Journal of Magnetism and Magnetic Materials 198–199 (1999) 611–616

Invited paper

Second harmonic generation from magnetic surfaces and thin films

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Abstract

In this paper we discuss the magneto-optical Kerr effect in the frequency doubled light (MSHG, magnetization-induced second harmonic generation) generated at interfaces of ultrathin ferromagnetic films and the surface of crystals having inversion symmetry. We demonstrate that the 'magnetic signals' like the nonlinear Kerr angle or the asymmetry can be strongly affected by the 'nonmagnetic' part of the second-order nonlinear susceptibility tensor, $\chi^{(2)}_{\mathrm{nonmag}}$. This changes of $\chi^{(2)}_{\mathrm{nonmag}}$ can be caused by the change of the electronic structure with film thickness (quantum well states in the Cu cover layer of Cu/Co/Cu(0 0 1)) or by changes of the surface morphology. One monolayer (ML) periodic oscillation during the layer-by-layer growth of Co films on Cu(0 0 1) were observed in the *magnetic* second order susceptibility $\chi^{(2)}_{\mathrm{nonmag}}$.

Keywords: Magneto-optics; Nonlinear optics; Thin-film magnetism

1. Introduction

Optical methods like the magneto-optical Kerr-effect (also called *linear Kerr effect* in this paper) have been applied with great success in investigations of magnetic properties of ultrathin films. Optical second-harmonic generation (SHG) is forbidden in the bulk of systems with inversion symmetry and becomes allowed only at the surface and buried interfaces where this inversion symmetry is broken. For the first time the magneto-optical Kerr effect in the frequency doubled light (sometimes named *nonlinear Kerr effect*) was discussed in the theoretical papers of Pan et al. [1] and Hübner and Bennemann [2]. The first experimental evidence was given by Reif et al. [3]. Meanwhile a number of publications proved this method to be a valuable tool in the investigation of magnetism at surfaces and interfaces [4–15].

Second harmonic generation arises from a nonlinear polarization $\boldsymbol{P}(2\omega)$ generated by an intense incident light beam. $\boldsymbol{P}(2\omega)$ can be written as

$$P_i(2\omega) = \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega) \tag{1}$$

with $\chi^{(2)}$ the third rank tensor of the second-order nonlinear susceptibility. Because $\chi^{(2)}$ is an odd rank tensor $\boldsymbol{P}(2\omega)$ vanishes in the bulk of a medium with inversion symmetry. In Eq. (1) only the electric dipole contributions are considered. There are higher-order contributions to $\boldsymbol{P}(2\omega)$ like electric quadrupole and magnetic dipole contributions but they are considered to be small compared to the dipole part. However, because they are symmetry allowed in the bulk (even rank tensor) they may be of comparable size in certain cases [13].

Symmetry selection rule restrict the number of nonzero elements in $\chi^{(2)}_{ijk}$ [1]. In the presence of a magnetization $\boldsymbol{M}$ the symmetry is reduced and therefore more elements of $\chi^{(2)}$ become nonzero. Considering only entirely *p*- or *s*-polarization of the incident light, the observed magneto-optical effects are similar to the magneto-optical Kerr effect in the reflected light: For a magnetization perpendicular to the optical plane a different

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0304-8853/99/$ – see front matter
PII: S0304-8853(98)01216-5

but *always entirely p-polarized second-harmonic* (SH) *intensity* for the magnetization in opposite directions is observed (transversal Kerr geometry), while for a magnetization in the optical plane (and $\boldsymbol{M} \parallel$ to the surface) the polarization of the SH light changes due to a magnetization induced *entirely s-polarized* component, which changes sign upon reversal of the magnetization direction (longitudinal Kerr geometry).

