Optical second-harmonic generation from magnetized surfaces

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We propose optical second-harmonic generation as a means to probe surface magnetization. It is shown that surface magnetization can induce a number of nonlinear susceptibility elements that would vanish otherwise. They are presented for the (001), (110), and (111) surfaces of a fcc centrosymmetric crystal. An order-of-magnitude estimate, using the microscopic expression of the nonlinear susceptibility, suggests that these induced elements are detectable by optical second-harmonic generation with appropriate polarization combinations. The second-harmonic signals from magnetized and nonmagnetized surfaces should exhibit characteristically different rotational anisotropy.

I. INTRODUCTION

The controversy over the observation of magnetically "dead" layers by Liebermann *et al.*[1] almost two decades ago has sparked continuting intensive studies in the field of surface magnetism.[2–13] From the basic research point of view, the fact that the surface and the bulk of the same material can have very different magnetic properties is certainly most interesting and intriguing.[6,7,11] Improved understanding of the role of surfaces in magnetic phase transitions will also help shed light on other physical phenomena such as surface melting.[2] From the application point of view, the fact that magnetic memory devices could be affected by surface magnetization naturally calls for a better understanding of surface magnetism. The surface magnetic properties of transition metals are also of pivotal importance for catalysis and metallurgy.

Experimental studies in this field have, however, been impeded by the limited number of analytical tools available. Techniques such as electron-capture spectroscopy,[8] inverse photoelectron spectroscopy,[9] Hall-effect measurement,[10] and angle-resolved photoelectron spectroscopy[12] have been used. Most of these methods require placing the probe along with the sample in an environment of ultrahigh vacuum. Recently, optical second-harmonic generation (SHG) has been proven to be a versatile probe for surface studies.[14] It has the advantages of being highly surface sensitive, capable of remote sensing and *in situ* measurement, and applicable to any interface accessible by light. One may question whether the technique can also be used to probe surface magnetization. Recently, Pan and Shen drew attention to this possibility by showing that the nonlinear optical susceptibility tensor for SHG for the (001) surface of a cubic crystal possesses a group of nonvanishing elements induced by the presence of a finite magnetization, **M**, parallel to the (100) axis.[15]

In this paper, we show in more detail the experimental feasibility of probing magnetized surface by optical second-harmonic generation. The nonlinear optical susceptibility tensors for SHG from magnetized (100), (110), and (111) surfaces of a fcc centrosymmetric crystal are derived and tabulated in Sec. II. The input-output polarization combinations needed for detecting the nonlinear susceptibility elements induced by surface magnetization are suggested in Sec. III. The SH signals from magnetized and nonmagnetized surfaces can exhibit different rotational symmetries. Section IV shows a first-order microscopic expression of the magnetization-induced surface nonlinear susceptibility, taking into account spin-orbit interaction of the conduction electrons. An order-of-magnitude estimate is presented, using nickel as an example.

II. SYMMETRY CONSIDERATIONS

In a centrosymmetric medium, the electric dipole contribution to the second-order optical nonlinearity is identically zero. At the surface, the inversion symmetry is broken, resulting in the high surface sensitivity of SHG. The magnetization of a material will not break the inversion symmetry of the bulk material, but can lower the surface symmetry, and hence modify the form of the nonlinear susceptibility tensors for surface SHG.

The surface nonlinear optical polarization at 2ω can be written as

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

where the surface nonlinear susceptibility third-rank tensor $\chi^{(2)}$ is a function of the surface magnetization **M** in general and $\mathbf{E}(\omega)$ is the fundamental field. The symmetry of $\chi^{(2)}(\mathbf{M})$ is dictated by the symmetry of the particular surface under consideration. The nonzero elements of

TABLE I. Independent nonvanishing elements of $\chi_s^{(2)}$ for (001), (110), and (111) surfaces of fcc crystals without surface magnetization. (Surface is in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane.)

