Nonlinear magneto-optical Kerr effect on a nickel surface

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Nonlinear surface optics is being developed as a useful new tool in surface science. In this work, we calculate the second-order magneto-optical response function in order to determine the nonlinear magneto-optical Kerr effect. This is applied to the surface of ferromagnetic nickel. We take into account the realistic spin-polarized nickel band structure and the spin-orbit coupling, but treat the transition-matrix elements as constants in a first approximation. We calculate nonlinear Kerr spectra which should be observable in surface second-harmonic-generation experiments. As a check of our calculations we determine the linear magneto-optical Kerr effect (MOKE) spectra for bulk nickel and find good agreement with experiment.

I. INTRODUCTION

Conventional techniques in surface science mostly use emission, capture, adsorption, or scattering of massive particles. But optical techniques are becoming increasingly important, because they are nondestructive, capable of *in situ* remote sensing with high spatial and temporal resolution at any interface accessible by light.[1] The main drawback is the general lack of surface sensitivity. In linear optical reflection, the bulk contributions dominate by far. So it becomes necessary to use nonlinear-optical probes for surface analysis.

Second-harmonic generation (SHG), which is forbidden in inversion-symmetric media within the electric-dipole approximation, is surface sensitive as the three-dimensional inversion symmetry is broken at the surface. It depends on the specific surface whether it is still two-dimensionally inversion symmetric. If not, the surface contribution dominates in SHG.

Surface second-harmonic generation has already been used to study a number of adsorbate systems such as rhodamine on quartz substrate, O_2/Si(111), CO/Cu(100), CO/Rh(111), and O_2/Rh(111).[1] Recently, SHG has also been used as a surface probe on alkaline-earth halides,[2] CO/Ag, pyridine/Ag,[3] and quinquethienyle/quartz.[4] Furthermore, there is interest to study ferromagnetic transition-metal surfaces with this technique.[5]

Theoretically, the field of nonlinear optics was opened by Göppert-Mayer in 1931.[6] Already in the 1960s Bloembergen, Pershan,[7] and Kelley[8] treated nonlinear optics within the general framework of response theory, Jha[9] used Boltzmann's equation. Pershan calculated nonlinearities from the anharmonic-oscillator model and solved nonlinear wave equations with the use of classical electrodynamics.[10] But at that time theoretical research concentrated on the prediction of new nonlinear effects. Therefore, a large number of nonlinear tensors were discussed and group-theoretically classified.[11,12] On the basis of these theories the angular distributions of nonlinear light intensities, especially for dielectrics, could be calculated in certain experimental situations at surfaces.[2] But it was not before 1986 that theorists became really interested in surface second-harmonic generation and calculated nonlinear intensities for "jellium" by means of the hydrodynamic model[13] and within density-functional theory.[14,15] Furthermore, nonlinearities were included in quasiparticle theories[16] for ferromagnetic insulators, but only for bulk material ("magnetoexcitonic polaritons").

So far, however, there exists no microscopic theory which could quantitatively connect electronic band structures of metals with experimental SHG spectra. Especially, no theory exists for the nonlinear magneto-optical Kerr effect (rotation of the polarization plane of the frequency-doubled light when reflected from a ferromagnetic metal surface). This effect could become important for the nanosecond and picosecond spectroscopy of ferromagnetic structures at transition-metal surfaces. This is interesting for new applications in memory technology and magneto-optical recording ("perpendicular recording").

II. THEORY

In this paper we calculate the nonlinear magneto-optical response function which is the basis for the description of the nonlinear magneto-optical Kerr effect. Concerning the response theory we use the self-consistent-field approach in the form proposed by Ehrenreich and Cohen[17] and extend it to second order. The linear optical dielectric function is defined by

$$\epsilon(\mathbf{q},\omega)=1-\frac{4\pi e^2}{q^2}\langle\langle\rho(\mathbf{q},t);\rho(-\mathbf{q})\rangle\rangle_\omega \ . \tag{1}$$

The linear dielectric polarization is given by

$$\mathbf{P}(\mathbf{q},\omega)=\chi^{(1)}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega) \ , \tag{2}$$

and the second-order polarization by

$$\mathbf{P}(2\mathbf{q},2\omega)=\chi^{(2)}(2\mathbf{q},2\omega)\mathbf{E}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega) \ , \tag{3}$$

where

$$\chi^{(1)}=\frac{\epsilon^{(1)}-1}{4\pi} \tag{4}$$

and $\chi^{(2)}$ are tensors of rank 2 and 3, respectively. We drop the tensor indices for notational simplicity.

