Phase effects in magnetic second-harmonic generation on ultrathin Co and Ni films on Cu(001)

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Phase relations in second-harmonic generation (SHG) have been studied systematically for Ni and Co films on Cu(001) as a function of thickness in the range 1–12 ML. Below two monolayers we observe, with *s*-polarized fundamental light and *P*-polarized second-harmonic light, phase shifts close to 180° of both films against the Cu substrate. Such large phase shifts in this polarization combination appear to be characteristic of the transition from *s*- to *d*-band metals. In the ferromagnetic thickness range the *relative phase* between odd and even tensor elements becomes important. For Ni films it is independent of film thickness for both $p \rightarrow P$ and $s \rightarrow P$ polarizations, and leads to the ratio $\chi_{xyy}^{\mathrm{odd}}/\chi_{zyy}^{\mathrm{even}} = 0.047 \pm 0.013$, in agreement with theoretical predictions. In the case of Co films the relative phase differs dramatically between these two polarization combinations. It is nearly independent of film thickness for $p \rightarrow P$ polarized SHG. However, for $s \rightarrow P$ polarization it varies from 135° at 3 ML to 60° at 10 ML, causing a sign change of the magnetic contrast at 90° near 6 ML. The ratio of odd to even second-harmonic field amplitudes was found to vary from 22% at 3 ML to 12.5% above 6 ML. From these results we conclude that measurements of the relative phase are necessary for deriving reliable information from SHG about the magnetization state of a sample.

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I. INTRODUCTION

Second-harmonic generation (SHG) in reflection is a versatile method to optically investigate electronic, structural, and magnetic properties of surfaces and interfaces of centrosymmetric materials.[1–3] Complete information about the nonlinear response—in a dipole approximation of the form $\mathbf{P}(2\omega) \propto \chi^{(2)}:\mathbf{E}(\omega)\mathbf{E}(\omega)$—requires knowledge of both the amplitude and phase of the second-harmonic (SH) radiation. While the amplitude is determined by the intensity, the phase can only be recorded relative to a reference field. Chang *et al.*[4] were the first to measure SHG phases. They compared, for three semiconductor materials, the phases of SH fields with that of a reference source, and from the phase shifts derived the relative size of the nonlinear susceptibilities. A more detailed discussion of how to determine phases was later given by Berkovic and Shvartsberg[5] and Stolle *et al.*[6] These authors also summarized all SH phase studies that had been reported up to the mid-1990's. A particularly interesting example was the demonstration that phases contain information about the orientation of dipolar adsorbates on surfaces.[6,7]

An additional phase enters for SHG on magnetized materials, as first pointed out by Pan *et al.*[8] This originates from the fact that the nonlinear susceptibility now contains two contributions, $\chi^{(2)}(\pm\mathbf{M}) = \chi^{(2)}_{\mathrm{even}} \pm \chi^{(2)}_{\mathrm{odd}}$, one which responds symmetrically (even) to magnetization reversal and another one which changes sign (odd). In the following we will denote this phase between even and odd parts of the SH field as the *relative* phase. This has been studied, for example, by Rasing and co-workers for magnetic multilayer systems like Co/Au, (Ref. 9) and Rh/Co/Cu.[10,11] In the same group an interferometric method was also developed for measuring relative phases in ultrahigh vacuum (UHV).[11,12]

Magnetic second-harmonic generation (MSHG), lacking any phase information, was reported by several groups for the following epitaxially grown ultrathin films: Fe/Cu(001),[13] Co/Cu(001),[14–18] and Ni/Cu(001).[16–18] The power of the technique became evident by observation of structural changes with thickness in Fe/Cu(001),[13] and by identifying periodic oscillations of surface magnetization with thickness in Co/Cu(001),[15] effects which are in principle not accessible to linear magnetooptical inspection. However, the difference in thickness dependence of the SH yields for the *s*- and *p*-polarized fundamental, first discovered by Jin *et al.*[15] for Co/Cu(001), proves that a mere intensity measurement does not suffice. The authors found that for $s \rightarrow P$ polarization the magnetic contrast

$$\rho = 2\frac{I^{\uparrow} - I^{\downarrow}}{I^{\uparrow} + I^{\downarrow}}, \tag{1}$$

calculated from the MSHG intensities $I^{\uparrow}(2\omega)$ and $I^{\downarrow}(2\omega)$ for opposite magnetic-field directions, changes sign between 5 and 6 ML, while for $p \rightarrow P$ polarization this is not the case. The latter implies that the magnetization direction of the Co film remains unchanged at such film thickness. Qualitatively, Jin *et al.*[15] explained the vanishing contrast as an exact cancellation of the contributions from the film surface and the Co/Cu interface. It was left open, however, why this effect appears only in MSHG with *s*-polarized incident light but not *p*-polarized incident light. In this paper we will prove that the sign change of the magnetic contrast around 5–6 ML for $s \rightarrow P$ polarization is exclusively a phase effect between the even and odd parts of the second-harmonic field, and that a similar effect does not appear in Ni/Cu(001).

To this purpose we investigated variations of the SH phase with thickness for ultrathin Co and Ni films on a Cu(001) substrate. At first, the magnetic contrast was monitored during film growth at a well-defined substrate temperature for *s*- and *p*-polarized incident light and opposite directions of an external magnetic field in transversal geometry. Then the phase of *P*-polarized SHG was measured at several film thicknesses for the two polarization directions of the

fundamental. For both film materials we find a similar behavior of the SH phase with thickness before the films turn ferromagnetic. In the magnetic range, however, the *relative* phases behave differently for Ni and Co films. In particular for Co films, variations of the $s \rightarrow P$ SHG with thickness show dramatic effects that are caused by changes of the relative phase which can even mimic a sign reversal of the magnetization. Our results highlight that information about thin-film magnetism derived from magnetic SHG requires a knowledge of the relative phase.

II. SH YIELD AS A FUNCTION OF FILM THICKNESS

The variation of the SH intensity was measured during film growth for the two polarization combinations $p \rightarrow P$ and $s \rightarrow P$. Those were chosen because they include different numbers of nonlinear susceptibility tensor components. If we define the geometry as $-z$ along the surface normal, x axis parallel to the plane of incidence, and the magnetic field in either the $+y$ ($\uparrow$) or $-y$ ($\downarrow$) direction, then, for a (001) surface, the $p \rightarrow P$ combination contains six components and the $s \rightarrow P$ combination consists of only two. For $p \rightarrow P$ polarization there exist three even components, χ_{zzz}^{even}, χ_{zxx}^{even}, and χ_{xzx}^{even}, and three odd ones, χ_{xxx}^{odd}, χ_{xzz}^{odd}, and χ_{zzx}^{odd}, which implies that the relative phase is effectively composed of all mutual phases of these six components. In contrast, $s \rightarrow P$ polarization involves only one even element, χ_{zyy}^{even}, and one odd element, χ_{xyy}^{odd},[19] and the relative phase between magnetic and nonmagnetic contributions is well defined.