Surfaces	Symmetry classes	Independent nonvanishing elements
(001)	$4m$	$xzx=xxz=yzy=yyz$, $zxx=zyy$, zzz
(110)	$mm2$	$xzx=xxz$, $yzy=yyz$, zxx, zyy, zzz
(111)	$3m$	$xxx=-xyy=-yxy=-yyx$, $xzx=xxz=yzy=yyz$, $zxx=zyy$, zzz

$\chi^{(2)}(\mathbf{M})$ can be obtained from invariance of $\chi^{(2)}(\mathbf{M})$ under symmetry operations:

$$\chi_{ijk}^{(2)}=T_{ii'}T_{jj'}T_{kk'}\chi_{i'j'k'}^{(2)},\quad i,j,k=x,y,z \tag{2}$$

where T is the transformation matrix for each symmetry operation, and summation over repeated indices is implied. The time-reversal properties of $\chi^{(2)}(\mathbf{M})$, neglecting dissipation, requires that the real part of $\chi^{(2)}(\mathbf{M})$ is an even function of $\mathbf{M}$, while the imaginary part of $\chi^{(2)}(\mathbf{M})$ is an odd function of $\mathbf{M}$. The latter group, nonvanishing only in the presence of a finite $\mathbf{M}$, can be useful for probing surface magnetization.

We consider the (100), (110), and (111) surfaces of fcc centrosymmetric crystals. In the absence of surface magnetization, the (001) and (110) faces are of 4mm and mm2 symmetries, respectively, while the (111) surface is of class 3m when more than two monolayers of the surface are considered. Nonvanishing elements of $\chi^{(2)}(\mathbf{0})$ for these symmetries can be found in numerous works, e.g., the recent paper by Guyot-Sionnest *et al.*[16] These are reproduced in Table I for later comparison. With surface magnetization, the symmetries are changed. We summarize our derivation for the nonvanishing surface-susceptibility tensor elements in the following. The coordinate system chosen for all cases is to have the surface in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane and the surface normal along $\hat{\mathbf{z}}$.

First we consider a magnetized (001) surface: With $\mathbf{M}$ parallel to the [100] direction ($\hat{\mathbf{x}}$), the fourfold symmetry of the surface about the surface normal is broken. The two independent symmetry operations are (i) reflection about the $\hat{\mathbf{x}}$-$\hat{\mathbf{z}}$ mirror plane, $x\to x$, $y\to -y$, and $\mathbf{M}\to-\mathbf{M}$, and (ii) reflection about the $\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$ mirror plane, $x\to -x$, $y\to y$, and $\mathbf{M}\to\mathbf{M}$. Using Eq. (2), one can show that there are ten independent nonvanishing elements: five of them ($\chi_{xxz}^{(2)}=\chi_{xzx}^{(2)}$, $\chi_{yyz}^{(2)}=\chi_{yzy}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zyy}^{(2)}$, $\chi_{zzz}^{(2)}$) are even in $\mathbf{M}$, while the other five ($\chi_{xxy}^{(2)}=\chi_{xyx}^{(2)}$, $\chi_{yxx}^{(2)}$, $\chi_{yyy}^{(2)}$, $\chi_{yzz}^{(2)}$, $\chi_{zyz}^{(2)}=\chi_{zzy}^{(2)}$) are odd in $\mathbf{M}$. If the surface magnetization $\mathbf{M}$ is parallel to the [110] direction, all of the 27 elements are nonzero, ten of which are independent. Actually, the latter can be obtained from the former case of $\mathbf{M}\|[100]$ by a coordinate transformation with $\hat{\mathbf{x}}'\|\hat{\mathbf{x}}+\hat{\mathbf{y}}$ and $\hat{\mathbf{y}}'\|\hat{\mathbf{x}}-\hat{\mathbf{y}}$. If the surface magnetization, $\mathbf{M}$, is parallel to the surface normal, i.e., the [001] direction, the fourfold symmetry of the surface is preserved. The symmetry operations are ($x\to x$, $y\to -y$, and $\mathbf{M}\to-\mathbf{M}$) and ($x\to -x$, $y\to y$, and $\mathbf{M}\to-\mathbf{M}$) for reflections about the $\hat{\mathbf{x}}$-$\hat{\mathbf{z}}$ and $\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$ planes, respectively, yielding five independent nonvanishing elements. Three of them are even in $\mathbf{M}$ and the others odd in $\mathbf{M}$. Table II lists all the nonvanishing susceptibility elements for the above cases.