Instead of a diagrammatic formulation we use an equation-of-motion formalism. Therefore, we consider Heisenberg's equation of motion,

$$i\hbar\dot{\rho}=[H,\rho]\ , \tag{5}$$

where

$$H=H_0+V(\mathbf{r},t) \tag{6}$$

is the Hamiltonian of the total system. H_0 is the Hamiltonian of the unperturbed solid which satisfies Schrödinger's equation,

$$H_0|\mathbf{k}l\rangle=E_{\mathbf{k}l}|\mathbf{k}l\rangle\ , \tag{7}$$

where $E_{\mathbf{k}l}$ is the energy corresponding to the Bloch state $|\mathbf{k}l\rangle=(1/\sqrt{\Omega})u_{\mathbf{k}l}e^{i\mathbf{k}\cdot\mathbf{r}}$ of wave vector $\mathbf{k}$ in the lth band. The Fourier transformation of the self-consistent potential is

$$V(\mathbf{r},t)=\sum_{\mathbf{q}'}V(\mathbf{q}',t)e^{-i\mathbf{q}'\cdot\mathbf{r}}\ . \tag{8}$$

This potential consists of the external plus the screening potential. In second order only the screening potential is present.

ρ denotes the density operator which we expand in the form

$$\rho=\rho^{(0)}+\rho^{(1)}+\rho^{(2)}+\cdots\ , \tag{9}$$

where $\rho^{(0)}$ satisfies the eigenvalue equation

$$\rho^{(0)}|\mathbf{k}l\rangle=f(E_{\mathbf{k}l})|\mathbf{k}l\rangle\ . \tag{10}$$

Here, f is the Fermi function. By taking into account only first-order terms and using Eqs. (7) and (10) we obtain from the equation of motion for the matrix elements of ρ between states $|\mathbf{k}l\rangle$ and $|\mathbf{k}+\mathbf{q},l'\rangle$

$$\begin{aligned}i\hbar\frac{d}{dt}\langle\mathbf{k}l|\rho^{(1)}|\mathbf{k}+\mathbf{q},l'\rangle&\equiv(-\hbar\omega+i\hbar\alpha)\langle\mathbf{k}l|\rho^{(1)}|\mathbf{k}+\mathbf{q},l'\rangle\\&=\langle\mathbf{k}l|[H_0,\rho^{(1)}]|\mathbf{k}+\mathbf{q},l'\rangle+\langle\mathbf{k}l|[V,\rho^{(0)}]|\mathbf{k}+\mathbf{q},l'\rangle\\&=(E_{\mathbf{k}l}-E_{\mathbf{k}+\mathbf{q},l'})\langle\mathbf{k}l|\rho^{(1)}|\mathbf{k}+\mathbf{q},l'\rangle+[f(E_{\mathbf{k}+\mathbf{q},l'})-f(E_{\mathbf{k}l})]V(\mathbf{q},t)\langle\mathbf{k}l|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},l'\rangle\ .\end{aligned} \tag{11}$$

The time dependence of the matrix elements is assumed to be $e^{i\omega t+\alpha t}$. α corresponds to some finite lifetime or, from the experimental point of view, instrumental resolution.

The polarization $\mathbf{P}(\mathbf{q},t)$ is related to the induced change in electron density in first order by

$$\begin{aligned}&\nabla\cdot\mathbf{P}^{(1)}(\mathbf{q},t)=en^{(1)}(\mathbf{q},t)\\&\quad\Longrightarrow i\mathbf{q}\cdot\mathbf{P}^{(1)}(\mathbf{q},t)=en^{(1)}(\mathbf{q},t)\ ,\end{aligned} \tag{12}$$

and in second order by

$$\begin{aligned}&\nabla\cdot\mathbf{P}^{(2)}(2\mathbf{q},t)=en^{(2)}(2\mathbf{q},t)\\&\quad\Longrightarrow 2i\mathbf{q}\cdot\mathbf{P}^{(2)}(2\mathbf{q},t)=en^{(2)}(2\mathbf{q},t)\ .\end{aligned} \tag{13}$$

