Theory for Spin-Polarized Oscillations in Nonlinear Optics due to Quantum Well States

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Using an electronic tight-binding theory we calculate the nonlinear magneto-optical response from an x-Cu/Fe/Cu(001) film as a function of frequency and Cu overlayer thickness ($x = 3-25$). We find very strong spin-polarized oscillations with periods of 6 and 11 monolayers due to quantum well states. These oscillations are enhanced by the large density of Fe d states close to the Fermi level acting as intermediate states for frequency doubling. The results show that optical second harmonic generation is a very sensitive probe of electronic structures and is even **k** sensitive. [S0031-9007(96)01235-5]

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The magnetism of low-dimensional metallic structures such as surfaces, thin films, and multilayer sandwiches has recently become an exciting new field of research and applications [1]. In particular, thin magnetic films and multilayers exhibit a rich variety of properties not previously found in bulk magnetism such as enhanced or reduced moments [2], oscillatory exchange coupling through nonmagnetic spacers [3], giant magnetoresistance [4,5], and the reorientation of the magnetic easy axis upon thickness and temperature variation [6]. Especially the observation of spin-polarized quantum well states (QWS) [7–10] in Cu/Co(001) has attracted a great deal of attention. It has become clear that quantum well states are indeed responsible for the important oscillatory behavior of the exchange coupling of ferromagnetic thin films via nonmagnetic spacers [11,12]. Presently mainly photoemission (PE) and inverse photoemission [7–10] have been used to identify QWS effects. Very recently a possible connection between thickness dependent changes in the nonlinear magneto-optical Kerr effect (NOLIMOKE) and QWS [13] has been proposed.

It is the goal of this Letter to show that also *nonlinear* optics, in particular NOLIMOKE, is a new sensitive tool for studying QWS. We find very interesting structure in the second harmonic generation (SHG) signal due to particular transitions in **k** space. This is very remarkable since it indicates that SHG is able to detect very sensitively **k**-dependent structures. This new effect seems to be of general interest for the physics of nonlinear optics and its relationship to the underlying electronic structure. Nonlinear optics, in contrast to linear optics, is able to give wave-vector resolved information about the underlying electronic structure. We demonstrate this by extending our previous work on the Fe/Cu(001) bilayer system [14] to the sandwich system x-Cu/1Fe/Cu(001) where the layer number x is varied between 3 and 25. We calculate the SHG yield $I_{(2\omega)}(\omega)$ and the magnetic intensity contrast $\Delta I_{2\omega} = \frac{I_{2\omega}(\mathbf{M}) - I_{2\omega}(-\mathbf{M})}{I_{2\omega}(\mathbf{M}) + I_{2\omega}(-\mathbf{M})}$ of SHG for these systems and find very large quantum well oscillations, originating from particular transitions in **k** space. Note linear optics is less informative, since it involves only one transition and since the Drude term of the dielectric function creates a strong background of transitions from all **k** directions.

A simple physical picture explains already that SHG and NOLIMOKE, involving optical transitions $E_l \overset{\hbar\omega}{\rightarrow} E_{l'} \overset{\hbar\omega}{\rightarrow} E_{l''} \overset{2\hbar\omega}{\rightarrow} E_l$ between initial, intermediate, and final states E_l, $E_{l'}$, and $E_{l''}$, respectively, should exhibit large oscillations due to quantum well states. We assume for simplicity that, for the x-Cu/Fe/Cu(001) sandwich initial and intermediate states E_l and $E_{l'}$ have little dispersion as expected for electronic d states in thin films and that the relevant unoccupied states above the Fermi level are Cu s-QWS, whose energies depend on the film thickness and which occur only for discrete values of the perpendicular wave vector $\mathbf{k}^{\perp}$. Then the final optical transition $E_{l'} \overset{\hbar\omega}{\rightarrow} E_{l''}$ must reach a quantum well state in order to contribute to SHG. For given $\hbar\omega$ this happens only for a certain film thickness and multiples of this. Thus oscillations arise. The period of the oscillations should depend characteristically on the photon energy and the electronic structure. The oscillations will eventually get washed out for thicker films, since the QWS get denser. The amplitude of the oscillations is strongly increased by the Fe interlayer, since SHG benefits from the high density of Fe states. Also it becomes clear that the spin polarization of the intermediate Fe states will cause a magnetization dependence of the period and a relative peak shift upon changing the magnetization direction **M** to $(-\mathbf{M})$ [see Eq. (1)]. The **k** selectivity is a consequence of the fact that unoccupied final states are necessary for a contribution to the SHG yield.