As for the linear Kerr effect we can define an asymmetry A in the case of the transversal Kerr geometry:

$$A = \frac{I(2\omega, M) - I(2\omega, -M)}{I(2\omega, M) + I(2\omega, -M)} = \frac{2R}{1+R^2}\cos\phi \qquad (2)$$

with $R = \chi^{(2)}_{\mathrm{mag}}/\chi^{(2)}_{\mathrm{nonmag}}$ the ratio of the magnitude of the effective 'magnetic' and 'nonmagnetic' tensor element and ϕ the phase difference between them. For the longitudinal Kerr geometry a (complex) Kerr angle can be defined as; $\tan \Phi_{\mathrm{K}} = E_{\mathrm{s}}(2\omega)/E_{\mathrm{p}}(2\omega)$. Magnitude and phase of Φ_{K} can be measured independently in this geometry.

Generally, it was found that the relative magneto-optical effect is orders of magnitude larger than the effects measured in the reflected light. Kerr angles up to 90° have been reported [8,10,11] or asymmetries close to 100% [11]. This indicates that the magnetization-induced part of the second order susceptibility $\chi^{(2)}$ is of the same order of magnitude as the 'nonmagnetic' part of $\chi^{(2)}$.

The description of the experimental setup can be found in Refs [15,16]. In brief, the light of a Ti-Sapphire laser ($\lambda = 720$–950 nm, pulse width 80 fs, repetition rate 80 MHz) is focused onto the sample in an UHV chamber (spot diameter about 25–100 μm, peak fluence below 2 mJ/cm^2). The SH light generated at the surface is detected by a photomultiplier. The light of the fundamental frequency is blocked by a combination of an interference filter and a colored glass filter. For the longitudinal Kerr geometry a calcite polarizer is placed in the outgoing beam path for polarization analysis of the frequency doubled light. The sample is magnetized by a dipole magnet with an external coil (magnetization along the (1 1 0) azimuth direction). The angle of incidence of the light beam was about 38°.

2. Surface sensitivity of MSHG

Surface sensitivity very often is tested by monitoring the signal of interest as a function of adsorption of a (reactive) gas like CO or O_2 [3,17]. A more direct proof is to measure the thickness dependence of the SH light as a function of a ferromagnetic ultrathin film [6,7]. Fig. 1 shows the SH intensity from a Co-wedge grown on Cu(0 0 1). The transversal Kerr geometry was used. In the middle panel the SH intensity for the magnetization in opposite directions is plotted as open and closed symbols as a function of the Co film thickness. The asymmetry

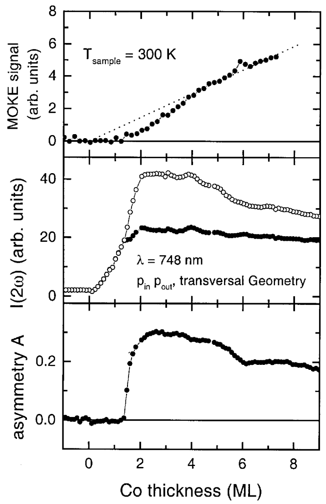

Fig. 1. SH intensity from a Co wedge grown on Cu(0 0 1) (middle panel) for the magnetization in opposite directions (open and filled symbols). Bottom panel the asymmetry calculated from the SH intensities above. Angle of incidence $\theta_i = 38°$. For comparison the linear Kerr signal is shown in the top panel measured with a HeNe laser in the longitudinal Kerr geometry.

calculated from the SH intensities is shown in the bottom panel. The SH intensity from the clean Cu surface is quite small because the photon energy of the fundamental light is below the threshold of d-electron excitation. With increasing Co thickness the SH intensity increases rapidly until at about 2 monolayers (ML) it reaches a more or less constant value. Similarly, the magnetic asymmetry is zero until at about 1.5 ML the Co film becomes ferromagnetically ordered. The maximum of the asymmetry is reached at about 2 ML as well. This immediately proves that the effective thickness in which the SH light is generated is of the order of 1–2 ML, both for the 'nonmagnetic' as well as for the magnetization induced part of SHG.

