Effects of Surface Magnetism on Optical Second Harmonic Generation

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We report on the first experiments showing the influence of surface magnetization on optical second harmonic generation in reflection at a Fe(110) surface. The magneto-optical Kerr effect modifies the hyperpolarizability of the surface in the optical field, leading to a dependence of the second harmonic yield on the direction of magnetization relative to the light fields. For the clean surface an effect of 25% was determined, which decays exponentially with surface contamination by the residual gas, thus demonstrating the high surface sensitivity of this technique.

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For more than two decades, the magnetic properties of thin films and surfaces of magnetic materials have been subject to intensive experimental [1–8] and theoretical [9–12] research, incited by the question of Liebermann, Fredkin, and Shore [1] whether or not the topmost two layers of these materials are magnetically dead. In addition to conventional techniques for studying surface magnetization, such as, e.g., spin-polarized electron spectroscopies [3,4], recently the use of surface-sensitive optical second harmonic generation (SHG) has been proposed [10–12]. This method combines the advantage of being a purely optical one, which allows investigations wherever light has access, with a pronounced surface sensitivity [13]. Since the generation of the second harmonic is, for symmetry reasons, forbidden in centrosymmetric materials, from a cubic crystal all signal originates in the surface region where the bulk symmetry is broken, i.e., from the first two to three atomic layers. Therefore, detailed information about electronic and magnetic surface properties, like band structure, exchange interaction, spin-orbit coupling, etc., may be expected from respective experiments and corresponding theory.

The magnetization dependence of the second harmonic generation may be understood in a similar way as the linear magneto-optical Kerr effect [14,15], which has been well established as a rapid optical probe for magnetization [2], the drawback of which, however, is the lack of surface sensitivity. The combined action of spin-orbit coupling and exchange interaction in ferromagnetic materials affects the polarization of the reflected light also in higher orders. As shown by Argyres [15], spin-orbit coupling acts like a magnetic field on the electrons which are forced to move in the current induced by the electric field of the incident light. (Nonlinear contributions to this current are at the origin of second harmonic generation.) The "Lorentz force" corresponding to this (spin-orbit) magnetic field rotates the direction of the reradiated electric light field with respect to the driving one. This effect is illustrated in Fig. 1 for a specific geometrical situation. Let us, for simplicity, consider only the oscillation of the electrons perpendicular to the surface, denoted by $\mathbf{e}_z$, as induced by the projected electric field of the p-polarized fundamental light, incident under 45° to the surface normal. (This is the oscillation giving the largest contribution to the generated second harmonic [16].) If the (spin-orbit) magnetic field is pointing "up" as shown in Fig. 1 (i.e., along the [001] direction which is the easy axis of magnetization in Fe), the Lorentz force leads to a small counterclockwise rotation of the macroscopic direction of oscillation [17], resulting in the oscillation denoted by $\mathbf{e}_-$. For the observation of p-polarized light in the direction of specular reflection, the respective projection obviously results in a *reduction* of intensity. Analogously, the reversed direction of the magnetic field *increases* the observed intensity. Whereas in paramagnetic materials both antiparallel spin directions, and thus the spin-orbit contributions to the equivalent magnetic field, are equally abundant, balancing out the two polarization rotations, in a ferromagnet exchange interaction leads to a different abundance of both spin directions. The consequence is a

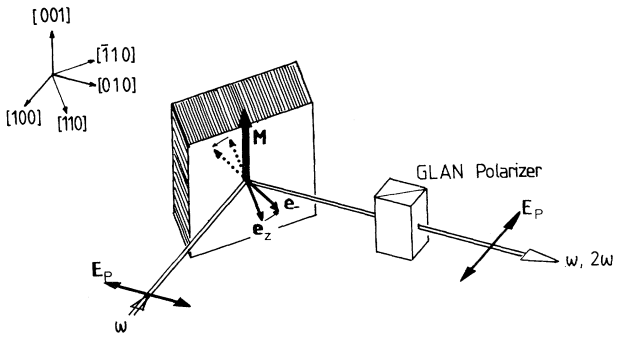

FIG. 1. Schematic of the experimental situation: The Fe(110) crystal is in a single magnetic domain state, with the magnetization along the ± [001] directions. p-polarized light of frequency ω (532 nm) is incident under 45° to the normal (i.e., [1̄00]), and the p-polarized second harmonic, as analyzed by a Glan polarizer, is observed under specular reflection (i.e., in the [010] direction). The effect of the magnetization on the induced electron oscillation perpendicular to the surface ($\mathbf{e}_z$) is sketched, resulting in a polarization rotation of the reradiated light field ($\mathbf{e}_-$). Inset: The relevant crystallographic directions.