With the electrical field

$$\mathbf{E}(\mathbf{q},t)=\frac{i\mathbf{q}}{e}V(\mathbf{q},t)\ , \tag{14}$$

and Eqs. (11) and (12), it follows for the linear optical dielectric response function

$$\begin{aligned}\chi^{(1)}(\mathbf{q},\omega)&=-\frac{e^2}{q^2}\frac{n^{(1)}(\mathbf{q},t)}{V(\mathbf{q},t)}\\&=\frac{-\frac{e^2}{q^2\Omega}\sum_{\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{\mathbf{k}',l,l'}\langle\mathbf{k}'+\mathbf{q},l'|e^{i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}'l\rangle\langle\mathbf{k}'l|\rho^{(1)}|\mathbf{k}'+\mathbf{q},l'\rangle}{V(\mathbf{q},t)}\ .\end{aligned} \tag{15}$$

We assume the time dependence $e^{i\omega t+\alpha t}$ for the external potential and therefore also for the screening potential (thus for the total self-consistent potential) as we did in (11) for the matrix elements $\langle\mathbf{k}l|\rho^{(1)}|\mathbf{k}+\mathbf{q},l'\rangle$. With this convention we obtain for the optical dielectric function (for photons $|\mathbf{q}|\ll 1/a$, a is the lattice constant, and longitudinal and transverse dielectric functions become identical[18]) ($\omega=cq$)

$$\chi^{(1)}(\mathbf{q},\omega)=-\frac{4\pi e^2}{q^2\Omega}\sum_{\mathbf{k},l,l'}|\langle\mathbf{k}l|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},l'\rangle|^2\frac{f(E_{\mathbf{k}+\mathbf{q},l'})-f(E_{\mathbf{k}l})}{E_{\mathbf{k}+\mathbf{q},l'}-E_{\mathbf{k}l}-\hbar\omega+i\hbar\alpha}\ . \tag{16}$$

To express the tensor character, $\chi^{(1)}(\mathbf{q},\omega)$ would have to be multiplied by $\mathbf{q}\otimes\mathbf{q}/q^2$. To calculate the second-order optical dielectric function, we extend this scheme in a straightforward manner, but note that $V^{(2)}=V_s^{(2)}(2\mathbf{q},t)$ (s stands for screening) because the external potential contributes to V only in first order. We assume the time dependence $e^{2i\omega t+2\alpha t}$ for the second-order matrix elements and the nonlinear screening potential and collect the second-order terms in the

equation of motion for the matrix elements $\langle \mathbf{k}l|\rho^{(2)}|\mathbf{k}+2\mathbf{q},l''\rangle$:

$$i\hbar\frac{d}{dt}\langle \mathbf{k}l|\rho^{(2)}|\mathbf{k}+2\mathbf{q},l''\rangle=\langle \mathbf{k}l|[\mathbf{H}_0,\rho^{(2)}]|\mathbf{k}+2\mathbf{q},l''\rangle+\langle \mathbf{k}l|[V^{(1)},\rho^{(1)}]|\mathbf{k}+2\mathbf{q},l''\rangle+\langle \mathbf{k}l|[V_s^{(2)},\rho^{(0)}]|\mathbf{k}+2\mathbf{q},l''\rangle$$

$$\Longleftrightarrow(-2\hbar\omega+2i\hbar\alpha)\langle \mathbf{k}l|\rho^{(2)}|\mathbf{k}+2\mathbf{q},l''\rangle$$

$$=(E_{\mathbf{k}l}-E_{\mathbf{k}+2\mathbf{q},l''})\langle \mathbf{k}l|\rho^{(2)}|\mathbf{k}+2\mathbf{q},l''\rangle+\langle \mathbf{k}l|[V^{(1)},\rho^{(1)}]|\mathbf{k}+2\mathbf{q},l''\rangle$$

$$+[f(E_{\mathbf{k}+2\mathbf{q},l''})-f(E_{\mathbf{k}l})]V_s(2\mathbf{q},t)\langle \mathbf{k}l|e^{-2i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q},l''\rangle\ . \tag{17}$$