A closer look to the data, however, reveals a more complicated behavior. Firstly, after reaching the maximum the SH intensity as well as the asymmetry do not remain constant with further increasing Co thickness but decrease again at about 5 ML. Secondly, a weak oscillatory contribution is visible with a period of 1 ML. The first effect is caused by a change of the electronic states at the surface and Co/Cu interface with Co film thickness. The second effect cannot be attributed to electronic changes of completely filled layers but is related to the variation in surface morphology. These two effects will be discussed in the following two sections.

3. Quantum well state resonances in the MSHG from Cu/Co/Cu(1 0 0)

As mentioned above the magneto-optical Kerr signal is influenced by electronic changes. An oscillatory component has been observed in the (linear) polar Kerr angle of Au/Fe/Au(0 0 1) sandwiches as a function of the Fe thickness [18] or Au/Co(0 0 0 1) as a function of the Au cover layer [19]. These results are interpreted as arising from strongly confined (spin polarized) quantum well states either in the Fe layer or in the Au cap layer. Similar but much stronger effects have been observed in the nonlinear Kerr signal [6,7,12]. Oscillations are seen not only in the magnetic signal like the asymmetry but in the (average) SH intensity as well. The question arises to what extend these oscillations are caused by the magnetization-induced part of $\chi^{(2)}$. Fig. 2(a) shows the SH intensity from a Cu wedge on a 10 ML thick Co film grown on Cu(0 0 1) for various wavelength of the incident light. The transversal Kerr geometry was used with *p*-polarized incident light. Open and solid symbols represent the SH intensity for the magnetization in opposite directions parallel to the ⟨1 1 0⟩ azimuth. Clearly a strong variation of the SH intensity with the Cu cover layer thickness can be observed for all incident wavelengths. A similar oscillatory variation of the SH intensity with the thickness variation of the nonmagnetic cover layer has been observed in the system Au/Co/Au(1 1 1) [12,20]. There the SH intensity as well as the magnetic asymmetry shows a more regular behavior compared to the result in Fig. 2(a). The oscillations can be described by a single damped cosine function but the oscillation amplitude was considerably smaller. Moreover, the oscillation period did not depend on the wavelength of the incident light contrary to the present case of Cu/Co/Cu(0 0 1). At $\lambda = 740$ nm an especially strong maximum is observed at about 12 ML Cu thickness which shifts to higher thickness with increasing wavelength. The intensity variations cannot be described by a simple cosine function and they are extremely high. Up to now there exists no theoretical model to describe the experiments quantitatively. However, several simple models have been proposed describing qualitatively the experimental results [21,22,16]. The main reason for the observed difference in the two cases is the different degree of *k*-vector selectivity [22]. While in the (0 0 1) surface mainly states close to $\bar{\Gamma}$ contribute to the SHG (but with a high density of states) in case of the (1 1 1) surface the contributing *k*-vectors are more spread across the Brillouin zone. A large number of different contributing *k*-vectors tend to smear out the oscillations in the SH intensity versus cover layer thickness because with each *k*-vector a different oscillation period is associated. On the other hand for the (0 0 1) surface the strong *k* selectivity leads to the strong intensity variations with cover layer thickness in the average SH intensity. Then the asymmetry shown in the Fig. 2(b) is no longer a good measure for $\chi^{(2)}_{mag}$ or even the surface /interface magnetization. The fast and strong oscillations in the thickness range about 5 ML and the sign change of about 18 ML at $\lambda = 740$ nm to 35 ML at $\lambda = 920$ nm are caused by a sign change of $\chi^{(2)}_{nonmag}$ rather than of $\chi^{(2)}_{mag}$. As can be seen from Eq. (2) a smooth zero crossing of $\chi^{(2)}_{nonmag}$ causes the characteristic 's'-shaped asymmetry curves in Fig. 2(b). A direct separation of magnetic and nonmagnetic contributions can be obtained in the longitudinal Kerr geometry. The result again for Cu/10 ML Co/Cu(0 0 1) as function of the Cu cover layer is shown in Fig. 3 for *p*-polarized incident light and *p*-polarized outgoing SH light (middle panel, entirely generated by $\chi^{(2)}_{nonmag}$) and *s*-polarized SH light (lower panel, entirely generated by $\chi^{(2)}_{mag}$). While the *p*-polarized SH intensity curve reproduces well the average SH intensity for $\lambda =$ 790 nm in Fig. 2(a) the SH intensity for the *s*-polarized SH intensity shows a completely different behavior. The strong maximum at about 13 ML does not appear in the magnetic SH contribution. With the exception of the first few monolayers there are no strong intensity variations with Co film thickness. Obviously magnetic effects like a spin splitting of the QWS in the Cu layer do not strongly influence the SHG from these sandwich systems and the oscillations in the asymmetry in Fig. 2(b) are caused mainly by a change of $\chi^{(2)}_{nonmag}$.