To verify this physical picture we performed calculations using our previous theory to evaluate the SHG intensity $I_{2\omega}(\omega)$ for opposite magnetization directions [15–17]. Employing an electronic theory for both the nonlinear susceptibility $\chi^{(2)}$ and the linear dielectric function $\epsilon(\omega)$ and separating $\chi^{(2)}$ into even and odd parts under magnetization reversal $\chi^{(2)}_{\text{even}}(\omega)$ and $\chi^{(2)}_{\text{odd}}(\omega)$, we get for the SHG yield within the electric-dipole approximation for the polar geometry (**M** is normal to the surface

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for a Fe monolayer) [18]

$$I_{2\omega}(\pm\mathbf{M}) \propto |E_0|^2 \, | f(\omega)^2 F(2\omega) \{\chi^{(2)}_{\text{even}}(\omega) \pm \chi^{(2)}_{\text{odd}}(\omega)\}|^2. \quad (1)$$

Here, $f(\omega)$ and $F(2\omega)$ are calculated from the linear Fresnel factors. The susceptibility $\chi^{(2)}$ which is a key quantity for the nonlinear optical response, is given by

$$\chi^2(\omega) = \sum_{l,l',l'',k^\perp,\sigma} M^3 \frac{1}{E_{l''} - E_l - 2\hbar\omega + 2i\hbar\alpha_1} \times \left\{ \frac{f(E_{l''}) - f(E_{l'})}{E_{l''} - E_{l'} - \hbar\omega + i\hbar\alpha_1} - \frac{f(E_{l'}) - f(E_l)}{E_{l'} - E_l - \hbar\omega + i\hbar\alpha_1} \right\}. \quad (2)$$

Here, $f(E_l)$ denote the Fermi distribution functions, α_1 is the Lorentzian broadening, and M are the dipole matrix elements. The sum is performed over all eigenstates E_l and all allowed $\mathbf{k}^\perp$ points [19]. Note that all eigenvalues E_l depend on $\mathbf{k}^\perp$ and spin σ and that the nonlinear susceptibility tensor $\chi^{(2)}(\omega)$ is material specific.

As input for the calculation of $\chi^{(2)}$ we used for the electronic band structure of the x-Cu/Fe/Cu(001) system a Cu bulk Hamiltonian combined with a Fe monolayer. The Hamiltonian is calculated within the combined interpolation scheme [20], the parametrization is according to Fletcher and Wohlfarth [21]. The parameters for the Cu bulk band structure are taken from Ref. [22]. For the Fe monolayer they have been obtained from a fit to an *ab initio* calculation [23]. We are evaluating the SHG response at $(k_x, k_y) = (0, 0)$, since for the (001) direction the high density of states due to the extremal Fermi surface diameter (caliper) at $\mathbf{k}^\parallel = (0, 0)$, which give the QW period from Ruderman-Kittel-Kasuya-Yoshida calculations [24], dominates the output [25,26]. The $\mathbf{k}$ summation is performed over $\mathbf{k}$ points along the $\mathbf{k}^\perp$ direction. QWS are introduced for the Cu 4s-band in which states occur only at equally spaced $\mathbf{k}^\perp$ values ($\Delta\mathbf{k}^\perp \propto 1/n$, n is the number of Cu overlayers).

To simplify our calculation, we assume constant matrix elements, which are fitted by the linear dielectric function $\epsilon(\omega)$ [17,27] and perform the summations in Eq. (2) using an appropriate interface cutoff. This approximation is reasonable because the $\mathbf{k}$ dependence of the matrix elements is expected to become less important in two dimensions due to the shrinking of the d-band width for the reduced coordination number [17]. To compare with experiment [28], we choose 1.61 eV as incident photon energy.