In the experiments, Co and Ni films on Cu(001) were prepared in an UHV chamber at a base pressure of 2×10^{-10} mbar. The uncertainty of the substrate surface orientation was $\leqslant 1°$. The film thickness was controlled by medium-energy electron diffraction and SHG. Both quantities were monitored simultaneously during film growth as described in detail in Ref. 18. After cleaning the Cu(001) surface by the usual sputtering and annealing cycles, Ni films were grown at substrate temperatures varying from 30 °C to 45 °C, while for Co films room temperature was used. Under these conditions there is no risk of interdiffusion.[20]

Light pulses of 30-fs width and a central wavelength of 800 nm were provided by a home-built Ti:sapphire laser at a repetition rate of 76 MHz. The *p*- or *s*-polarized laser beam with an average power of about 400 mW was focussed by a fused silica lens (focal length 30 cm) through the UHV entrance window onto the sample at an angle of incidence of 45°. Only *P*-polarized SH light, controlled by a Glan-Thomson prism, was recorded by a photomultiplier in a single-photon-counting mode. During film growth, an external magnetic field was applied perpendicular to the plane of incidence, which saturated the in-plane magnetization of the film. Its direction was alternately reversed, and for each magnetization direction the polarization of the fundamental was turned from *s* to *p*. A typical growth rate was 0.2 ML/min. In general, we observe a 25 times larger SH intensity for the $p \rightarrow P$ polarization combination compared to the $s \rightarrow P$ combination, which leads to a correspondingly poorer signal-to-noise ratio for the latter (cf. Figs. 1 and 2). The reason for

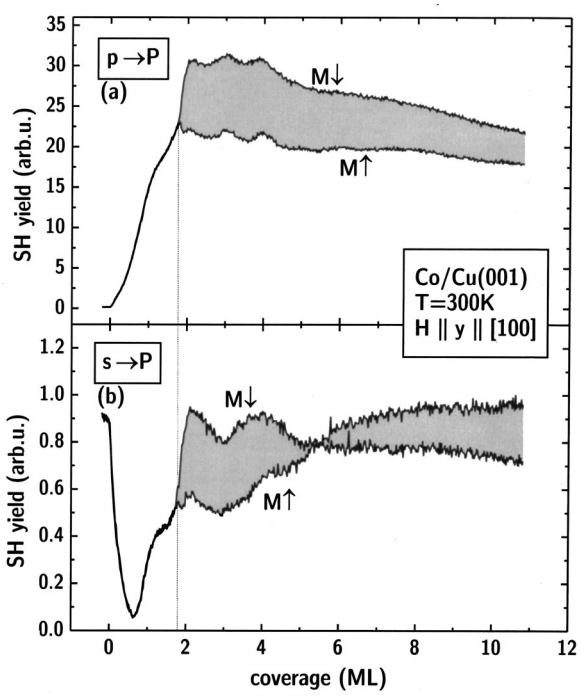

FIG. 1. Dependence of *P*-polarized SHG on Co film thickness for opposite magnetic-field directions oriented in plane perpendicular to the plane of incidence. Results in (a) and (b) are obtained with *p*- and *s*-polarized incident light, respectively.

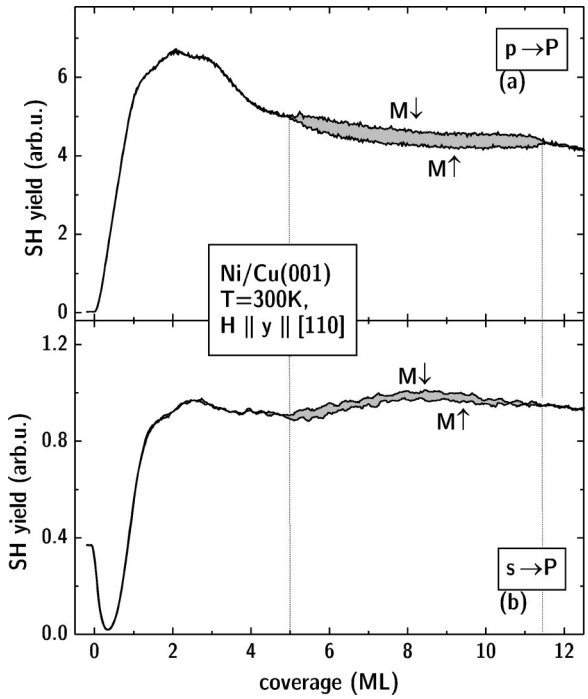

FIG. 2. *P*-polarized second harmonic yield as a function of Ni film thickness for opposite magnetic-field directions oriented in plane perpendicular to the plane of incidence. (a) shows the results for *p*-polarized light, and (b) results for *s*-polarized incident light. The onset of ferromagnetic coupling at 5 ML and the reorientation transition between 11 and 12 ML are indicated by dotted lines.

this is the different number and character of the susceptibility components involved.

A. Co/Cu(001)

The variation of the *P*-polarized SH yield with film thickness and magnetization direction is displayed in Fig. 1 for *p*- and *s*-polarized fundamental light. We remark that there is general agreement with the data reported by Jin *et al.*[15] In detail, however, minor discrepancies exist which are probably caused by different film qualities like impurity concentration and roughness, but these will not be discussed here further. Of interest to us are the following dominant features: (1) the steep rise of $p \rightarrow P$ SHG during the first 3 ML; (2) the drop of the $s \rightarrow P$ yield to almost zero below 1 ML; (3) the splitting of both yield curves for opposite magnetization directions above 2 ML; and (4) the sign change of the magnetic contrast [defined in Eq. (1)] for $s \rightarrow P$ polarization near 5.5 ML.

Features (1) and (2) are caused by the development of the Co/Cu interface and connected changes of the absolute phase in a thickness range where the film is still paramagnetic. For a clean Cu(001) surface the $p \rightarrow P$ SHG yield is very small for fundamental light of 800 nm. An increase by about two orders of magnitude during the first 2 ML reflects the nonlinear response of *d* electrons, which strongly enhances the SH yield even for small coverages, long before the first monolayer is completed. This demonstrates the superb surface sensitivity of SHG, and justifies the neglect of nonlocal contributions to the SHG intensity. The slow overall decrease beyond the maximum yield around 3 ML indicates a gradual change in weight of SHG from the Co/Cu interface to that from the film surface. Up to 4 ML we also observe small maxima indicating layer completion,[15] which can be utilized for checking the film thickness.

The $s \rightarrow P$ yield behaves totally different. Below 1 ML it drops to almost zero, then increases and levels off to about the same yield as for the pure Cu(001) surface. Phase measurements presented below show that the minimum around 0.7 ML originates from a large phase shift between *s*- and *d*-band metals, which in the ideal case may amount to 180°. The exact position of the minimum depends on the ratio of SHG for thick films to the one for clean Cu(001), which can be seen by comparing Figs. 1 and 2.

Feature (3) in Fig. 1(a), the splitting of the yield curves for opposite magnetization directions, demonstrates ferromagnetic coupling with the in-plane magnetization direction. The onset at a film thickness of 1.9 ML for a substrate temperature of 300 K agrees well with the Curie temperature reported in the literature.[15,21] For $p \rightarrow P$ polarization the contrast for opposite magnetization directions persists throughout the measured range, implying that *no reorientation* of the magnetization takes place. We note, however, that splitting decreases linearly by about a factor of 2 between 2 and 12 ML. To interpret this reduction, knowledge of the relative phase is required, and we will return to this point later.