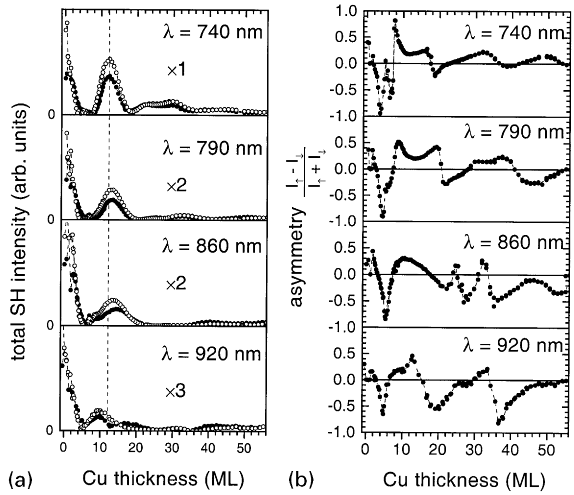

Fig. 2. SH intensity from Cu/10 ML Co/Cu(0 0 1) sandwich as a function of the Cu cover layer thickness for various wavelength λ of the incident light measured in the transversal Kerr geometry with *p*-polarized incident light.The intensities are normalized against a quartz reference and scaled by the indicated factors for the different incident wavelength. (b) The Kerr asymmetries calculated from the SH intensities shown in (a). Open and filled symbols indicate the SH intensity for opposite magnetization directions.

The measurement of the pure magnetic *s*-component of the SH light is complicated by its relative smallness compared to the *p*-component which is up to 30 times larger. Due to small misalignment of the incident polarization SHG from nonmagnetic tensor elements contribute to the signal so that an intensity difference is

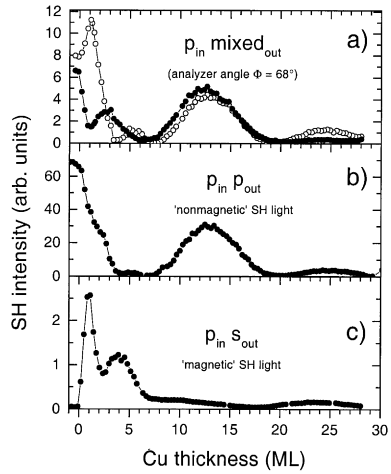

Fig. 3. Comparison of the *p*-polarized (b) and *s*-polarized (c) SH intensity from a Cu/10 ML Co/Cu(0 0 1) sandwich as a function of the Cu cover layer for *p*-polarized incident light at $\lambda = 790$ nm. Longitudinal Kerr geometry. For comparison the SH intensity at an analyzer angle of 68° is shown in the top panel. Open and filled symbols indicates the SH intensity for opposite magnetization directions.

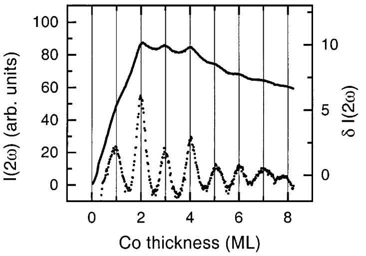

Fig. 4. *p*-polarized SH intensity for *p*-polarized incident light monitored during the growth of the Co film on the Cu substrate (left scale, top curve). The bottom curve (right scale) displays the difference of the SH intensity and its average over 50 data points, $\delta I(2\omega)$.