preferred direction of the Lorentz force and thus a net effect on the polarization of the reflected second harmonic light. Since here we want to concentrate on the most significant effect of reversing the direction of the average magnetization in the irradiated region, we can simplify the argument of Pan, Wei, and Shen [10], and distinguish between magnetization-dependent ("odd-parity") and -independent ("even-parity") contributions to the second-order optical susceptibility [18] $\chi^{(2)}$. The electric field of the generated wave at the second harmonic frequency may thus be written as

$$\mathbf{E}^{\pm}(2\omega) \propto (\chi_0^{(2)} \pm \chi_{\mathrm{mag}}^{(2)})\mathbf{E}^2(\omega)\,, \qquad (1)$$

and the observed second harmonic intensity is given by the square of Eq. (1). ($\pm$ refers to the two possible directions of the magnetic field.)

In this Letter we report on the first experiments revealing the influence of surface magnetization on optical second harmonic generation at a Fe(110) surface under ultrahigh-vacuum conditions (basic pressure below 10^{-7} Pa). The experimental arrangement was chosen according to the above considerations and is schematically sketched in Fig. 1: The magnetization is parallel to the [001] direction on the (110) surface, thus being perpendicular to the plane spanned by the incident fundamental light and the specularly reflected second harmonic light, both at 45° to the surface normal ("plane of incidence"). Both light beams are *p* polarized; i.e., the electric fields oscillate in the plane of incidence, and thus both have one component parallel and one component perpendicular to the surface [18]. In detail, a single crystal of Fe(110) is fixed between the jaws of an electromagnet to align the magnetic domains. For sample preparation, the crystal was sputtered and annealed, thus guaranteeing a clean and well-ordered surface [19,20]. As the fundamental light, 532 nm from a frequency-doubled neodymium-doped yttrium-aluminum-garnet laser was used, providing pulses of 6-ns duration with an intensity of $\approx 5\times10^6$ W/cm^2 at the sample, at a repetition rate of 20 Hz. For both beams *p* polarization was well controlled by means of Glan prisms with an extinction ratio $> 10^6$. The generated second harmonic of this radiation (266 nm) was detected by a photomultiplier equipped with a solar-blind Cs-Te cathode in order to minimize interferences by the reflected fundamental light. In addition, several UV transmitting edge filters were applied, partly in front of the analyzing Glan prism to avoid nonlinear effects. For each laser pulse, the analog photomultiplier signal was processed in a gated integrator, digitized, and transferred to a microcomputer where it was stored. The influence of laser power fluctuations was minimized by normalizing each pulse of the SHG signal to a frequency-doubled reference signal produced from an idle reflection of the incident beam. One experimental cycle consisted in taking 250 laser shots with the magnetization in the "up" direction, 100 pulses with a glass plate blocking the generated UV light as a reference, and 250 pulses with reversed magnetization ("down"). In order to improve the statistics, several experimental cycles were superimposed to yield results like the one in Fig. 2. Finally, the data were averaged over the respective regions of interest ("up" or "down").

The typical result is shown in Fig. 2: In part (a), data from several runs, all taken during the first 45 min after freshly sputtering the surface are superimposed (220 cycles), normalized to the mean value between the two regions with field up and down, i.e., to the expectation without magnetization. Obviously, there is a pronounced magnetization-dependent contribution to the second harmonic yield to be seen from the difference between the