By using Poisson's equation for the nonlinear screening potential

$$\nabla^2V_s^{(2)}=-4\pi e^2n^{(2)}\ , \tag{18}$$

if follows that

$$V_s^{(2)}(2\mathbf{q},t)=\frac{\pi e^2}{q^2\Omega}\sum_{\mathbf{k}',l,l''}\langle \mathbf{k}'+2\mathbf{q},l''|e^{2i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}'l\rangle\langle \mathbf{k}'l|\rho^{(2)}|\mathbf{k}'+2\mathbf{q},l''\rangle\ . \tag{19}$$

Inserting Eqs. (3), (13), and (19), the first-order result for $\langle \mathbf{k}l|\rho^{(1)}|\mathbf{k}+\mathbf{q},l'\rangle$, and summing over $\mathbf{k}$, l, l', and l'', finally leads to the nonlinear-optical dielectric function

$$\chi^{(2)}(2\mathbf{q},2\omega)=\frac{-ie^3}{2q^3\Omega}\sum_{\mathbf{k},l,l',l''}\left\{(\langle \mathbf{k}+2\mathbf{q},l''|e^{2i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}l\rangle\langle \mathbf{k}l|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},l'\rangle\langle \mathbf{k}+\mathbf{q},l'|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q},l''\rangle)\right.$$

$$\times\frac{\left[\dfrac{f(E_{\mathbf{k}+2\mathbf{q},l''})-f(E_{\mathbf{k}+\mathbf{q},l'})}{E_{\mathbf{k}+2\mathbf{q},l''}-E_{\mathbf{k}+\mathbf{q},l'}-\hbar\omega+i\hbar\alpha}-\dfrac{f(E_{\mathbf{k}+\mathbf{q},l'})-f(E_{\mathbf{k}l})}{E_{\mathbf{k}+\mathbf{q},l'}-E_{\mathbf{k}l}-\hbar\omega+i\hbar\alpha}\right]}{E_{\mathbf{k}+2\mathbf{q},l''}-E_{\mathbf{k}l}-2\hbar\omega+2i\hbar\alpha}$$

$$\left.\times\frac{1}{1-\dfrac{\pi e^2}{q^2\Omega}\displaystyle\sum_{\mathbf{k},l,l''}|\langle \mathbf{k}l|e^{-2i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q},l''\rangle|^2\dfrac{f(E_{\mathbf{k}+2\mathbf{q},l''})-f(E_{\mathbf{k}l})}{E_{\mathbf{k}+2\mathbf{q},l''}-E_{\mathbf{k}l}-2\hbar\omega+2i\hbar\alpha}}\right\}\ . \tag{20}$$

To restrict our theory to the surface, we replace $\mathbf{q}$ by $\mathbf{q}_\parallel$ (parallel to the surface), the volume Ω by the surface A, and the three-dimensional Fourier transformations by two-dimensional ones. This procedure corresponds to the result[19–22] for the linear surface dielectric function $g(\mathbf{q}_\parallel,\omega)$, first derived by Persson *et al.* by integrating the Poynting vector over the metal surface,

$$\mathrm{Img}(\mathbf{q}_\parallel,\omega)=\frac{2\pi^2}{q_\parallel A}\sum_{\gamma,\gamma'}|\langle\gamma|\Phi_1|\gamma'\rangle|^2(f_\gamma-f_{\gamma'})\delta(\varepsilon_\gamma-\varepsilon_{\gamma'}-\hbar\omega+i\hbar\alpha)\ , \tag{21}$$

where $|\gamma\rangle,|\gamma'\rangle$ are the single-particle wave functions of the solid, and

$$\Phi_n=[1-g(\mathbf{0},n\omega)]e^{-in\mathbf{q}_\parallel\cdot\mathbf{r}_\parallel-nq_\parallel z}\ . \tag{22}$$

Now we want to consider the nonlinear magneto-optical Kerr effect at ferromagnetic transition-metal surfaces. Although Kerr observed the rotation of the polarization plane of light reflected from ferromagnets already in 1877, the underlying mechanism was not found before 1955, when Argyres[23] showed that the combination of the exchange interaction and the spin-orbit coupling is responsible for the Kerr effect: As spin-orbit coupling acts like an external magnetic field,

$$-i\hbar\dot{\mathbf{p}}=[H_{\mathrm{s.o.}},\mathbf{p}]=[\lambda\mathbf{L}\cdot\mathbf{S},\mathbf{p}]=\lambda\mathbf{p}\times\mathbf{S}\ , \tag{23}$$