For $s \rightarrow P$ SHG a sign change of the magnetic contrast occurs around 5.5 ML [feature (4) in Fig. 1(b)], which is caused by phase shifts between odd and even contributions to the SH field, as will be shown below. The magnetic contrast has a maximum shortly after the onset of magnetization, then decreases with increasing film thickness, changes sign, and increases again with opposite sign for thicker films. Looking only at this sign change of magnetic contrast could lead to the improper conclusion of a magnetization reversal near 5.5 ML. This emphasizes the importance of measuring the relative phase.

B. Ni/Cu(001)

In Fig. 2 we show the *P*-polarized SH yield as a function of Ni-film thickness for *p*- and *s*-polarized incident light and opposite external magnetic-field directions. Compared to Co films, we note a similar trend of the overall SH intensity; the magnetic properties, however, are entirely different, as reported previously.[18] The beginning of film growth is again characterized by a steep increase of the $p \rightarrow P$ yield, reaching a maximum around 2 ML, while the $s \rightarrow P$ yield drops to about zero below 0.5 ML. As for Co films, both features are related to the different electronic structure and the correlated phase change. For $p \rightarrow P$ polarization the layer completion is also clearly discernible at 2 and 3 ML.

Ferromagnetic coupling of the Ni film appears in both polarization combinations around 5 ML, in agreement with the Curie temperature for this thickness.[22] Apart from the onset point, the data reproduce the well-known fact that the magnetization is at first oriented in plane, and due to stress inside the film reorients around 10 ML into the direction perpendicular to the film plane.[23,24] We find that the relative phases do not vary throughout the measured range of ferromagnetic coupling for both $p \rightarrow P$ and $s \rightarrow P$ polarization combinations.

III. PHASE MEASUREMENTS

In principle, the phase of the SH fields can be measured by time- or frequency-domain interferometry with regard to a nonlinear reference source. Which of the two techniques applies depends on whether or not sample and reference pulses overlap in time. If they overlap, the interference is measured in the time domain by altering the optical phase delay between the reference source and the sample.[5,6] This is usually done by varying the light path in gases, liquids, or other media with suitable phase velocity dispersion. In air, for example, changing the optical path by about 5 cm leads to a phase shift of 2π for a fundamental wavelength of 800 nm.

Such time-domain interferometry cannot be utilized in experiments with short laser pulses when the group velocity dispersion of a medium separates sample and reference pulses. In that case interferometry must be performed in the frequency domain, as demonstrated by Veenstra *et al.*[11] This method is necessary, for example, when phase measurements are to be carried out on a sample mounted in an UHV chamber, with the SH reference source located outside the UHV, as indicated in Fig. 3. The different group velocities of fundamental and SH light within the UHV window separate

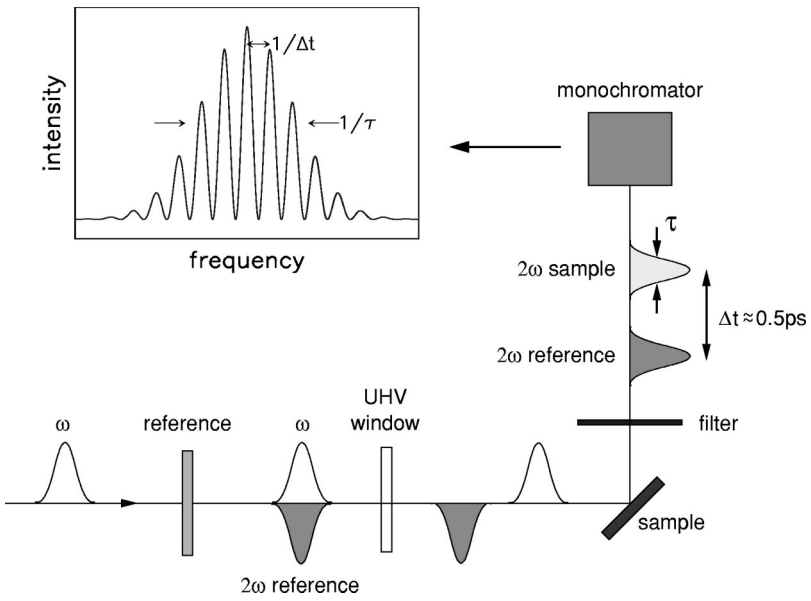

FIG. 3. Principal scheme for frequency-domain interferometry on thin metallic films in ultrahigh vacuum. Second harmonic pulses are shaded, darker ones originate from the reference source. The inset shows a typical interference pattern in the frequency domain.

reference and sample pulses by much more than the pulse width τ, and interference in the time domain vanishes. In the frequency domain, however, a temporal separation Δt gives rise to a modulation frequency $1/\Delta t$ spread over a spectral range of $1/\tau$ (see the inset of Fig. 3). The phase of the modulations, depending on the relative phase between sample and reference pulses, can then be measured with a monochromator without the need of moving optical elements.[11,25] Ultrashort laser pulses with their broadened spectrum, together with a polychromator, even permit real-time phase spectroscopy, as demonstrated by Wilson *et al.*,[25] who with this technique investigated the bias dependence of SH amplitude and phase of a Si metal-oxide-semiconductor capacitor.

For our phase measurements we used a 250-μm-thick *z*-cut quartz crystal as reference source. It was mounted outside the UHV chamber between the focusing lens and the 3-mm-thick fused silica UHV window. The different group velocities of fundamental and SH light within the UHV window separate reference and sample pulses by about 0.5 ps, which is more than an order of magnitude longer than the pulse width of $\tau \approx 30$ fs. The resulting interferogram was recorded by a 0.5-m grating monochromator with better than 0.1-nm resolution using a scanning speed of 0.2–0.5 nm/min at a sampling time of 1 sec. By rotating the reference quartz plate about its surface normal, the amplitude of the reference pulse could be varied[26] to match the SH signal strength originating from the sample, in order to achieve an optimized interference contrast at any given polarization direction.

In the following we will briefly summarize the way to extract the phase from the interference of sample and reference SH fields. Typical interferograms are shown in Fig. 4 for $s \rightarrow P$ SHG on a 6-ML Co film and opposite magnetic-field directions. Two main features characterize these patterns. One is the oscillation with a period of about 1 nm caused by the temporal separation $\Delta t = 0.53$ ps of SH reference and sample pulses after passing the UHV window (cf. Fig. 3). The second feature are the two maxima of the envelope which arise from SHG in the reference crystal. These are known as ''Maker fringes,'' and are most pronounced when the SH yield of the sample is weak, as is the

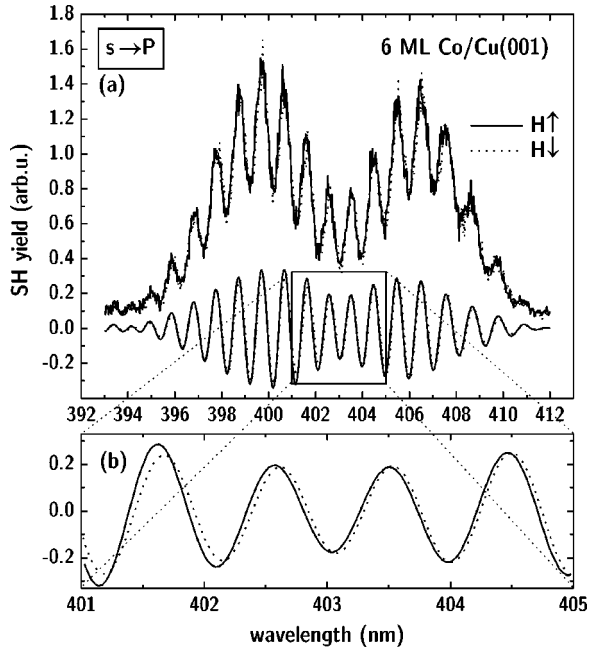

FIG. 4. Illustration of Fourier filtering for an interferogram recorded with $s \rightarrow P$ polarization on a 6-ML Co film for opposite magnetic field directions. The Fourier transform of the original data in (a) produces satellites around $\Delta t = \pm 0.53$ ps. Transforming these back produces the interferograms displayed below the original curves. Its magnified central part in (b) visualizes the phase difference between opposite magnetization directions.

