induced second harmonic generation hysteresis curves for 3 and 7 monolayers Fe on Cu(100).

amplitude of the 3 ML film exceeds that of the 7 ML film by about a factor of 2. However, because the average SH signal for 3 ML is higher by the same factor, the asymmetry remains unchanged. These features of the 3 and 7 ML film turn out to be characteristic for the two phases I and II. The full thickness dependence of MSHG was determined on a wedge ranging from 0 to 12 ML as shown in Fig. 3. The upper part of Fig. 3 depicts the MSHG signal for both directions of magnetization as it was measured in remanence at a temperature of 220 K as well as the asymmetry calculated from these values. In the lower part of the picture the MOKE ellipticity is plotted for comparison. Four different thickness ranges can be distinguished, as indicated by the dashed lines. Up to approximately 1 ML the SH intensity increases nearly linearly with the Fe coverage and is independent of the direction of the magnetic field. Between 1.3 ML and about 10 ML two regions with fairly constant MSHG signals on different absolute levels exist, sharply separated by the transition from phase I to phase II. However, the asymmetry A is seen to be nearly independent of the transition. Finally, above 10 ML A gradually disappears because the film collapses into the bcc structure with in-plane magnetization.

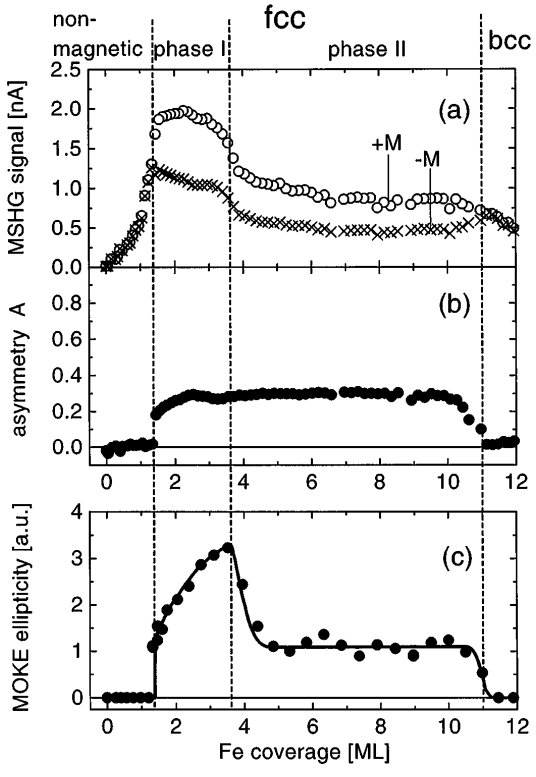

FIG. 3. Thickness dependence of the magnetization induced second harmonic generation signals for positive and negative magnetization (a) and the resulting asymmetry $A(\alpha = 105°)$ (b) between 0 and 12 monolayers Fe on Cu(100). For comparison in (c) the linear MOKE ellipticity is depicted. Both the linear and the nonlinear Kerr effects were measured in remanence at $T = 220$ K.

The almost linear increase below 1 ML is due to the increasing coverage of the Cu substrate which, despite deviations from a perfect layer by layer growth, is nearly linear up to 0.9 ML [21]. After the onset of ferromagnetism at 1.3 ML there is still a significant increase in the asymmetry which cannot be explained by the strong thickness dependence of the Curie temperature in this thickness range. Together with the slight maximum around 2.5 ML it might indicate a small thickness dependent variation of the magnetic moment at the surface. However, a merely electronic origin cannot be excluded. Certainly the most striking result of our investigations is the nearly constant and equal asymmetry within the main parts of phase I and phase II, in marked contrast to linear MOKE. While in phase I linear MOKE ellipticity suggests roughly homogeneous magnetization of the entire film, the only very weak variation of the asymmetry proves that the surface magnetization is comparatively thickness independent with only the possible small deviations from constancy already discussed. Because of the extreme surface sensitivity of MSHG the constant asymmetry in phase II not only proves that the magnetization is located at the surface, indeed, but also confirms its thickness independence in agreement with linear MOKE and low-energy electron diffraction spectroscopy (LEED) investigations [4]. Because of the different Curie temperatures in both phases an extrapolation to 0 K would increase the asymmetry in phase II with respect to phase I by roughly 10%. The fact that the surface magnetization is nearly equal in both phases is easily understood in the context of the existence of a well defined high-spin phase. According to the results of [3] and [4] the unit cell volume of the top layer in phase II is nearly the same as in phase I, which suggests the magnetic moments at the surface in both phases to be nearly equal. However, as the asymmetry shows characteristic deviations from constancy, a weak influence of the highly different reconstructions on the surface magnetization seems to be visible.

The strong drop of the nonmagnetic part of the MSHG signals given by the average SH intensity going from phase I to phase II may be attributed to special features of the different reconstructions within both phases. The lowering of the symmetry due to reconstruction involving only lateral shifts of the atoms should not effect the SH yield to a first approximation because the light spot of diameter 40 μm averages over all structural domains. However, as, e.g., the SH yield can be enhanced drastically on vicinal surfaces [22] compared to low indexed surfaces, layer relaxation and buckling certainly may influence the SH output. Therefore, in phase I the 4×1 and the 5×1 reconstructions may account for the observed higher SH intensity, whereas for the 2×1 reconstruction in phase II no buckling is reported [4], possibly resulting in a lower average SH yield. The occurrence of ridgelike bcc precipitates in phase II [21]

cannot be responsible for the observed difference in the SH intensity between phases I and II. Although they are observed at thicknesses as low as 4.6 ML, their density increases rapidly with thickness at thicknesses above 6 ML while the average SH intensity is entirely constant up to 10 ML. Similar statements are true for the different degree of long range order between and within the two phases [4,23].

As the inversion symmetry is broken also at the interface between Fe and Cu substrate, in principle a contribution to MSHG could arise from the interface to Cu, too, as found, for example, for Co/Cu(100) [24]. However, the large difference in the average SH intensity between the two phases in contrast to the nearly constant asymmetry strongly suggests that for fcc Fe on Cu(100) the buried interface does not contribute significantly to the MSHG signal: The absolute level of the MSHG signals is mainly governed by the different superstructures. The dominant role of the surface contribution can also be demonstrated by adsorption of very small dosages of oxygen ($T = 170$ K): For a 3 ML Fe film the MSHG asymmetry decreases linearly by nearly 40% upon oxygen exposure up to 0.5 L in contrast to a decline of the linear Kerr angle of only 7%. Significant quadrupolelike bulk contributions from a few ML Fe films are not to be expected, in agreement with our data (otherwise a linear increase with thickness should be visible).

In summary, we have shown that for RT-grown Fe films on Cu(100) the surface magnetization is to a good approximation equal in the two structurally distinct fcc phases below and above ≈ 4 ML. Thereby direct evidence of surface magnetism in the thickness range between 5 and 11 ML is given. The equal surface magnetization can be explained by identical atomic volumes at the surface in both phases. While the different reconstructions strongly infuence the average SH yield, only a very weak influence on the surface magnetization is observed.

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