In Fig. 1 we show results of our calculation for the SHG signal of the x-Cu/Fe/Cu(001) system as a function of the Cu overlayer thickness demonstrating the pronounced QWS oscillations (nearly 100% of the signal) and their strong spin dependence. Most striking is the dominant oscillation period of 11 monolayers (ML)

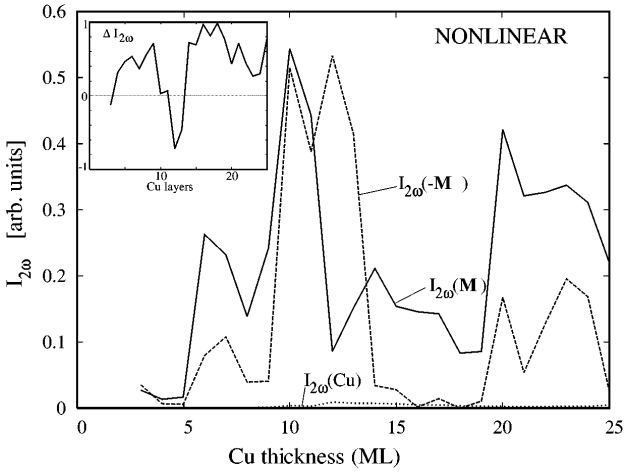

FIG. 1. SHG yield for opposite magnetization directions $\mathbf{M}$ and $-\mathbf{M}$. The dominating 11 ML period is due to a $2\hbar\omega$ resonance between Cu d states and quantum well states, drastically enhanced by the Fe d bands and thus demonstrating the $\mathbf{k}$ selectivity of SHG. In the absence of the Fe bands the SHG yield $I_{2\omega}(\mathrm{Cu})$ is nearly indistinguishable from zero on this scale. The peak shift between the $\mathbf{M}$ and $-\mathbf{M}$ signal is due to the spin polarization of the Fe d bands. The inset shows the magnetic contrast $\Delta I_{2\omega} = \frac{I_{2\omega}(\mathbf{M}) - I_{2\omega}(-\mathbf{M})}{I_{2\omega}(\mathbf{M}) + I_{2\omega}(-\mathbf{M})}$.

of the SHG signal for both magnetization directions $\mathbf{M}$ and $-\mathbf{M}$ and the relative peak shift upon changing $\mathbf{M} \rightarrow -\mathbf{M}$. A smaller period of 6 ML is also present. The enhancement of the SHG signal due to the Fe d bands becomes apparent if we compare $I_{2\omega}(\pm\mathbf{M})$ with the nonlinear response $I_{2\omega}(\mathrm{Cu})$ of the system without the Fe interlayer (but keeping the confinement for the Cu overlayer), which is 50 times weaker, in good agreement with experiment [28]. The inset of Fig. 1 showing results for the magnetic contrast ΔI_{2w} gives further evidence for the importance of the Fe d bands. The result indicates clearly that the exchange splitting of the Fe interlayer is heavily involved. The magnetic contrast varies between 100% and -80% and changes sign several times, due to the equal amplitudes of the SHG intensity for both magnetization directions. Our results for the period, the amplitude, and the magnetic contrast are in excellent agreement with experiment [28].

In Fig. 2 we show for comparison the *linear* dielectric function $\epsilon(\omega)$, and the linear Kerr angle for the same system as a function of the Cu overlayer thickness. Two oscillation periods for the imaginary part of the dielectric function $\epsilon(\omega)$ for both magnetization directions can be detected, a dominant one with period 6 ML and a less pronounced oscillation with a period of 3 ML. In contrast to nonlinear optics, the amplitude of the oscillation is much smaller (5% of the signal), in agreement with experimental observations [29]. Furthermore, an overall increase of the linear signal with Cu thickness is observed, since it results not only from the interface, but from all layers. Note the magnetic effect is 3 orders of magnitude smaller than for the nonlinear signal. This small magnetic effect becomes

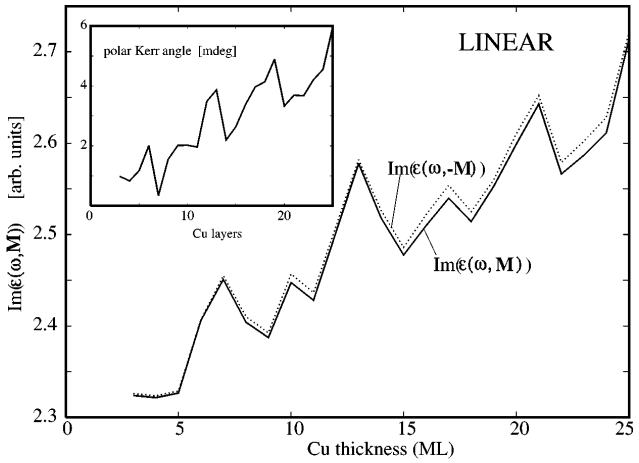

FIG. 2. Linear dielectric function of the x-Cu/Fe/Cu(001) sandwich for opposite magnetization as a function of the Cu layer thickness. Note the 6 ML period as fundamental period is visible, while the 11 ML period is completely absent. The magnetic contrast is much smaller than for the SHG signal. The inset shows the linear Kerr angle Φ_{Kerr} as a function of the Cu layer thickness.