case in Fig. 4. This phenomenon will not be discussed here further; instead we refer to the literature.[27]

Of relevance to our purpose are the high-frequency oscillations which contain the phase shift between the opposite magnetization directions. To extract the phase angles we adopted the filtering procedure described by Veenstra *et al.*[11] It involves that only the satellites of the Fourier transform at $\pm\Delta t$ will be taken into account. Backtransformation of these satellites into the frequency domain then produces the bandpass filtered interferograms from which the angular shift between the opposite magnetization directions can be extracted. To demonstrate the power of such a filtering process, we purposely picked the rather noisy $s\rightarrow P$ interferograms in Fig. 4(a). In the original data a modulation period of about 1 nm at 400 nm can be observed, but the phase shift between the opposite field directions is not discernible. In contrast, the Fourier-filtered interferograms, shown in the same frame below the original data clearly exhibit the phase shift, as illustrated in the magnified central segment in Fig. 4(b). This amounts to $11°\pm1°$. The same procedure was applied to derive all phase shifts for Co and Ni films of various thicknesses discussed below.

A. Phase change for nonmagnetic films

SHG on ultrathin films is composed of a coherent superposition of interface and surface-to-vacuum response. Both contributions come into play when the film-substrate interface is formed. Their relative weight varies with film thickness, and the question is how the total phase changes during the growth process. To investigate this the SH phase must be well defined, and polarization combinations involving several tensor components do not qualify. Therefore, we used $s\rightarrow P$ SHG, which includes only one tensor element χ^{even}_{zyy}, in the nonmagnetic thickness range. Also, we normalized the SH phase of the film to the one of the clean Cu substrate by measuring under identical conditions film and substrate phases with respect to a SH reference field.

In Figs. 1 and 2 we see, during the first 2 ML, an abrupt increase of the SH intensity for $p\rightarrow P$ polarization. In contrast, for $s\rightarrow P$ polarization, a rapid drop before 1 ML is followed by a steep increase up to the maximum around 2 ML. This general pattern is similar for Co and Ni films, suggesting that in both cases it reflects the evolution of an interface and the increased action of *d* electrons. To test whether the observed behavior is governed by a phase change, we have performed phase measurements on Co films using the $s\rightarrow P$ polarization. Figure 5(a) presents typical Fourier-filtered interferograms obtained with a clean Cu(001) surface, with 0.2-ML Co coverage, and with a 1.4-ML Co film. A magnified part in the lower frame [Fig. 5(b)] shows the phase shifts in more detail. Relative to the phase of clean copper (solid curve) one can recognize a shift of about 13° for 0.2-ML coverage (dashed curve) and 143° for the 1.4-ML Co film (dotted curve).

The important result is that the phase shift increases monotonously with Co coverage up to 2 ML and does not show any particularity near the minium of the SHG. Hence the minimum in the SH yield must be explained by assuming

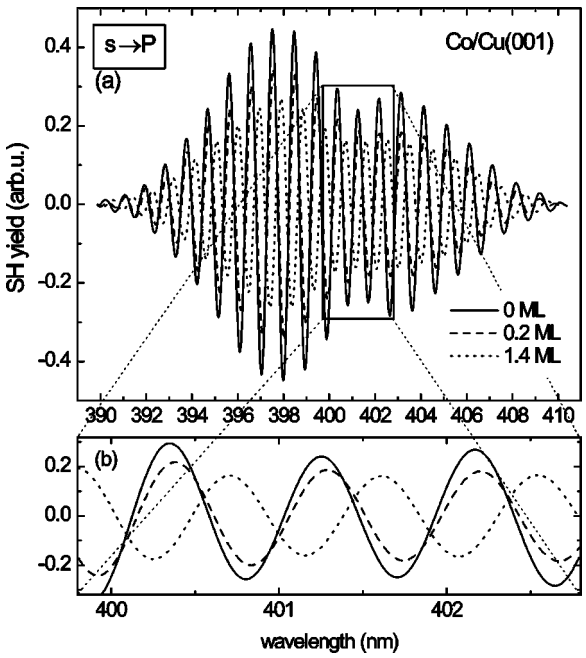

FIG. 5. SH phase changes for the initial nonmagnetic stages of Co-film growth. (a) Fourier-filtered interferogram recorded with $s\rightarrow P$ polarization on a pure Cu(001) surface and one with 0.2- and 1.4-ML Co coverages. (b) Magnified central part of the interferogram illustrating the phase shifts.

that there exists a phase shift of at least 143° for the nonlinear response of *s* and *d* electrons, as illustrated in Fig. 6. Here we replotted the $s\rightarrow P$ yield variation with coverage of Fig. 1(b), together with the results of the phase measurements. Vector diagrams on top of the figure attempt to explain the minimum. It is easy to see that such a minimum

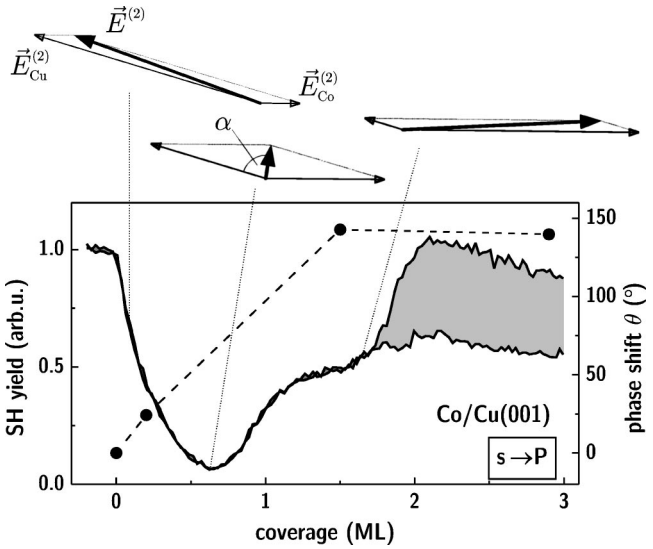

FIG. 6. SH phase shifts (dots) for the initial stages of Co-film growth compared to the $s\rightarrow P$ polarized SHG (solid curve) for opposite magnetization directions. The shaded area indicates the magnetic contrast of the film. Vector diagrams illustrate the phase shift at three coverages to explain the minimum of the SH yield around 0.65 ML.

occurs for the resulting SH field when the Co field increases with increasing coverage, provided it is out of phase by more than 90° to the Cu field. Simultaneously the Cu field decreases, since beyond a thickness of about 2 ML its contribution has vanished, as indicated by constant phase and total field. Of course, the cancellation would be complete for a phase shift of 180°, and we suggest that this value is reached under ideal conditions. Deviations from 180° could be caused by the small fraction of *s* electrons in Co, by possible contributions from surface states,[28] and by film imperfections and impurities. In fact, it is known that perfect growth of Co films does not proceed until 2 ML (Ref. 29) are completed. In contrast, Ni films on Cu(001) grow layer by layer, and consequently the conspicuous minimum of the $s \rightarrow P$ SHG on Ni/Cu(001) around 0.3 ML in Fig. 2 comes very close to zero which corroborates the proposition of a 180° phase shift between *s* and *d* electrons. Moreover, here a more or less constant yield is reached already at a smaller thickness possibly reflecting the better growth in this range.