it rotates the polarization plane of linearly polarized light. In nonferromagnetic materials the effects for left-handed and right-handed circularly polarized light (the superposition of which builds up the linear polarization) cancel out so that no net effect occurs. But in ferromagnets the exchange interaction splits the band structure, and consequently spin-up and spin-down states are not equally occupied. This fact allows a net rotation of the polarization plane of about 0.1° (in nickel). The sign and absolute value of the Kerr angle show a pronounced frequency dependence which has not yet been fully understood. The theories of the 1960s derived the magneto-optical response functions for the linear Kerr (or Faraday) effect and discussed the different intraband and interband contributions.[24,25] But, at that time, theorists did not dare to compare with experimental spectra. Today the situation is not better, maybe even worse than 25 years ago. Although now some spin-polarized ferromagnetic band-structure calculations for bulk nickel[26,27,28] (even at finite temperatures[29]) and for the Ni(001) surface[30,31] are available, only one attempt[32] has so far been made to connect them to the experimental Kerr spectra.

The results are not completely satisfactory. On the other hand, before having achieved good agreement of the different measurements, experimental interest moved from pure ferromagnetic materials to intermetallic alloys. The search for large Kerr-angle materials became important in the 1980s because of their application in magneto-optical memories and data processing ("compositionally modulated films", "perpendicular recording").

We calculate the nonlinear magneto-optical response function by taking into account exchange interaction and spin-orbit coupling in (20). We denote the spin-polarized band structure by the index σ (e.g., $E_{\mathbf{k}l\sigma}$) and sum over σ. Spin-orbit interaction is included within first-order Heitler-Ma perturbation theory in the coupling constant λ according to the procedure proposed by Cohan and Hameka for externally applied magnetic fields in gases and liquids.[33] If we apply this to the product of three matrix elements,

$$\langle \mathbf{k}+2\mathbf{q}, l''\sigma|e^{2i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}l\sigma\rangle\langle \mathbf{k}l\sigma|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}, l'\sigma\rangle\langle \mathbf{k}+\mathbf{q}, l'\sigma|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q}, l''\sigma\rangle ,$$

we use first-order perturbation theory for each of the six wave functions and dipole operators which come into play by expanding the exponential and retaining only the $\mathbf{q}\cdot\mathbf{r}$ interband terms. Then we collect all first-order terms, i.e., those which are perturbed in *one* wave function or dipole operator and unperturbed in the other *eight* quantities (wave functions or dipole operators). So we obtain the following *nonlinear magneto-optical* surface response function:

$$\begin{aligned}\chi^{(2)}(2\mathbf{q}_\parallel,2\omega)=\frac{e^3\hbar}{4m^2c^2\mathbf{q}_\parallel^2 A}\sum_\sigma\Bigg\{\sum_{\mathbf{k},l,l',l''}\Bigg[\sum_{\mathbf{k}_1}P\Bigg[\frac{V_{\mathbf{k}_1;\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma}\mathbf{k}_1\times(\mathbf{k}+2\mathbf{q}_\parallel)\langle\sigma\rangle}{E_{\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma}-E_{\mathbf{k}_1}}\langle\mathbf{k}_1|e^{2i\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}l\sigma\rangle\langle\mathbf{k}l\sigma|e^{-i\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}_\parallel,l'\sigma\rangle \\ \times\langle\mathbf{k}+\mathbf{q}_\parallel,l'\sigma|e^{-i\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma\rangle\Bigg] \\ +Q[V_{\mathbf{k}l\sigma;\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma}\mathbf{k}\times(\mathbf{k}+2\mathbf{q}_\parallel)\langle\sigma\rangle\langle\mathbf{k}l\sigma|e^{-\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}_\parallel,l'\sigma\rangle \\ \times\langle\mathbf{k}+\mathbf{q}_\parallel,l'\sigma|e^{-i\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma\rangle]\Bigg] \\ \times\frac{\left[\dfrac{f(E_{\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma})-f(E_{\mathbf{k}+\mathbf{q}_\parallel,l'\sigma})}{E_{\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma}-E_{\mathbf{k}+\mathbf{q}_\parallel,l'\sigma}-\hbar\omega+i\hbar\alpha}-\dfrac{f(E_{\mathbf{k}+\mathbf{q}_\parallel,l'\sigma})-f(E_{\mathbf{k}l\sigma})}{E_{\mathbf{k}+\mathbf{q}_\parallel,l'\sigma}-E_{\mathbf{k}l\sigma}-\hbar\omega+i\hbar\alpha}\right]}{E_{\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma}-E_{\mathbf{k}l\sigma}-2\hbar\omega+2i\hbar\alpha} \\ \times\frac{1}{1-\dfrac{\pi e^2}{q_\parallel A}\displaystyle\sum_{\mathbf{k},l,l''}|\langle\mathbf{k}l\sigma|e^{-2i\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma\rangle|^2\frac{f(E_{\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma})-f(E_{\mathbf{k}l\sigma})}{E_{\mathbf{k}+2\mathbf{q}_\parallel,l''\sigma}-E_{\mathbf{k}l\sigma}-2\hbar\omega+2i\hbar\alpha}}\Bigg\}.\end{aligned} \tag{24}$$