Similarly, we can find the nonvanishing $\chi^{(2)}$ elements for a magnetized (110) surface as shown in Table III. We choose the $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ axes to be along the $[\bar{1}10]$ and [001] directions, respectively. For $\mathbf{M}\|[001]\|\hat{\mathbf{y}}$, there are ten independent nonvanishing elements; five of them are even and the other five odd in $\mathbf{M}$. For the case of $\mathbf{M}\|[110]\|\hat{\mathbf{z}}$, there are eight independent nonzero elements; five of them are even and the other three odd in $\mathbf{M}$. Note that the symmetry of $\chi^{(2)}(\mathbf{M})$ for the (110) surface is identical to that for the (001) surface.

Finally, our results for a magnetized (111) surface are given in Table IV. The $[2\bar{1}\bar{1}]$ and $[01\bar{1}]$ directions are

TABLE II. Independent nonvanishing elements of $\chi_s^{(2)}(\mathbf{M})$ for the (001) surface of fcc crystals with surface magnetization $\mathbf{M}$ parallel to the [100], [110], and [001] directions. ($\hat{\mathbf{x}}$ is along the [001] direction and the surface is in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane.)

Direction of $\mathbf{M}$	Independent nonvanishing elements: Even parity	Odd parity
[100]	$xzx=xyz$, $yzy=yyz$, zxx, zyy, zzz	$xyx=xxy$, yxx, yyy, yzz, $zyz=zzy$
[110]	$xyz=xzy=yzx=yxz$, $xzx=xxz=yzy=yyz$, $zxx=zyy$, zzz, $zxy=zyx$	$xxx=-yyy$, $xyy=-yxx$, $xzz=-yzz$, $xxy=xyx=-yxy=-yyx$, $zxz=zzx=-zyz=-zzy$
[001]	$xzx=xxz=yzy=yyz$, $zxx=zyy$, zzz	$xyz=xzy=yzx=yxz$, $zxy=zyx$

TABLE III. Independent nonvanishing elements of $\chi_s^{(2)}(\mathbf{M})$ for the (110) surface of fcc crystals with surface magnetization **M** parallel to [001] and [110] directions. ($\hat{\mathbf{y}}$ is along the [001] direction and the surface is in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane.)

Direction of **M**	Independent nonvanishing elements: Even parity	Odd parity
[001]	$xzx=xxz$, $yzy=yyz$, zxx, zyy, zzz	xxx, xyy, xzz, $yxy=yyx$, $zxz=zzx$
[110]	$xzx=xxz$, $yzy=yyz$, zxx, zyy, zzz	$xyz=xzy$, $yzx=yxz$, $zxy=zyx$

chosen to be the $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ axes. The cases for $\mathbf{M}\|[2\bar{1}\bar{1}]\|\hat{\mathbf{x}}$ and $\mathbf{M}\|[111]\|\hat{\mathbf{z}}$ have been studied. Eighteen and seven independent nonvanishing elements are found, respectively. The parities of these elements with respect to **M** are indicated in the table.

III. SECOND-HARMONIC GENERATION AS A PROBE FOR SURFACE MAGNETISM

We have shown that certain surface nonlinear susceptibility tensor elements are nonvanishing only in the presence of a finite **M**. With appropriate combinations of input and output beam polarizations, different elements of $\chi^2(\mathbf{M})$ can be selectively measured by surface SHG. In the following discussion, we shall use the experimental geometry shown in Fig. 1. The interface of medium I (air or vacuum) and medium II (which can be magnetized) is in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane, with the surface normal being the $\hat{\mathbf{z}}$ axis. The laser beam is incident at an angle θ with respect to the $\hat{\mathbf{z}}$ axis, whereas θ' is the refraction angle in medium II. The $\hat{\mathbf{x}}'$ and $\hat{\mathbf{y}}'$ axes in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane are chosen to be parallel and perpendicular to the plane of incidence, respectively, and ϕ is the angle between $\hat{\mathbf{x}}$ and $\hat{\mathbf{x}}'$. The notation (s,p) denotes that the incident fundamental beam is p polarized while the SH output is s polarized, and so on. The SH signal reflected from a centrosymmetric medium actually consists of not only a surface contribution but also a bulk contribution. The latter, however, tends to be weaker than the former in the case of metals.[16] The