The phase variation of the $s \rightarrow P$ SHG with coverage reflects its sensitivity to the electronic structure of the interface and film at a fundamental photon energy of 1.55 eV. In this energy range below the Fermi level *s* electrons in Cu, but mostly *d* electrons in Co with a higher density of states are excited.

B. Relative phase between even and odd SH fields

As mentioned above, for magnetic materials the *relative* phase between the even and odd fields is important.[8,30] This becomes evident when the MSH intensity is written in terms of the nonmagnetic and magnetic SH response fields

$$I^{\uparrow\downarrow}(2\omega) \propto |\mathbf{E}(2\omega)_{\text{even}} \pm \mathbf{E}(2\omega)_{\text{odd}}|^2 \tag{2a}$$

$$\propto E_{\text{even}}^2 + E_{\text{odd}}^2 \pm 2E_{\text{even}}E_{\text{odd}} \cos\phi. \tag{2b}$$

Here $\mathbf{E}(2\omega)$ can be expressed in the form[31,32]

$$\mathbf{E}(2\omega) = \frac{2i\omega}{c}\mathbf{F}(2\omega)\chi^{(2)}\mathbf{f}(\omega)|\mathbf{E}(\omega)|^2\delta z, \tag{3}$$

which factorizes the nonlinear response $\chi^{(2)}$ and the linear optical properties at fundamental and doubled frequencies contained in the Fresnel factors $\mathbf{f}(\omega)$ and $\mathbf{F}(2\omega)$, respectively. The interference term in Eq. (2b) depends on the relative phase ϕ which can severely affect the SH intensity of magnetized surfaces and interfaces. Upon magnetization reversal the nonlinear susceptibility $\chi^{(2)} = \chi^{(2)}_{\text{even}} + \chi^{(2)}_{\text{odd}}$ can undergo phase shifts between 0° and 180° while the Fresnel factors in Eq. (3) are barely altered by the linear magnetooptical effect. That odd tensor elements indeed have opposite phases for opposite magnetization directions was verified by Stolle *et al.*[10] using polarization-dependent SHG measurements on Rh/Co/Cu multilayers.

The relative phase ϕ cannot be measured directly with interferometric techniques. Figure 7 illustrates the situation. Of interest is the angle ϕ between the even- and odd-field contributions while measurements only provide the phase

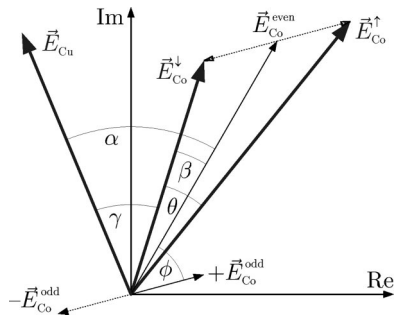

FIG. 7. Vector diagram of SH fields illustrating the connection between the measured phase shift θ between up ($\uparrow$) and down ($\downarrow$) magnetic field directions and the relative phase ϕ between the even and odd parts. Also included is the SH field from pure Cu(001) which served as reference field.

change θ and the intensity ratio, $I^{\downarrow}/I^{\uparrow}$, for opposite magnetization directions. These three quantities are connected, however. Starting from Eq. (2b), geometrical analysis on the basis of Fig. 7 leads to the following relations:[33]

$$\cos\phi = \frac{1 - I^{\downarrow}/I^{\uparrow}}{[(1 + I^{\downarrow}/I^{\uparrow})^2 - 4\, I^{\downarrow}/I^{\uparrow} \cos^2\theta]^{1/2}}, \tag{4}$$

$$\frac{|E_{\text{odd}}|}{|E_{\text{even}}|} = \left[\frac{1 + I^{\downarrow}/I^{\uparrow} - 2\sqrt{I^{\downarrow}/I^{\uparrow}}\cos\theta}{1 + I^{\downarrow}/I^{\uparrow} + 2\sqrt{I^{\downarrow}/I^{\uparrow}}\cos\theta}\right]^{1/2}. \tag{5}$$

The difficulty lies in the fact that $|E_{\text{odd}}|$ is generally small compared to $|E_{\text{even}}|$, which makes θ small even when ϕ is large. Thus, for a reliable determination of ϕ and $|E_{\text{odd}}|/|E_{\text{even}}|$, one has to measure θ and $I^{\downarrow}/I^{\uparrow}$ with high precision, which requires a good signal-to-noise level.

To demonstrate the typical accuracy of the raw data, interferograms obtained with a 8.3 ML Co/Cu(001) film are shown in Fig. 8 for $p \rightarrow P$ and $s \rightarrow P$ polarizations. The main feature is the oscillation with $\Delta\lambda \approx 1$ nm caused by the UHV window (cf. Fig. 3). Again, the ''Maker fringes''[27] are most pronounced for the $s \rightarrow P$ yield, which, in this case, is about four times smaller compared to the one for $p \rightarrow P$. The ratio of the yields, however, depends critically on the angular position of the reference crystal and is therefore not a measure of the actual ratio of sample contributions. As discussed above, the phase shift θ between the opposite magnetization directions can be derived from the high-frequency oscillations using the Fourier filtering procedure,[11] an example of which is displayed in Fig. 4 for a 6-ML Co film.

From Fig. 7 it is obvious that the relative phase shift ϕ between odd and even contributions can be understood as the difference between the phases of even and odd SH fields with regard to a reference. We chose the SH field from the pure Cu(001) surface as reference, and measured these absolute phases for a few film thicknesses to crosscheck the results for the relative phases.