Here, $P(\ )$ denotes the sum of six permutations of first-order terms (in spin-orbit coupling) with perturbed wave functions (containing one extra energy denominator) and $Q[\ ]$ means the sum of three terms (containing no extra energy denominator) with one of the three dipole operators replaced by the spin-orbit operator (leaving the wave functions unperturbed).[33] All matrix elements have in principle a z dependence defined by (22). This nonlinear response function $\chi^{(2)}(2\mathbf{q}_\parallel,2\omega)$ shows in a very obvious manner the effects of frequency doubling, spin-orbit interaction, exchange splitting, and the band structure itself. The tensor character is hidden in the $\mathbf{r}$ dependence of the matrix elements. For a detailed discussion of the group-theoretical aspects of the nonlinear surface magneto-optical problem, we refer the reader to the recent work of Pan, Wei, and Shen.[34] Equation (24) reduces to their result (23) if (1) the terms $Q[\ ]$ are neglected, (2) nonlinear screening is neglected, and (3) the $\mathbf{q}_\parallel$ dependence is neglected.

The main problem in the evaluation of (24) for nickel results from the spin-polarized band structure and the surface matrix elements. In this paper we treat the matrix elements as constants neglecting intraband contributions which are exponentially small at energies larger than 0.5 eV. It is

$$\langle\mathbf{k}_1|e^{ni\mathbf{q}_\parallel\cdot\mathbf{r}}|\mathbf{k}_2\rangle\approx niq_\parallel\times10^{-11}\text{ m},\quad n=1,2$$

where 10^{-11} m is the extension of a hydrogenlike $3d$ orbital of nickel (nuclear charge 28). We use the semiempirical spin-polarized band structure of Weling and Callaway[35] which appears to describe photoemission experiments quite well. Thus we use a weighted superposition (for the correct counting of the electronic states) of

three spheres of the radii $\overline{\Gamma L}$, $\overline{\Gamma K}$, and $\overline{\Gamma X}$, respectively, to approximate the anisotropy of the first Brillouin zone (truncated octahedron) corresponding to fcc nickel:

$$\chi^{(2)}(2\mathbf{q}_{\parallel},2\omega)=a\chi^{(2)}_{\Gamma L}(2\mathbf{q}_{\parallel},2\omega)+b\chi^{(2)}_{\Gamma K}(2\mathbf{q}_{\parallel},2\omega)+c\chi^{(2)}_{\Gamma X}(2\mathbf{q}_{\parallel},2\omega)\ ,$$

with $a=1.220$, $b=1.000$, and $c=0.1064$. These values correspond to the best agreement of the linear magneto-optical response function with magneto-optical Kerr effect (MOKE) data. $\chi^{(2)}_{\Gamma L}$, for instance, is the response function which contains the sphere of radius $\overline{\Gamma L}$. The main contributions to the magneto-optical yield should come from the singularities in the joint density of states which predominantly occur in the high-symmetry directions. The good reproduction of the linear Kerr spectra clearly shows that our approximation contains all relevant band-structure features (see Sec. III).