measured for the magnetization in opposite direction which should not be present in the case of perfect alignment. Actually the arithmethic average $(I(2\omega, +\boldsymbol{M}) + I(2\omega, -\boldsymbol{M}))/2$ is plotted in the bottom panel of Fig. 3. From the comparison with the SH intensity at $\Phi = 68°$ (top panel) it can be concluded that $\chi^{(2)}_{\mathrm{mag}}$ changes sign at about 2–3 ML Cu thickness. At 1 ML Cu coverage, therefore, $\chi^{(2)}_{\mathrm{mag}}$ has a strong peak. It rapidly decreases and changes sign at about 2–3 ML. Then the magnitude of $\chi^{(2)}_{\mathrm{mag}}$ smoothly decreases again. The fact that $\chi^{(2)}_{\mathrm{mag}}$ of the uncovered Co film is small indicates that $\chi^{(2)}_{\mathrm{mag}}$ at the Co/vacuum surface, $\chi^{(2,\mathrm{surf})}_{\mathrm{mag}}$, and $\chi^{(2)}_{\mathrm{mag}}$ at the buried Cu substrate/Co interface, $\chi^{(2,\mathrm{int})}_{\mathrm{mag}}$, are of very similar magnitude. The strong changes upon coverage with 1 ML Cu are probably caused by the electronic hybridization effects of Cu and Co at the interface. It has been shown, that they lead to strong changes in the magnetic properties of the Co film [23,24]. In the present case the relative change of $\chi^{(2,\mathrm{surf})}_{\mathrm{mag}}$ upon Cu coverage is even more enhanced because the contribution from the Cu substrate/Co interface $\chi^{(2,\mathrm{int})}_{\mathrm{mag}}$ strongly reduces the net magnetic signal for the uncovered Co film.

4. One monolayer periodic oscillations in the magnetization-induced second-order susceptibility during the layer-by-layer growth of Co on Cu(0 0 1)

The effect of surface/interface roughness on the SHG can be quite significant [14,25]. The 1 ML period oscillations in Fig. 1 demonstrate, that even atomic level roughness is visible in (M)SHG. These oscillations are even more visible in Fig. 4 where the *p*-polarized SH intensity for *p*-polarized incident fundamental light in the longitudinal geometry is shown. The SH intensity was recorded *during* the growth of Co on Cu(0 0 1). For experimental details see Ref. [15]. At room temperature Co grows in a layer-by-layer mode. Co islands periodically nucleate, grow in size, and finally coalesce. The average island size at half filled layers is about 5–10 nm diameter resulting in a fraction of 10–20% of atoms sitting on step edges [26]. The enhanced number of step edge atoms leads in the present case to a reduction of the total SH intensity generated at the surface and the buried Cu/Co interface.

In this geometry no magnetization-induced tensor elements of $\chi^{(2)}$ contribute. Therefore, the observed oscillations are cause entirely by $\chi^{(2,\mathrm{surf})}_{\mathrm{nonmag}}$. As discussed in the previous section it is quite difficult to extract the magnetic information from the SH intensities if both, $\chi^{(2)}_{\mathrm{mag}}$ and $\chi^{(2)}_{\mathrm{nonmag}}$, are affected by the externally controlled parameter, which in this case is the Co film thickness. We searched therefore for a condition where $\chi^{(2)}_{\mathrm{nonmag}}$ is largely insensitive to the morphology changes of the surface during the layer-by-layer growth. Fig. 5(a) shows the SH intensity for *s*-polarized incident light in the transversal Kerr geometry with otherwise identical conditions to that in Fig. 4. The arithmetic average of the SH intensity for the two opposite magnetization directions shown in Fig. 5(c) exhibits only some weak intensity variations with Co film thickness after the strong increase up to 2 ML. No 1 ML periodic signal can be detected even in the enlarged view of Fig. 5(e). Contrary to the average signal, the asymmetry shown in Fig. 5(b) shows well resolved 1 ML periodic oscillations over a slowly varying course. After the onset of ferromagnetic order at about 1.5 ML the asymmetry has a relatively small value and even changes sign at about 4 ML. We want to emphasize, that the asymmetry in this case is *not* directly proportional to the surface magnetization. Two important factors have to be considered. Firstly, the asymmetry results