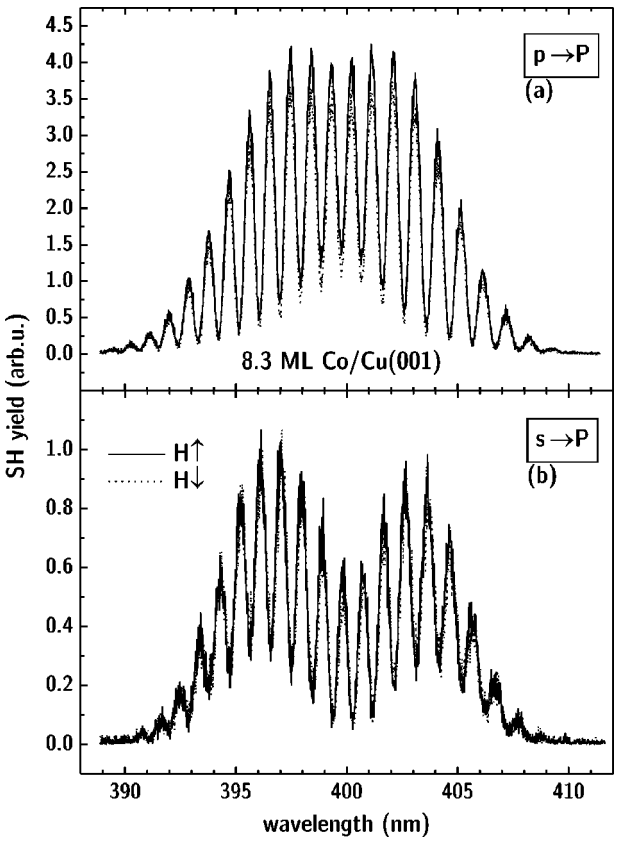

FIG. 8. Typical SH interference patterns of pulses from a reference source and from a 8.3-ML Co film on Cu(001) for $p \rightarrow P$ (a) and $s \rightarrow P$ (b) polarization combinations and opposite magnetization directions along $\pm y$, indicated by solid and dotted lines. Note the different scale for $p \rightarrow P$ and $s \rightarrow P$ spectra.

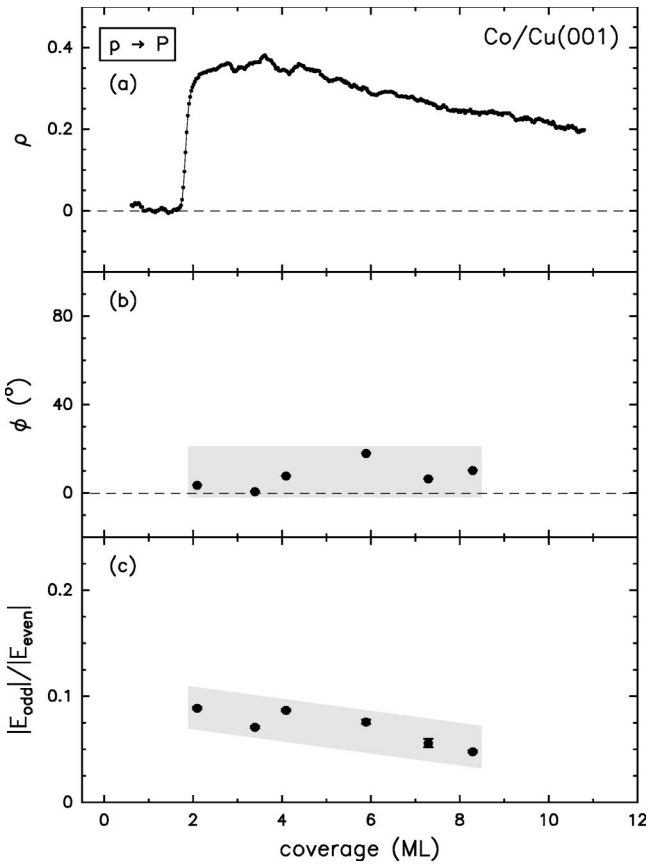

FIG. 9. Dependence on Co film thickness of the $p \rightarrow P$ polarized magnetic contrast (a), the relative phase ϕ between even- and odd- field contributions (b), and the ratio of odd- to even-field amplitudes (c).

IV. RELATIVE PHASE AND MAGNETIC CONTRAST

A. $p \rightarrow P$ polarized SHG on Co/Cu(001)

The following proportionality exists between magnetic contrast ρ, relative phase ϕ, and ratio of odd- and even-field amplitudes:

$$\rho \approx \frac{|E_{\mathrm{odd}}|}{|E_{\mathrm{even}}|} 2 \cos \phi. \tag{6}$$

This relation can be derived from Eq. (2b) with the realistic assumption $|E_{\mathrm{odd}}|/|E_{\mathrm{even}}| \ll 1$. Hence the magnetic contrast can be influenced by both the relative phase and the ratio of odd- and even-field amplitudes. This is visualized in Fig. 9, where the contrast ρ of the $p \rightarrow P$ polarized SH yield presented in Fig. 1(a) is compared to the independently measured phase angle ϕ. The onset of ferromagnetic coupling around 1.9 ML is followed by a maximum contrast at 2 ML, which then decreases almost linearly in the measured thickness range. At 12 ML the contrast is reduced by a factor of 2 [Fig. 9(a)]. Since the relative phases in Fig. 9(b) remain constant we find that, according to Eq. (6), the ratio of odd- to even-field amplitudes decreases by the same amount, as shown in Fig. 9(c). Assuming that $|E_{\mathrm{even}}|$ follows the average yield of the opposite magnetization directions, which is only reduced by 30% between 2 and 12 ML, we can conclude that the change of contrast is predominantly caused by $|E_{\mathrm{odd}}|$.

When speculating about the reasons for the decline of $|E_{\mathrm{odd}}|/|E_{\mathrm{even}}|$ with thickness two reasons are conceivable. One could be that for small thicknesses the magnetization of the Co film is stronger compared to thicker films,[34] and therefore a larger $|E_{\mathrm{odd}}|$ contributes to SHG. The other reason has to do with the fact that the field amplitudes and the relative phase are effective quantities which actually consist of three contributions. The mutual phases between the odd tensor elements $\chi_{xxx}^{\mathrm{odd}}$, $\chi_{xzz}^{\mathrm{odd}}$, and $\chi_{zzx}^{\mathrm{odd}}$ might shift with film thickness because only two of them depend on z. With $p \rightarrow P$ polarized SHG, including phase measurements, there is no chance to decide between these two possibilities, and we conclude that experiments in this polarization combination are in principle not sufficient to provide information about the relative size of interface and film magnetizations.

B. $s \rightarrow P$ polarized SHG on Co/Cu(001)

Since $s \rightarrow P$ SHG contains only one even ($\chi_{zyy}^{\mathrm{even}}$) tensor element and one odd ($\chi_{xyy}^{\mathrm{odd}}$) tensor element, the relative phase is well defined, and we expect unambiguous information from this polarization combination. Indeed, as can be