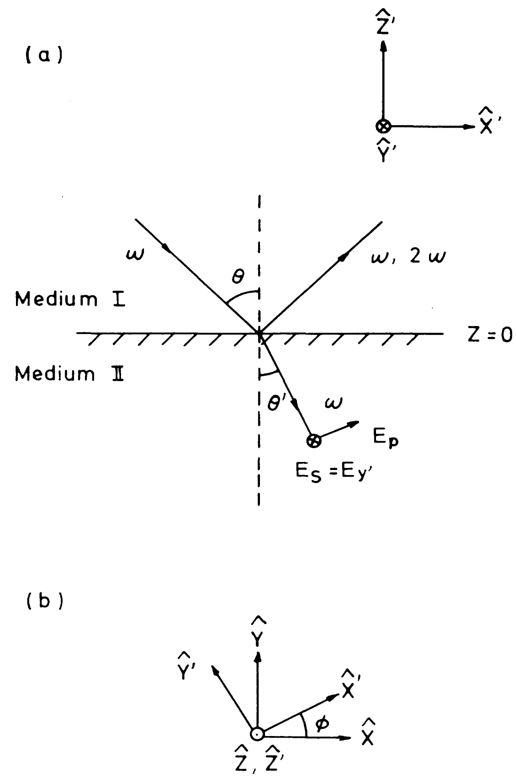

FIG. 1. (a) Geometry of second-harmonic generation in reflection from an interface between two media. (b) Beam coordinates $\hat{\mathbf{x}}'$, $\hat{\mathbf{y}}'$, and $\hat{\mathbf{z}}'$ relative to crystal coordinates $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$.

effective surface nonlinear polarization can be written as

$$\mathbf{P}_{\text{eff}}=\mathbf{P}_s(M)+\mathbf{P}_b\ , \tag{3}$$

where $\mathbf{P}_s(M)$, defined in Eq. (1), is the surface contribution to $\mathbf{P}_{\text{eff}}$ and $\mathbf{P}_b$ is the equivalent surface polarization due to the bulk quadrupole.[14,17] We shall assume that only the surface layer is magnetized.

A. (001) surface

For a normally incident beam with the (s,s) polarization combination, the reflected SH signal vanishes for

TABLE IV. Independent nonvanishing elements of $\chi_s^{(2)}(\mathbf{M})$ for the (111) surface of fcc crystals with surface magnetization **M** parallel to the $[2\bar{1}\bar{1}]$, and [111] directions. ($\hat{\mathbf{x}}$ is along the $[2\bar{1}\bar{1}]$ direction and the surface is in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane.)

Direction of **M**	Independent nonvanishing elements: Even parity	Odd parity
$[2\bar{1}\bar{1}]$	xxx, xyy, xzz, $xzx=xxz$, $yzy=yyz$, $yxy=yyx$, zxx, zyy, zzz, $zxz=zzx$	$xyx=xzy$, $xxy=xyx$, yxx, yyy, yzz, $xzx=yxz$, $zyz=zzy$, $zxy=zyx$
[111]	$xxx=-xyy=-yxy=-yyx$, $xzx=xxz=yyz=yzy$, zxx, zyy, zzz	$xyz=xzy=-yzx=-yxz$, $xxy=xyx=yxx=-yyy$