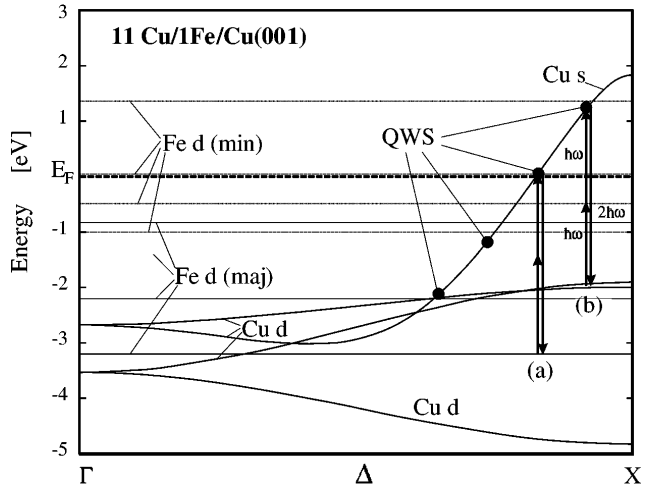

FIG. 3. Band structure of the x-Cu/Fe/Cu(001) sandwich along $\mathbf{k}^{\perp}$ for 11 Cu monolayers. Bands with energy less than -5 eV are not drawn. The filled dots mark some of the QWS as derived from the Cu bulk band structure for 11 ML. The contributing transitions giving the dominant peak of the SHG yield at 11 ML (and 22 ML) are indicated. Transition (b) is resonant for $2\hbar\omega$ and only possible in nonlinear optics. For the case of 6 ML only the QWS at E_F and at -2.1 eV is present. Thus the peak of the SHG yield at 6 ML and multiples results mainly from transition (a).

obvious from the linear Kerr angle Φ_{Kerr} shown in the inset of Fig. 2. Φ_{Kerr} is of the order of mdeg, whereas the nonlinear Kerr angle is 2 to 3 orders of magnitude larger [23]. The polar Kerr angle also displays the 6 ML oscillation period, and the overall increase with increasing layer thickness is again due to the large probing depth of the magneto-optical Kerr effect.

Our results for the pronounced oscillations of $I_{2\omega}(\omega)$ due to QWS can be understood in view of Fig. 3, where the electronic structure of the x-Cu/Fe/Cu(001) system for $x = 11$ ML along $\mathbf{k}^{\perp}$ is sketched [30]. The QWS (filled dots) result from the confinement of the s electrons in thin Cu films, causing an equally spaced discretization in the $\mathbf{k}^{\perp}$ direction, whereby the number of $\mathbf{k}$ points equals the number of Cu layers. Only the four rightmost QWS are displayed in Fig. 3 for simplicity. Clearly this discretization of the $\mathbf{k}$ values affects the SHG intensity, since photon transitions $E_{l'} \rightarrow E_{l''}$ are limited to these distinct $\mathbf{k}^{\perp}$ points. The appearance of a QWS above E_F as a final state for the nonlinear optical transition results in an increase of the nonlinear response. This occurs only for a certain film thickness.

Apparently only if the QWS is at resonance for a signal frequency $\hbar\omega = 1.61$ eV, two incident photons are able to excite electrons from the Cu d band to the Cu s-QWS [transition (b)]. Then a $2\hbar\omega$ photon may be emitted resonantly, generating the frequency-doubled nonlinear response [31]. Transitions of this kind are mainly responsible for the peak at 11 ML and multiples thereof in Fig. 1 for both magnetization directions and a signal frequency of 1.61 eV. At 11 ML also the second QWS close to E_F contributes [nonlinear transition (a), Fig. 3]. Consequently, this gives an additional contribution to the SHG yield. Nevertheless, there is no general increase of the SHG with layer thickness, since the SHG results only from the Fe/Cu interface. A transition similar to (b) in Fig. 3, which involves the Fe minority bands as intermediate states, gives additional resonances for the minority transitions, thus resulting in a peak shift and broadening for magnetization $-\mathbf{M}$ at 11 ML; see Fig. 1. This peak shift then results in the strong magnetic contrast; see inset of Fig. 1.