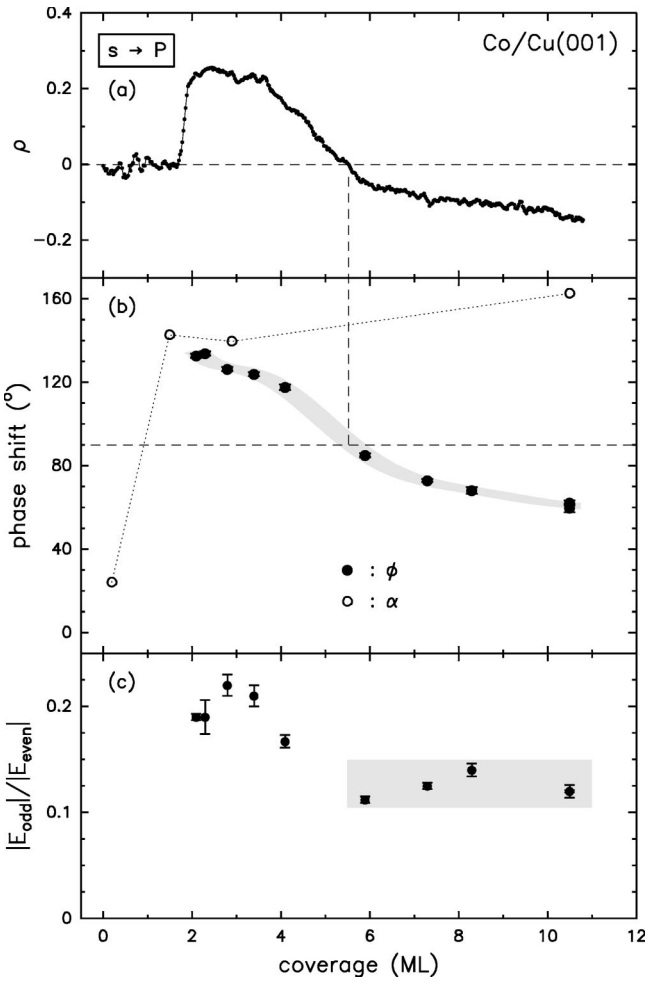

FIG. 10. Dependence on Co film thickness of the $s \rightarrow P$ polarized magnetic contrast (a), the relative phase ϕ (dots) between even- and odd- field contributions (b), and the ratio between the two field amplitudes (c). The variation of the phase shift α for the even field with regard to the Cu surface is indicated in (b) by open circles.

seen in Fig. 10(a), the observed variation of contrast with thickness derived from Fig. 1(b) differs dramatically from the one for $p \rightarrow P$ polarization. As expected, the onset of magnetization at 1.9 ML agrees with that measured with $p \rightarrow P$ polarization. The difference is that the magnetic contrast reaches its maximum somewhat later between 2.5 and 3 ML, then decreases with increasing film thickness and even changes sign near 6 ML. Beyond this point it increases again with opposite sign, but reaches no saturation within the measured range. The relative phase plotted in Fig. 10(b) varies in exactly the same manner as the magnetic contrast, and identifies the sign change as a mere phase effect. The phase angle turns from 133° at 2 ML to 60° between 10 and 11 ML, intersecting 90° near 6 ML, at exactly the same thickness where the magnetic contrast changes sign.

In Fig. 10(b) we also included the phase angle α between the even part of the SH field and that of Cu(001) (cf. Fig. 7). The first three values in the nonmagnetic thickness range have been discussed in connection with Fig. 6. The two phases at 2.8 and 10.5 ML have been extracted from the intensity ratio $I^{\downarrow}/I^{\uparrow}$, the phase shift θ for opposite field directions, and the angle γ between the field $E^{\downarrow}_{Co}$ and the bare Cu surface using the relation $\alpha=\beta+\gamma$. The angle β is obtained by the expression

$$\cos\beta = \frac{\sqrt{I^{\downarrow}/I^{\uparrow}} + \cos\theta}{[1 + I^{\downarrow}/I^{\uparrow} + 2\sqrt{I^{\downarrow}/I^{\uparrow}}\cos\theta]^{1/2}}, \tag{7}$$

derived from the cosine law for the triangles in Fig. 7. The important result of this analysis is that the phase shift of the even part varies by only 23° between 2.8 and 10.5 ML, while the relative phase ϕ between even and odd fields changes by as much as 73°. Since the phase shift of the odd field with regard to the Cu reference is the sum of the shift for the even part and the relative phase angle, we obtain for the odd part about 270° and 223° at 2.8 and 10.5 ML, respectively [see Fig. 10(b)]. That means most of the relative phase change of about 73° between 2.8 and 10.5 ML originates from the phase shift of the odd part.

The origin of the thickness dependence of the relative phase in Fig. 10(b) is not clear. It is definitely not caused by the varying path length ($\sqrt{2}d$ at 45° angle of incidence) of the fundamental and/or SH from the interface. Using the refractive indices $n_{co}(\omega)=2.5$ and $n_{Co}(2\omega)=1.6$,[35] one can estimate a phase shift with thickness of $\Delta\phi=2.4°/\text{nm}$, much too small to explain the observed variation.[36] It is also far less than the uncertainty of the relative phases observed for $p \rightarrow P$ polarization (Fig. 9). A possible explanation for the phase change are magnetostrictive effects. For example, Allenspach[37] found a sign change of the stress in Co/Cu(001) films between 3 and 5 ML, depending on temperature and preparation conditions. It is conceivable that such variations of the film stress correlate with the relative phase between even and odd SH fields.

The ratio of odd to even field amplitudes derived from magnetic contrast and relative phase [Eq. (6)] is shown in Fig. 10(c). The contribution of the odd SH field starts close to 2 ML, where the Co film becomes ferromagnetic at room temperature. Contrary to $p \rightarrow P$ polarization [cf. Fig. 9(c)], here we note a significant variation with thickness which reflects a magneto-optical property of the film, and is not caused by any phase effect. Around 3 ML the amplitude ratio reaches a pronounced maximum; beyond 4 ML, it decreases to and then remains constant above 6 ML. In principle, such variation can originate from either field, but of main interest are changes of $|E_{\text{odd}}|$ with film thickness since those would indicate a difference between film and interface magnetizations. To investigate this question we separated even- and odd- field amplitudes, assuming that $|E_{\text{even}}|$ is proportional to the averaged SH yield for opposite magnetization directions. Inserting this value together with the phase angles ϕ and the contrast ρ into Eq. (6) results in values for $|E_{\text{odd}}|$ which show exactly the same trend as the amplitude ratio in Fig. 10(c). Hence we conclude that the variation with film thickness originates exclusively from the odd contribution to the SH field.

The result of Fig. 10(c) is that the odd-field contribution to the SHG is maximal around 3 ML, and is smaller by a factor of 2 and constant from 6 ML on. This implies a cor-

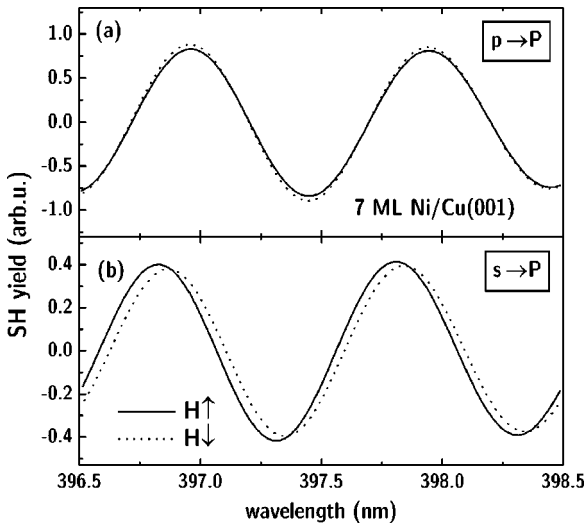

FIG. 11. Phase shifts θ between opposite magnetization directions along $\pm y$ obtained from Fourier-filtered interferograms measured with a 7-ML Ni film on Cu(001). Shifts for $p \rightarrow P$ polarization are diplayed in (a), and those for $s \rightarrow P$ polarization in (b).

respondingly stronger magnetization between 2 and 4 ML. Again, as for the phase, magnetostrictive effects could be responsible for this enhancement, although it seems a bit large. Another explanation would be the one mentioned above for $p \rightarrow P$ polarization in connection with Fig. 9, namely, an enhancement of the magnetization for thin films. For example, for a 2.1-ML Co film Srivastava *et al.*[34] observed a 20% larger magnetic moment compared to bulk. Most likely both effects, magnetostriction due to film stress and a gradual change of magnetic moments contribute to the observed behavior. Also, the constancy of $|E_{\mathrm{even}}|$ and $|E_{\mathrm{odd}}|$ for films thicker than 6 ML shows that the band structure is then well established, and no longer affected by film thickness. That there is still some influence of the changing fraction of interface to surface SHG can be seen from the slight variation of the magnetic contrast and the relative phase in Fig. 10.