$\mathbf{M}=0$. In the presence of a magnetized surface, $\mathbf{M}\|[100]$ or [110], the y' component of the surface nonlinear polarization is

$$P_{s,y'}(\mathbf{M})=\chi^{(2)}_{y'y'y'}(\mathbf{M})E_{y'}E_{y'} .$$

Applying Eq. (2), we get

$$\begin{aligned}P_{s,y'}(\mathbf{M})&=\{[2\chi^{(2)}_{xxy}(\mathbf{M})+\chi^{(2)}_{yxx}(\mathbf{M})]\sin^2\phi\cos\phi\\&\quad+\chi^{(2)}_{yyy}(\mathbf{M})\cos^3\phi\}E_{y'}E_{y'}\\&\propto C_1\cos\phi+C_2\cos(3\phi) ,\end{aligned} \tag{4}$$

where C_1 and C_2 are linear combinations of the nonlinear susceptibility tensor elements and the pump fields. It is seen that $P_{s,y'}$ has two components with onefold and threefold rotational symmetries, respectively, about the surface normal. The equivalent surface nonlinear polarization due to the bulk quadrupole for an incident angle θ is[18]

$$P_{b,y'}\propto\sin(4\phi)\sin\theta . \tag{5}$$

Therefore, for a normally incident beam, $P_{b,y'}$ is zero. Thus, $P_{\text{eff},y'}=P_{s,y'}$. We note that even if $\theta\neq0$, $P_{b,y'}$ has a different rotational symmetry than $P_{x,y'}$.

If $\mathbf{M}$ is parallel to $\hat{\mathbf{z}}\|[001]$, the SH signal with the (s,s) combination vanishes. With the (s,p) combination, we find

$$\begin{aligned}P_{s,y'}(\mathbf{M})&=\chi^{(2)}_{y'x'x'}(\mathbf{M})E^2_{x'}+2\chi^{(2)}_{y'x'z'}(\mathbf{M})E_{x'}E_{z'}+\chi^{(2)}_{y'z'z'}(\mathbf{M})E^2_{z'}\\&=-\chi^{(2)}_{xyz}(\mathbf{M})E_p^2\sin(2\theta') ,\end{aligned} \tag{6}$$

where E_p is the electric field amplitude and $\chi^{(2)}_{xyz}(\mathbf{M})$ is an odd function of $\mathbf{M}$. As one would expect physically, $P_{x,y'}$ is rotationally isotropic with respect to $\hat{\mathbf{z}}$. The quadrupole contribution from the bulk is again given by Eq. (5). The total SH field as a function of ϕ is

$$E_s(2\omega)=C_1+C_2\sin(4\phi) ,$$

with the constant term arising from the magnetized surface. Thus from the rotational anisotropy, the contribution of the magnetized (001) surface can be uniquely determined. For $\mathbf{M}=0$, the SH intensity, $I(2\omega)$, is proportional to $\sin^2(4\phi)$ and exhibits an eightfold symmetry. For $\mathbf{M}\neq0$, $I(2\omega)$ assumes a fourfold symmetry and its minima no longer vanish.

B. (110) surface

For the case of $\mathbf{M}\|[001]$, the (s,s) polarization combination yields

$$\begin{aligned}P_{s,y'}&=\{(2\chi^{(2)}_{yyx}(\mathbf{M})-\chi^{(2)}_{yyy}(\mathbf{M})]\sin\phi\\&\quad-[\chi^{(2)}_{xxx}(\mathbf{M})+2\chi^{(2)}_{yyx}(\mathbf{M})-\chi^{(2)}_{xyy}(\mathbf{M})]\sin(3\phi)\}E^2_{y'} ,\end{aligned} \tag{7}$$

which is nonvanishing only for $\mathbf{M}\neq0$. The equivalent surface nonlinear polarization due to the bulk quadrupole is

$$P_{b,y'}\propto k_{x'}(\omega)[\tfrac{1}{2}\sin(2\phi)+\tfrac{3}{4}\sin(4\phi)]\zeta E^2_{y'} , \tag{8}$$

where $k_{x'}(\omega)$ is the x' component of the wave vector of the pump field. ζ is a phenomenological constant describing the anisotropic contribution to $P_{b,y'}$.[18] For a normally incident s-polarized laser beam, $k_{x'}(\omega)=0$, the reflected SH signal is generated by $P_{s,y'}$ only. If the incidence angle is nonzero, the contribution of the surface magnetization to the nonlinear polarization can still be identified by inspecting the ϕ dependence of the reflected SH signal.