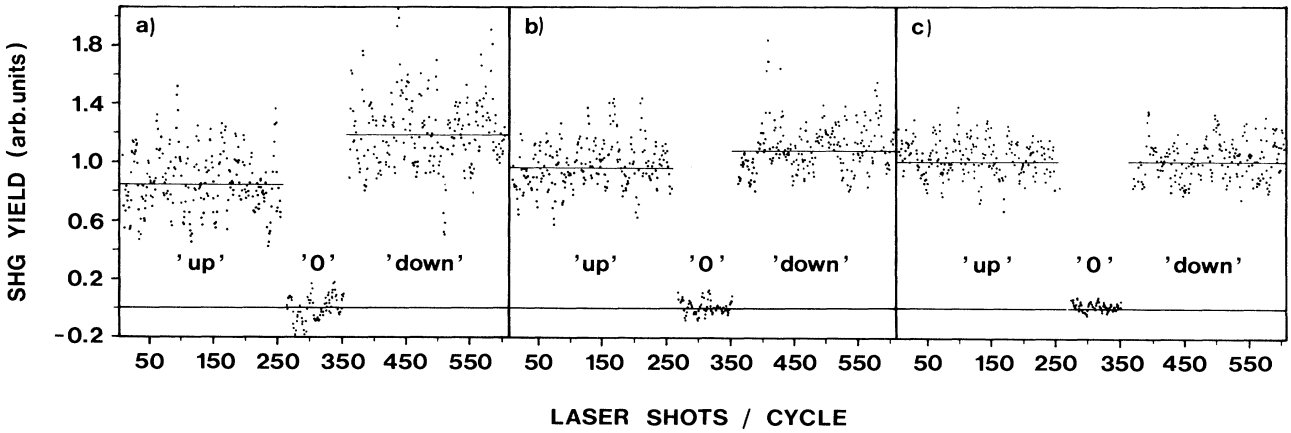

FIG. 2. Relative magnetization dependence of second harmonic signal for three different times elapsed since sample preparation [(a) $\approx$45 min, (b) $\approx$60 min, (c) $\geq$ 180 min]. Shown is, in each panel, an averaged [superposition of (a) 220, (b) 550, and (c) 750 cycles] experimental cycle, consisting of 250 pulses with magnetization "up," 100 pulses with no SHG signal (obtained by means of a UV blocking glass filter), and 250 pulses with magnetization "down." All signals are normalized to the expected value without influence of magnetization [cf. Eq. (1)]. The solid lines represent the average of the respective regions of interest.

magnetization up and down signals. Part (b) of Fig. 2 (550 cycles) was obtained in the same way from surfaces with about 60 min elapsed time, whereas part (c) (750 cycles) is typical for surfaces, which had not been cleaned for at least 3 h. The horizontal lines give the average values in the respective regions of interest. The results are summarized in Table I. In order to gain confidence in the experimental result, we checked our setup by looking for the second harmonic signal with both light polarizations being parallel to the magnetization. As expected [10], no magnetic signal could be detected.

It is obvious from the experiment that the magnetization-dependent contribution to the nonlinear susceptibility decays with time elapsed from the surface preparation. This decay with time is analyzed in more detail in Fig. 3: For three series of measurements and the data of Fig. 2, all at a residual pressure of about 9×10^{-8} Pa, the relative magnetization-dependent susceptibility $\chi^{(2)}_{\rm mag}/\chi^{(2)}_0$ is plotted versus the time passed since surface preparation. We find an exponential decay with time constant

$$\tau = 1835\ \text{s} = 30.6\ \text{min}\,, \tag{2}$$

and an initial ratio

$$\chi^{(2)}_{\rm mag}/\chi^{(2)}_0 = 0.25 \tag{3}$$

for a freshly prepared surface.

This ratio of nonlinear susceptibilities has to be compared to a simple theoretical estimate. The nonmagnetic susceptibility $\chi^{(2)}_0$ for a free-metal surface may be derived from the experimental result of Murphy *et al.* [21] for Al(111) (cf. Ref. [22]). For the magnetic contribution, because of lacking reliable data for iron, we use Hübner's predictions for nickel [12]. The resulting ratio $\chi^{(2)}_{\rm mag,Ni}/\chi^{(2)}_{0,\rm Al} = 0.069$ is then scaled by the ratio of bulk magnetic moments [23], for iron and nickel $\mu_{\rm Fe}/\mu_{\rm Ni} = 2.15/0.56$, to obtain

$$\chi^{(2)}_{\rm mag,Fe}/\chi^{(2)}_0 = 0.27\,. \tag{4}$$

This result is in surprisingly good agreement with the experimental value. That may be, however, purely accidental with regard to the gross approximation when estimating the iron contribution from that of nickel.

The observed decay of magnetization dependence is attributed to CO adsorption from the residual gas [24] at a background pressure in our experiment on the order of several 10^{-8} Pa. Previous experiments under identical conditions [24] have shown that the only major contaminant is CO, whereas water and O_2 are negligible. It is well known that CO chemisorbs on iron at room temperature and then slowly dissociates [19]. Already at slightly higher temperature (385 K) the adsorption is completely dissociative. So, with the inevitable transient surface heating by absorbed fractions of the incident laser light, the surface is likely to enrich with dissociated C and O, either by dissociative adsorption or by thermal dissociation. The increasing uptake of C and O with time results in a decrease of the surface magnetization, which explains the decrease of the magnetic contribution to the second harmonic generation. This dramatic influence of contamination demonstrates clearly the excellent surface sensitivity of the technique.