V. RELATIVE PHASES FOR NI/CU(001)

Figure 2 shows that, apart from the size, the magnetic contrast is similar for $p \rightarrow P$ and $s \rightarrow P$ polarization in the case of Ni films. For that reason we decided to measure the relative phase only at one thickness (7 ML) located in the in-plane magnetization range. Using the procedure described above we obtained for the shift of the relative phase between opposite external field directions the result displayed in Fig. 11 and listed in Table I.

To obtain the ratio of odd to even tensor elements we analyzed the data in a slightly different way compared to the previous discussion. We substitute the SH field by the susceptibility tensor $\chi^{(2)}$ times the Fresnel factor which describes the linear optical properties of the material at 2ω. Then the SH intensity for opposite magnetization directions can be expressed as

$$I^{\uparrow\downarrow}(2\omega) \propto |A\chi^{(2)}_{\mathrm{even}} \pm B\chi^{(2)}_{\mathrm{odd}}|^2 I^2(\omega), \tag{8}$$

TABLE I. Phase ϕ and ratio of odd and even SH field contributions for 7 ML Ni/Cu(001).

Polarization combination	ϕ	$\lvert B\chi^{(2)}_{\mathrm{odd}}/A\chi^{(2)}_{\mathrm{even}}\rvert$
$p \rightarrow P$	$(33 \pm 7)°$	0.024 ± 0.003
$s \rightarrow P$	$(62 \pm 11)°$	0.020 ± 0.005

where A and B are the effective Fresnel factors in the case that χ contains several components. Equation (4) remains unchanged, and Eq. (5) now represents the ratio $|B\chi^{(2)}_{\mathrm{odd}}/A\chi^{(2)}_{\mathrm{even}}|$. The magnetic contrast takes the form

$$\rho = \frac{4|B\chi^{(2)}_{\mathrm{odd}}/A\chi^{(2)}_{\mathrm{even}}|}{1+|B\chi^{(2)}_{\mathrm{odd}}/A\chi^{(2)}_{\mathrm{even}}|^2}\cos\phi, \tag{9}$$

and the ratio of odd- to even-field contributions can be derived from the relative phase and the magnetic contrast.

Needless to say, there is no chance to extract any more details from the result for $p \rightarrow P$ polarization. For $s \rightarrow P$ polarization, however, which contains only one even tensor component and one odd tensor component, their ratio can be derived. Introducing the explicit expressions for the Fresnel factors one obtains the relation[33]

$$\left|\frac{B\chi^{(2)}_{\mathrm{odd}}}{A\chi^{(2)}_{\mathrm{even}}}\right| = \left|\left[\frac{1}{N^2\sin^2\vartheta} - \frac{1}{\mathrm{N}^4}\right]^{1/2}\right| \frac{|\chi^{\mathrm{odd}}_{xyy}|}{|\chi^{\mathrm{even}}_{zyy}|}, \tag{10}$$

where N is the refractive index for SH light and ϑ the angle of incidence which in our case was 45°. For the refractive index we can use the bulk value which for 400 nm amounts to $N = (1.70 + i2.69) \pm 2\%$.[38] This is justified by the observation of Wierenga *et al.*[14] that the linear magnetooptical Kerr signals of Co films thicker than 3 ML can be described by bulk constants. Inserting N and ϑ, for the absolute value of the square root we obtain the value 0.43 ± 0.01, which together with the measured ratio given in Table I leads to $|\chi^{\mathrm{odd}}_{xyy}|/|\chi^{\mathrm{even}}_{zyy}| = 0.047 \pm 0.013$ for the 7-ML Ni film. Hence the odd tensor element amounts to only 5% of the even one. Pan *et al.*[8] and Hübner[30] predicted 7%, but used the magnetic moment $0.68\mu_B$ of a free Ni(001) surface. However, measurements of x-ray circular dichroism on 4-ML Ni/Cu(001) films resulted in $(0.275 \pm 0.1)\mu_B$.[34] If we extrapolate this value to 7 ML, we obtain a magnetic moment of about $0.43\mu_B$ for the 7-ML film. Using this value reduces the predictions by Pan *et al.* and Hübner for the ratio of odd to even tensor elements to 0.044, in excellent agreement with our result.

VI. CONCLUSION

We have investigated the dependence of SH yield on thickness up to 12 ML for Co and Ni films on Cu(001), using the two polarization combinations $p \rightarrow P$ and $s \rightarrow P$ of fundamental and SH light. Comparing the two films, a significant difference was found for the magnetic contrast which was correlated to the relative phase between even and odd SH field contributions in the case of Co films. Phase shifts were measured in the frequency domain, and analyzed by Fourier filtering the data, following the scheme introduced

by Veenstra *et al.*[11] In general, we find that the $p \rightarrow P$ polarization combination is not suited for unambiguous phase measurements, since it involves three even and three odd tensor components, which allows one to derive only effective phase angles. Instead, a polarization combination like $s \rightarrow P$ should be employed which consists of just one even component and one odd component for a (001) surface. Using this, we observe for both Co and Ni coverages in the nonmagnetic thickness range below 1 ML, a drop of the SH yield to almost zero which we attribute to a phase shift of 180° between the nonlinear response of *s* electrons in the case of a bare Cu surface and *d* electrons of the Co or Ni films.

In the ferromagnetic regime the relative phase between the even and odd parts of the SH field and their amplitude ratio were determined. For Co/Cu(001) we find with $p \rightarrow P$ polarization, a monotonic decrease of the magnetic contrast by a factor of 2 between 2 and 12 ML, which is not caused by the relative phase but instead by a corresponding decrease of the amplitude ratio $|E_{\mathrm{odd}}|/|E_{\mathrm{even}}|$. In contrast, the sign change of the magnetic contrast for $s \rightarrow P$ polarization between 5 and 6 ML was identified as a mere phase effect. This shift of the relative phase was shown to originate mainly from the odd SH field. In addition, the amplitude ratio was enhanced by a factor of 2 in the thickness range around 3 ML compared to values for films thicker than 6 ML. We suggest that both the phase shift and the variation of amplitude ratio originate from a combined action of stress-induced magnetostriction and higher magnetic moments for thinner films. Future investigations are necessary to reveal more details.

In the case of Ni/Cu(001) the magnetic contrast differs in size but otherwise behaves similarly for $p \rightarrow P$ and $s \rightarrow P$ polarization. For this reason we measured the relative phase only at a thickness of 7 ML, well beyond the onset of the in-plane magnetization. From the data for $s \rightarrow P$ polarization, we derived the ratio $|\chi_{xyy}^{\mathrm{odd}}|/|\chi_{zyy}^{\mathrm{even}}| = 0.05 \pm 0.01$. This result agrees well with predictions in the literature provided that a magnetic moment of $0.43\mu_B$ is used for the Ni(001) surface, a value which can be extrapolated from x-ray magnetic circular dichroism.

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