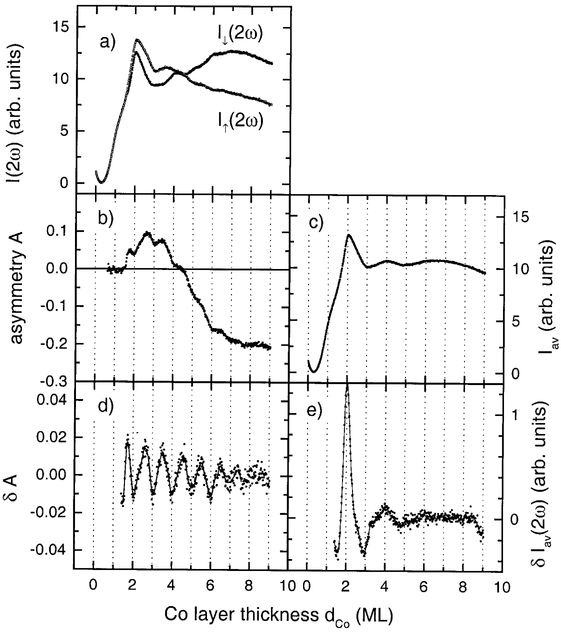

Fig. 5. (a) Measured total SH intensity as a function of the Co film thickness for *s*-polarized incident light in the transversal Kerr geometry for the magnetization in opposite directions. (b) magnetic asymmetry and (c) average SH intensity calculated from the SH intensities in (a). In (d) the difference of the magnetic asymmetry and its running average over 50 points is plotted. In (e) the similar difference as in (d) is plotted for the average SH intensity I_{av}.

from the coherent superposition of surface as well as interface contributions which tend to reduce the asymmetry measured in the total SH intensity in this case. Secondly, the changes of the electronic structure with (filled) Co layer thickness causes a change of surface and interface nonlinear susceptibility with Co film thickness. At a 4 ML film the magnetic contribution from the surface is exactly compensated by the interface. From the analysis of thick Co films we know that at a thickness larger than 4 ML the contribution from the Co/Cu(0 0 1) interface exceeds that of the surface, which leads to the conclusion that $\chi^{(2,surf)}_{mag}$ is enhanced at half filled layers [15]. In part due to the destructive interference of magnetic surface and interface SHG the relative amplitudes of these oscillations are strongly enhanced even further increasing the already quite high surface sensitivity of MSHG.

It is expected that the magnetic moment of atoms at step edges is somewhat enhanced compared to the magnetic moment of atom in the flat surface layer [27,28]. A quantitative estimate of an enhanced surface magnetization due to the presence of steps is not straight forward [15]. If we take the ratio of the amplitude of the 1 ML periodic part of the asymmetry and the asymmetry resulting from the surface asymmetry alone a ratio of $\delta A/A_s = 0.03$ results which has the right order of magnitude expected from the theoretical calculations [28].

5. Conclusion

In conclusion we have shown, that magnetization-induced second harmonic generation can be used as very sensitive tool in the investigation of surface/interface magnetism. However, because of the relative large magneto-optical effects, the magnetic signals like the nonlinear Kerr angle and the asymmetry can be strongly affected by changes in the non-magnetic part of $\chi^{(2)}$. We demonstrated this on the extreme case of QWS resonances in Cu/Co/Cu(0 0 1) sandwiches. MSHG is even sensitive to changes of the surface morphology on an atomic level. Also in this case a careful analysis is necessary to separate the magnetization induced changes in changes in $\chi^{(2)}$.

Acknowledgements

This work has been supported in part by the EC through grant No. RB-EMRX-CT96-0015 (TMR NOMOKE). Q.Y. Jin has been supported by the Alexander von Humbold Foundation.

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