We take $\hbar\alpha=0.35\times10^{-19}$ J$=0.218$ eV for the quartz-optical range (below $E=5$ eV) and $\hbar\alpha=0.7\times10^{-19}$ J$=0.437$ eV otherwise. For the spin-orbit interaction we use the value of 70 meV as calculated by Callaway's[32] and Freeman's groups.[31]

The nonlinear screening term in (24) is neglected in this paper. Its effect could be estimated as follows: The correction in the denominator of Eq. (24) is roughly of the order of the linear response function $\chi^{(1)}(2\mathbf{q},2\omega)$ which is about unity for $\hbar\omega=0.5$ eV and has decreased to 0.15 for $\hbar\omega=2$ eV. So it becomes a minor correction for not too small frequencies ω. Furthermore, a detailed calculation of the nonlinear screening term would be possible only on the basis of the knowledge of all the transition-matrix elements, because of the tensor character of this term:

$$[1-\chi^{(1)}(2\mathbf{q}_{\parallel},2\omega)]^{-1}\rightarrow[\delta_{ij}-\chi^{(1)}_{ij}(2\mathbf{q}_{\parallel},2\omega)]^{-1}\ .$$

In contrast to insulators, local-field effects should be negligible due to the extended character of the Bloch wave functions in metallic nickel.

III. RESULTS AND DISCUSSION

Figure 1 shows the experimental results of Krinchik,[36] Yoshino,[37] and Erskine[38] [which are consistent with Thiel's and Hoffmann's[39] values for the Ni(100) surface] and the calculated values of Callaway[32] for the imaginary part of the *linear* off-diagonal bulk conductivity of nickel (times the frequency ω) as a function of this frequency ω. Our results for this quantity are displayed in Fig. 2. (Notice that the vertical axis is scaled differently from Fig. 1.) The intraband transitions would only result in a small constant contribution to the quantity $\omega\,\mathrm{Im}\sigma_{xy}(\omega)=\omega^2\,\mathrm{Re}\chi^{(1)}_{xy}(\omega)$. Figure 3 gives the real and imaginary parts of the *nonlinear* magneto-optical response function $\chi^{(2)}$ as a function of the frequency ω according to (24) for the same nickel parameters as in the linear case. The vertical scale indicates that the nonlinear susceptibility leads to a polarization $\mathbf{P}(2\mathbf{q}_{\parallel},2\omega)$ which is 7 orders of magnitude lower in a field of the order of MV/m than the linear polarization $\mathbf{P}(\mathbf{q},\omega)$ [see Eqs. (2) and (3)]. We assumed that only the topmost layer (of the order of Å in thickness) contributes to the nonlinear signal as this is the range where the electronic charge density falls off from its bulk value to zero (due to metallic screening).

Nevertheless, the nonlinear magneto-optical Kerr effect should be observable in experiment, as second-

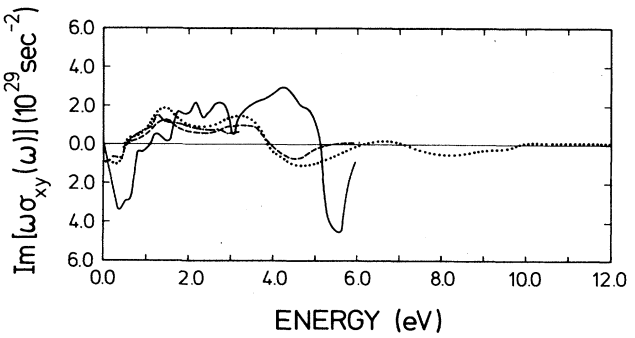

FIG. 1. Im$[\omega\sigma^{(1)}_{xy}(\omega)]$ for bulk nickel from the experiments of Krinchik and Artemjev (dashed curve), of Yoshino and Tanaka (dashed-dotted curve), and of Erskine (dotted curve) compared with the theoretical results of Wang and Callaway (solid curve).

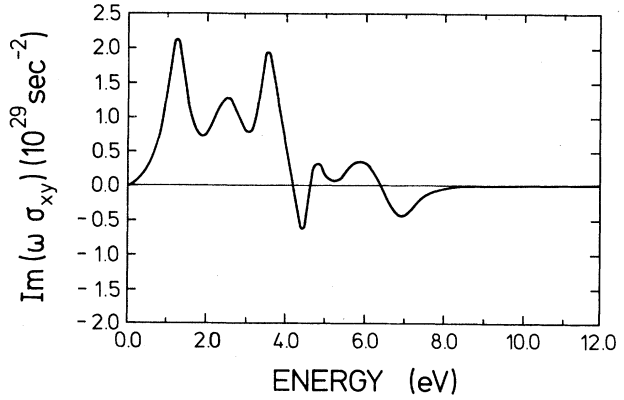

FIG. 2. Im$[\omega\sigma^{(1)}_{xy}(\omega)]$ for bulk nickel from this work.