With $\mathbf{M}\|[110]$, one can show that, for the (s,p) polarization combination,

$$\begin{aligned}P_{s,y'}&=\{[\chi^{(2)}_{yyz}(\mathbf{M})-\chi^{(2)}_{xxz}(\mathbf{M})]\sin(2\phi)\\&\quad+[\chi^{(2)}_{yxz}(\mathbf{M})+\chi^{(2)}_{xyz}(\mathbf{M})]\cos(2\phi)\\&\quad+[\chi^{(2)}_{yxz}(\mathbf{M})-\chi^{(2)}_{xyz}(\mathbf{M})]\}E_{x'}E_{z'}\end{aligned} \tag{9}$$

and

$$\begin{aligned}P_{b,y'}&\propto[\tfrac{3}{2}k_{x'}(\omega)E^{(2)}_{x'}\\&\quad-k_{2z'}(\omega)E_{x'}E_{z'}+k_{x'}E^2_{z'}]\zeta\sin(2\phi)\\&\quad-k_{x'}(\omega)E^2_{x'}\zeta\sin(4\phi) ,\end{aligned} \tag{10}$$

where $k_{2z}(\omega)$ is the z component of the wave vector of the refracted light in the magnetic material. In the absence of surface magnetization, $\chi^{(2)}_{yyz}=\chi^{(2)}_{xxz}\neq0$, while $\chi^{(2)}_{yxz}=\chi^{(2)}_{xyz}=0$. As a result, $P_{s,y'}=0$. The reflected SH signal is contributed solely by the bulk. For $\mathbf{M}\neq0$, it is possible to identify unambiguously the SH signal due to the magnetized surface by employing geometries with $\phi=0$ or $\phi=\pi/2$, at which $P_{b,y'}=0$, according to Eqs. (9) and (10), while $P_{s,y'}=\chi^{(2)}_{yxz}(\mathbf{M})E_p^2\sin(2\theta')$ for $\phi=0$, and $P_{s,y'}=-\chi^{(2)}_{xyz}(\mathbf{M})E_p^2\sin(2\theta')$ for $\phi=\pi/2$.

C. (111) surface

Let us consider the (s,s) polarization combination. For $\mathbf{M}\|[2\bar{1}\bar{1}]$, i.e., $\mathbf{M}$ in the mirror plane, we have

$$\begin{aligned}P_{s,y'}&=[-\chi^{(2)}_{xxx}(\mathbf{M})\sin^3\phi-\chi^{(2)}_{xyy}(\mathbf{M})\sin\phi\cos^2\phi\\&\quad-2\chi^{(2)}_{yyx}(\mathbf{M})\sin\phi\cos^2\phi+2\chi^{(2)}_{xxy}(\mathbf{M})\sin^2\phi\\&\quad+\chi^{(2)}_{yxx}(\mathbf{M})\sin^2\phi\cos\phi+\chi^{(2)}_{yyy}(\mathbf{M})\cos^3\phi]E^2_{y'}\end{aligned} \tag{11}$$

and

$$P_{b,y'}\propto\zeta E^2_{y'}\sin(3\phi) . \tag{12}$$

Examining Eqs. (11) and (12), we find $P_{s,y'}=\chi^{(2)}_{yyy}(\mathbf{M})E^2_{y'}$ while $P_{b,y'}=0$ for $\phi=0$. Both the surface and bulk contributions to the nonlinear polarization are identically zero in the absence of surface magnetization for $\phi=0$, but the former is nonvanishing for $\mathbf{M}\neq0$.

For M along the [111] axis, the (s,s) polarization combination gives

$$P_{s,y'}=[\chi^{(2)}_{xxx}(\mathbf{M})\sin(3\phi)+\chi^{(2)}_{yyy}(\mathbf{M})\cos(3\phi)]E^2_{y'} \tag{13}$$

and

$$P_{b,y'}\propto k_{2z'}(\omega)\xi E^2_{y'}\sin(3\phi) . \tag{14}$$

Both $P_{s,y'}$ and $P_{b,y'}$ exhibit a threefold rotational symmetry about [111]. The former, induced by **M**, can be unambiguously determined by choosing $\phi=0$.