In a sandwich with $x = 6$ ML of Cu, however, only the QWS at E_F and at -2.1 eV are present, giving rise to a strong contribution to $I_{2\omega}(\omega)$ due to the transition indicated by (a). This transition causes the oscillation period of 6 ML.

Next we discuss the oscillation due to QWS for the *linear* response. For the linear dielectric function $\epsilon(\omega)$ a resonance between the Cu s and d bands, which is responsible for the very strong peak in SHG at 11 ML, [transition (b) in Fig. 3] is not possible. Therefore the period of 11 ML as a fundamental period is absent. Only the upper transition in (a) of Fig. 3 with absorbed and emitted photon energy $\hbar\omega$ is involved [32]. Since this QWS at E_F is present at 6 ML and is in resonance with Fe majority d band at -2.1 eV, we find a dominant oscillation period of 6 ML. The smaller 3 ML period is due to a QWS at -2.1 eV, which occurs at 3 ML and multiples thereof and which allows for a resonant transition to the minority Fe d band near E_F. The strong influence of the nonmagnetic intraband transitions on the linear signal is responsible for the suppression of the magnetic effect as observed in the linear Kerr angle [33], which exhibits mainly the 6 ML period (see inset).

It becomes obvious from Eq. (2) that oscillations in SHG are much stronger than in linear optics, since two resonant energy denominators may occur and since the sum runs independently over all three energies E_l, $E_{l'}$, and $E_{l''}$, thus exploiting the large density of d states of both Fe and Cu. This yields a strong enhancement of effects due to QWS in SHG compared to linear optics. In our electronic structure the Cu d states cause this strong enhancement of the SHG oscillations, whereas the Fe d states in addition are responsible for the strong magnetic contrast. Since this amplification mechanism is not operative in linear optics, the oscillatory contribution to the linear signal is much weaker.

It becomes clear from our analysis that the oscillation period will depend on the photon energy. For the studied system we expect an increase of the period with increasing photon energy, since the dominant resonance between the Cu d and s bands is then due to a QWS at a $\mathbf{k}^{\perp}$ vector closer to the Brillouin-zone edge, thus resulting in a larger period. However, in general the oscillation period will depend on the electronic structure. If the QWS are involved as intermediate states, as might be the case for the x-Au/Co(0001)/Au(111) sandwich, the frequency dependence of the oscillation period might be largely reduced [34] due to (i) the large dispersion of the states above E_F acting as final states and (ii) a relatively narrow energy interval where confinement may occur (iii) the enhanced importance of the QWS symmetry compared to the energy denominators [35].

In conclusion, we showed that QWS give rise to strongly enhanced SHG oscillations. The electronic origin of this strong enhancement is analyzed. We get that SHG and consequently also NOLIMOKE is able to probe particular transitions in $\mathbf{k}$ space. Our results demonstrate that, although the period is caused by the s-QWS, the amplitude of the oscillation is enhanced due to the high density of Fe d states. Periods different from the fundamental period found in PE experiments are possible, depending on the position of resonant d bands below E_F. In contrast to linear optics, in SHG even $2\hbar\omega$ resonances strongly influence the oscillation. In the considered sandwich structure, this makes the larger period dominate the spectrum.

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[30] Of course, in the $\mathbf{k}^{\perp}$ direction there is no dispersion of the Fe monolayer bands.
[31] Note that the states involved in the transitions are controlled by $\hbar\omega$. One expects particularly strong contributions to SHG if $\hbar\omega$ matches the electronic resonances. Nonmatching effects become directly clear from the energy denominator in Eq. (2).
[32] To give a contribution to the linear response, an occupied and an unoccupied electronic state have to be involved. Therefore, transitions between two occupied d states such as the lower transition of (a) in Fig. 3 do not contribute.
[33] Furthermore, the square-root term in the formula for the polar Kerr angle suppresses the influence of the (spin polarized) interband contributions (see Ref. [23]).
[34] A. Kirilyuk and Th. Rasing (private communication).
[35] This case can be analyzed within our theory employing the symmetry of the matrix elements M in Eq. (2).