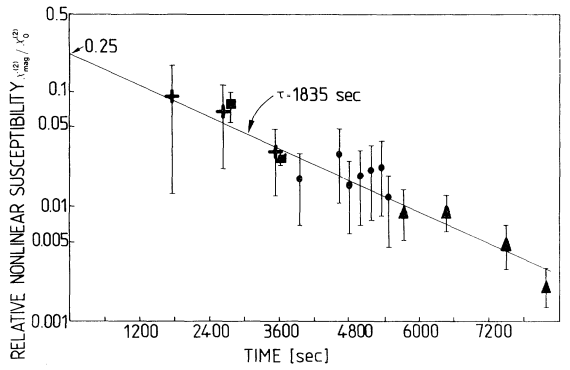

FIG. 3. Relative magnetization-dependent nonlinear susceptibility $\chi^{(2)}_{\rm mag}/\chi^{(2)}_0$ as a function of the time elapsed since surface preparation. [The ordinate is on a logarithmic scale; the three sets of symbols (+, ●, and ▲) represent three independent sets of measurements; the symbols ■ mark the respective positions for the data of Figs. 2(a) and 2(b).] By regression analysis, we find an exponential decay (time constant 1835 s = 30.6 min), and a relative nonlinear susceptibility for the clean surface of $\chi^{(2)}_{\rm mag}/\chi^{(2)}_0(t=0) = 0.25$. The correlation factor is $r^2 = 0.92$.

TABLE I. Relative magnetization dependence of second harmonic generation signal for three different times elapsed since sample preparation.

Time from surface preparation (min)	Relative signal ("1" is no magnetization) Magnetization "up"	Magnetization "down"
45	0.85 (±0.27)	1.16 (±0.33)
60	0.95 (±0.20)	1.06 (±0.21)
180	1.00 (±0.16)	1.00 (±0.16)

It should be noted that the contamination influences only the *magnetic* contribution to the second harmonic yield, other than in the case of CO on Ni, where the *total* second harmonic yield is decreased by the adsorbate [25]. Furthermore, from the decrease in magnetic influence, we exclude the formation of a ferromagnetic adsorbate, as observed by Johnson and co-workers [26], since the total gas exposure is roughly 1 order of magnitude less than the O_2 exposure necessary to form Fe_3O.

The energy coupled from the light field to the surface was sufficiently low, so as not to reach the Curie temperature or even the temperature for the transition from bcc to fcc structure at ≈ 1230 K. (An estimate along the lines of Bechtel [27] indicates a transient temperature increase of < 250 K during each laser pulse.) It is worth noting, however, that the magnetization dependence of

the hyperpolarizability also vanished, once the surface was intentionally damaged by too strong a laser pulse.

In conclusion, the existence of a magnetic contribution to optical second harmonic generation has been shown, for the first time, experimentally. We demonstrate the excellent surface sensitivity of this nonlinear magneto-optical Kerr effect. The extrapolated ratio between magnetization-dependent and -independent susceptibilities is extraordinarily large ($\approx 25\%$), in particular, in comparison to the linear Kerr effect, where it is extremely difficult to detect the equivalent effect of one or two monolayers [2]. The magnitude of the magnetic contribution to the hyperpolarization agrees surprisingly well with a theoretical estimate.

The effect is neither directly dependent on an external field, which in our experiment is only used to align the magnetic domains in the irradiated surface spot, nor is it restricted, like in many other techniques, to the investigation of remanent magnetization. The technique is also applicable to interfaces between two different materials, provided the light has access [28]. So, it should be possible to study the magnetic properties of a ferromagnetic surface or layer, buried under a thin (compared to the light penetration depth) nonmagnetic layer. This might bring about a unique way to investigate interfacial magnetic structures; however, one has to be cautious with respect to transient heating of the system, the thermal conductivity, and the Curie temperature of thin layers being different from bulk properties. The use of shorter laser pulses (picoseconds and below) might overcome this problem and also allow one to investigate magnetization dynamics by pump-probe techniques [29].

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