IV. THE MAGNETIZATION-INDUCED $\chi^{(2)}(\mathbf{M})$

In the previous section we have suggested several experimental geometries to probe the surface magnetization. It is, however, important to know whether the magnetization-induced components of $\chi^{(2)}(\mathbf{M})$ are large enough to give detectable SH signals. In this section we will estimate these components to the linear order in **M**. Consider Ni(001) as an example. We estimate $\chi^{(2)}_{xxy}(\mathbf{M})/\chi^{(2)}_{xxy}(0)\approx 0.1$ since it should be of the same order as the ratio of the linear optical susceptibility components $\chi^{(1)}_{xy}(\mathbf{M})/\chi^{(1)}_{xx}(0)$, which is about 0.1.[19]

It was first pointed out by Kittel[20] in an order-of-magnitude estimate that it is the change of the electronic wave functions, rather than the shift of energy eigenvalues due to spin-orbit coupling, which is responsible for the magnetization-induced $\chi^{(1)}_{xy}(\mathbf{M})$ in a ferromagnetic material. In the calculation for $\chi^{(1)}_{xy}(\mathbf{M})$ of Ni and Fe, Argyres[21] showed that this theory does give reasonable predictions. Here, we apply the same method to estimate $\chi^{(2)}_{xxy}(\mathbf{M})/\chi^{(2)}_{xxz}(\mathbf{0})$.

In the electric dipole approximation, the nonlinear susceptibility for SHG (Ref. 22) is

$$\chi^{(2)}_{ijk}(2\omega)=\frac{e^3}{\hbar^2}\sum_{\mathbf{k},v,c,c'}\left[\frac{\langle r_i\rangle_{vc}\langle r_j\rangle_{cc'}\langle r_k\rangle_{c'v}}{(2\omega-\omega_{cv})(\omega-\omega_{c'v})}+5\text{ similar terms}\right]f_v(\mathbf{k})\ , \tag{15}$$

where $\mathbf{k}$ denotes the electron wave vector; v,c,c' are band indices for the valance and conduction bands; $f_v(\mathbf{k})$ is the Fermi distribution function for the state $|v,\mathbf{k}\rangle$; $\langle r_i\rangle_{vc}$ is a matrix element for the ith component of the electronic displacement vector for the transition $c\leftrightarrow v$; and $\omega_{cv}=(E_c-E_v)/\hbar$.

The Hamiltonian for a magnetized system is

$$H=H_0+H_{\text{s.o.}}\ ,$$

where

$$H_0=\left[\frac{1}{2m}\right]p^2+V(\mathbf{r}) \tag{16}$$

and

$$H_{\text{s.o.}}=\left[\frac{1}{2m^2c^2}\right][\nabla V(\mathbf{r})\times\mathbf{p}]\cdot\mathbf{S}\ . \tag{17}$$

Treating the spin-orbit coupling Hamiltonian as a perturbation, we find that the electron wave functions with spin functions $\alpha(\pm 1)$ are[21]

$$\phi_{\lambda,\pm 1}=[\psi_n(\mathbf{k},\mathbf{r})\pm\chi_n(\mathbf{k},\mathbf{r})]\alpha(\pm 1) \tag{18}$$

and the corresponding eigenenergies are

$$\epsilon_{\lambda,\pm 1}=E_n(\mathbf{k})\pm\delta\ , \tag{19}$$

where ψ_n is the unperturbed eigenfunction with $H_0\psi_n=E_n\psi_n$ and $\chi_n(\mathbf{k},\mathbf{r})$ is a linear combination of $\psi_m(\mathbf{k},\mathbf{r})$ with $m\neq n$, i.e.,

$$\chi_n(\mathbf{k},\mathbf{r})=\sum_{m\ (\neq n)}b_{nm}\psi_m(\mathbf{k},\mathbf{r})\ . \tag{20}$$