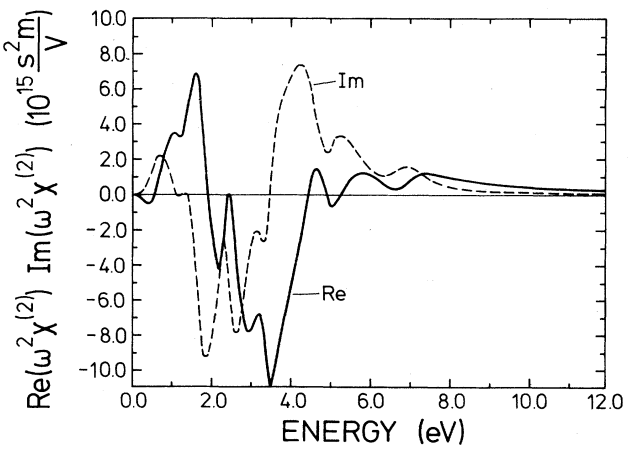

FIG. 3. The real (solid line) and imaginary (dashed line) parts of the nonlinear magneto-optical response function $\chi^{(2)}(2\mathbf{q}_{\parallel},2\omega)$ times the frequency ω^2.

harmonic-generation experiments[2] usually can cope with even lower intensities such as in insulators like BaF_2: The lowest detectable value[1] for $|\omega^2\chi^{(2)}(2\mathbf{q}_\parallel, 2\omega)|$ with some MW/cm^2 laser intensities is in the range from 5×10^9 to 5×10^{10} s^{-2}m/V. Even if the experiments could not reach the theoretical effectiveness for the frequency-doubling process and for the detection of the 2ω photons, it would be possible to see the nonlinear magneto-optical Kerr effect, as the nonlinear *magneto-optical (Kerr)* susceptibility for nickel is larger than the nonlinear *optical* susceptibility (for *usual SHG*) for insulators like BaF_2.

Therefore, this effect could become a new probe for the analysis of the electronic (including relativistic), magnetic (including magnetization anisotropy), and structural (by varying polarization and incident angle) properties of solid surfaces and surface states. Furthermore, one might think about dynamical applications of this effect (and surface second-harmonic generation in general) in order to study adsorbate motion and chemical reactions at surfaces. If one includes finite temperatures, the exploration of domain walls, surface magnons, and of the critical behavior would be possible.

Concerning the *linear* MOKE, which comes out in a natural way from our theory, we find good agreement between our results and the experiments. For a more detailed comparison, see Erskine's original figure,[38] where the vertical axis is scaled as in Fig. 2. We are able to reproduce the correct order of magnitude and the three prominent peaks at 1.4, 3.5 (positive sign), and 4.5 eV (negative sign) as well as approximately those at 6 (positive sign) and 7 eV (negative sign). They reflect the fact that the imaginary part of the off-diagonal conductivity σ_{xy} is proportional to the joint density of states:[40]

$$\rho_{\mathbf{k},l;\mathbf{k}+\mathbf{q},l'}(\hbar\omega) \propto \frac{1}{4\pi^3}\int dS \frac{|\langle \mathbf{k}l|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},l'\rangle|^2}{\nabla_{\mathbf{k}}(E_{\mathbf{k}+\mathbf{q},l'}-E_{\mathbf{k}l})|_{E_{\mathbf{k}+\mathbf{q},l'}-E_{\mathbf{k}l}=\hbar\omega}} . \tag{25}$$

This indicates that interband transitions are responsible for the main features of the MOKE spectra. This good reproduction of the linear Kerr effect gives us hope that our nonlinear Kerr spectra are not too bad.

Of course, concerning the linear MOKE, the single-particle band structure should in principle be refined by many-body (self-energy) corrections. The exact structure of $\frac{1}{48}$ or, with spin-orbit coupling, $\frac{3}{48}$ of the Brillouin zone and the detailed form of the matrix elements should be included. But even in the nonlinear case some improvements over our first approximation are necessary and, within the limits of computational time, possible. We are presently investigating such improvements. Especially a more detailed computation of the matrix elements (at the surface) seems inevitable to us for establishing the nonlinear magneto-optical effect and the optical second-harmonic generation in general as a new tool in surface science.

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