From Eqs. (18) and (19), the expression for $\chi^{(2)}_{ijk}$ in Eq. (15) can be rewritten as

$$\chi^{(2)}_{ijk}=\chi^{(2)}_{ijk}(\mathbf{M}=\mathbf{0})+\chi^{(2)}_{ijk}(\mathbf{M})\ , \tag{21}$$

where

$$\chi^{(2)}_{ijk}(\mathbf{M}=\mathbf{0})=\frac{e^3}{\hbar^2}\sum_{\mathbf{k}}\sum_{v,c,c',\sigma}\left[\frac{\langle r_i\rangle_{vc}\langle r_j\rangle_{cc'}\langle r_k\rangle_{c'v}}{(2\omega-\omega_{cv})(\omega-\omega_{c'v})}+5\text{ similar terms}\right]f_v(\mathbf{k}) \tag{22}$$

and

$$\chi^{(2)}_{ijk}(\mathbf{M})=\frac{e^3}{\hbar^2}\sum_{\mathbf{k},\sigma}\sum_{v,c,c}\left[\sum_m\pm b^*_{vm}\frac{\langle r_i\rangle_{vc}\langle r_j\rangle_{cc'}\langle r_k\rangle_{c'm}}{(2\omega-\omega_{cv})(\omega-\omega_{c'v})}+35\text{ similar terms}\right]f_v(\mathbf{k},\sigma)\ . \tag{23}$$

Here, σ is a spin index, and the $\pm$ signs correspond to spin up and down, respectively. If both spin states of $|v,\mathbf{k}\rangle$ are filled, their contributions in Eq. (23) are canceled exactly. Thus only the partially filled spin states contribute in the summation.

Calculating the tensor elements in Eq. (22) and Eq. (23) would require detailed information on the wave functions. Instead, we will calculate only the ratio of the magnetization-induced element $\chi^{(2)}_{\alpha,\beta,\gamma}(\mathbf{M})$ to the magnetization-independent nonvanishing element $\chi^{(2)}_{ijk}(\mathbf{0})$. We assume all nonvanishing $\chi^{(2)}_{ijk}(\mathbf{0})$ are alike and all $\chi^{(2)}_{\alpha,\beta,\gamma}(\mathbf{M})$ are alike. From Eqs. (22) and (23), we find

$$\chi^{(2)}_{\alpha,\beta,\gamma}(\mathbf{M})/\chi^{(2)}_{ijk}(\mathbf{0})\approx u_b\sum_m 6b_{vm}\ , \tag{24}$$

where u_b is the number of Bohr magnetons per surface atom.

We take the approximation by Argyres,[21]

$$b_{vm}=\frac{A}{i(E_v-E_m)}\ , \tag{25}$$

and consider only the m band just above or below the v band in the summation over m. For Ni, we take $A=1.0\times 10^{-13}$ erg,[21] the average nearest band separation of 4 eV$=6.4\times 10^{-12}$ erg,[21] and $u_b=0.68$ for a free surface,[5] we get

$$\chi^{(2)}_{\alpha,\beta,\gamma}(\mathbf{M})/\chi^{(2)}_{ijk}(\mathbf{0})\approx 0.07i\ . \tag{26}$$

This is in excellent agreement with our early estimate based on the known ratio of $\chi^{(1)}_{xy}(\mathbf{M})/\chi^{(1)}_{xx}(\mathbf{0})$.

Knowing that for a metal surface $\chi^{(2)}_{ijk}(\mathbf{0})\sim 10^{-15}$ esu,[16] we should expect $\chi^{(2)}_{\alpha,\beta,\gamma}(\mathbf{M})\sim 10^{-16}$ esu. This is certainly detectable, considering that the detection limit of surface SHG is $\chi^{(2)}<10^{-17}$ esu.[14]

V. SUMMARY

We have shown that surface magnetism can lower the surface symmetry and make several elements of the surface nonlinear susceptibility tensor for surface SHG no longer vanishing. These elements are derived and tabulated for (001), (110), and (111) surfaces of fcc centrosymmetric crystals. They are of the order of 10^{-16} esu for nickel, as estimated from the microscopic derivation. Based on this estimate, it is believed that optical SHG can be used to probe surface magnetization. Suitable input-output polarization combinations are suggested for the probing of the (001), (110), and (111) surfaces with various directions of **M**. It is also predicted that SHG signals from the magnetized and nonmagnetized surfaces in certain experimental geometries will exhibit characteristically different rotational anisotropy.

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