Symmetry Analysis of the Nonlinear Optical Response: Second Harmonic Generation at Surfaces of Antiferromagnets

A. Dähn, W. Hübner, and K. H. Bennemann
Institute for Theoretical Physics, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

(Received 21 June 1996)

Using symmetry arguments we show how optical second harmonic generation (SHG) can be used to detect antiferromagnetism at surfaces and in thin films. Based on the group theoretical analysis of the nonlinear electric susceptibility we propose a new nonlinear magneto-optical effect, which allows even in the presence of unit-cell doubling for the unambiguous discrimination of antiferromagnetic surface spin configurations from ferromagnetic or paramagnetic ones. As an example for this effect we discuss the polarization dependence of SHG from the fcc (001) surface of NiO in some detail. [S0031-9007(96)01558-X]

PACS numbers: 78.20.Ls, 42.65.Ky, 75.30.Pd, 75.50.Ee

In the last decade optical second harmonic generation (SHG) has become a well-established probe for the investigation of the geometrical and electronic properties of surfaces and interfaces. In particular, the nonlinear magneto-optical Kerr effect (NOLIMOKE) has been demonstrated both theoretically and experimentally as a powerful technique for the study of surface and interface ferromagnetism due to its enhanced surface sensitivity [1–6]. For example, recent NOLIMOKE measurements at fcc Fe films by Straub *et al.* [7] yield the result of magnetically active layers directly at the surface, which cannot be detected by other techniques. Moreover, enhanced Kerr rotations [8] and quantum well oscillations [9,10] demonstrate the unique options of NOLIMOKE and also its significance for *in situ* imaging of chemical bond formation via magnetism [11] (for instance, during the oxidation) as well as for femtosecond spectroscopies [12].

To apply NOLIMOKE not only to ferromagnetism, but also to an analysis of antiferromagnetism and thus also to magnetic domain structures, it is of considerable interest to extend our theory correspondingly [13]. By performing a symmetry analysis of the susceptibility tensor, we show that the SHG signal already discriminates characteristically antiferromagnetism from ferromagnetism or paramagnetism. At first sight this seems surprising, since both the paramagnetic and antiferromagnetic states exhibit time reversal symmetry. However, as will be shown by our detailed symmetry classification of the nonlinear electric susceptibility tensor, we obtain characteristic differences of the susceptibilities in the paramagnetic, ferromagnetic, and antiferromagnetic phases, which then can be detected by using different polarizations of the incoming light. Our analysis proposed here is different from the recent pioneering studies of antiferromagnetic bulk domains of Cr_2O_3 by Fiebig *et al.* [14,15]: They observed antiferromagnetic 180° domains of bulk Cr_2O_3 from a strong intensity contrast in SHG transmission and explained this effect by the interference of the nonlinear electric susceptibility (nonzero only in the antiferromagnetic phase) and magnetic susceptibility (allowed in both phases) [16]. While the phenomenon in Cr_2O_3 results from the simultaneous action of spin-orbit coupling and trigonal crystal distortion [17], we show here that SHG may also probe antiferromagnetism at surfaces of cubic crystals (where a center of inversion guarantees—within the electric dipole approximation—the absence of bulk contributions) without involving interference effects or crystal distortions.

Because of their rich magnetic phases, transition-metal oxides are of special interest for an analysis. Also they might change their magnetic properties during oxidation which is of interest to be observed. In particular, owing to available data obtained with various experimental techniques we apply our theory to NiO.

We start our theory from the symmetry analysis of the nonlinear susceptibility using classical electrodynamics. The nonlinear response is described by the nonlinear electrical polarization $P_{\mathrm{el}}^{(2\omega)}$ acting as a source term in the wave equation and related to the incident photon field by the nonlinear electrical susceptibility $\chi_{\mathrm{el}}^{(2\omega)}$:

$$P_{\mathrm{el}}^{(2\omega)} = \chi_{\mathrm{el}}^{(2\omega)} \colon E^{(\omega)} E^{(\omega)}. \tag{1}$$

Here, $\chi_{\mathrm{el}}^{(2\omega)}$ is the nonlinear electrical susceptibility in dipole approximation. It is a polar tensor of rank three which is nonzero only at the surface of a cubic material. According to Neumann's principle this susceptibility (which is a property tensor) has to remain invariant under any symmetry transformation $l_{n,n'}$ ($n = i,j,k$, $n' = i',j',k'$) leaving the lattice invariant [18,19]:

$$\chi_{\mathrm{el},i'j'k'}^{(2\omega)} = l_{i'i} l_{j'j} l_{k'k} \chi_{\mathrm{el},ijk}^{(2\omega)}, \qquad i,j,k = x,y,z\,. \tag{2}$$

If time inversion R: $t \rightarrow -t$ alone or in combination with any space operation l belongs to the classifying symmetry elements, Eq. (2) must be replaced by

$$\chi_{\mathrm{el},i'j'k'}^{(2\omega)} = \pm l_{i'i} l_{j'j} l_{k'k} \chi_{\mathrm{el},ijk}^{(2\omega)}, \qquad i,j,k = x,y,z\,, \tag{3}$$

where $-$ $(+)$ refers to the case when $\chi^{(2\omega)}$ changes sign under time-inversion R, denoted as c tensor (remains invariant, i tensor) [18].

0031-9007/96/77(18)/3929(4)$10.00

Using now the symmetry transformations for paramagnetic, ferromagnetic, and antiferromagnetic states we can immediately determine the resulting nonvanishing elements of $\chi^{(2\omega)}_{\mathrm{el},ijk}$. Since, depending on the magnetic state, different tensor elements vanish, it is possible to detect optically antiferromagnetism by varying the polarization of the incoming light. The allowed tensor elements resulting from Eqs. (2) and (3) are given in Table I.

The new predicted nonlinear magneto-optical effect results from the fact that the point groups obtained for antiferromagnetic configurations are different from the ones describing paramagnetic or ferromagnetic states of the same surfaces, since all three phases have characteristically different symmetry features: A ferromagnetic surface never exhibits time inversion symmetry R, but R may occur in combination with spatial symmetry operations (i.e., the symmetry group is magnetic). In the paramagnetic state, however, a surface always remains invariant under time reversal. Hence, for surfaces of cubic crystals the paramagnetic state exhibits the same time-inversion symmetry as the antiferromagnetic state. But the two states usually differ in the allowed space transformations, because in the paramagnetic phase no spin configuration has to be regarded.

In order to demonstrate that SHG yields a new effect, which sensitively probes antiferromagnetic surface spin configurations, we proceed as follows: (i) We determine the magnetic space group of the surface lattice including the spin configuration. We find that all examined antiferromagnetic (001), (110), and (111) surface configurations are highly symmetric: There always exists a translation T so that time-reversal R becomes a symmetry element of the lattice in combination with this translation. (ii) Since the nonzero elements of the property tensors rigorously follow from the point groups of a crystal, we restrict ourselves to the corresponding operations replacing all translations by the identity [18]. Thus, time-inversion R remains a symmetry element of all examined antiferromagnetic spin configurations. Consequently unit-cell doubling occurring for most of the antiferromagnetic spin configurations does not affect the classification. (iii) R has to be excluded from the analysis, since SHG is a dynamical process with a preferred direction of time [17]. In this case Neumann's principle is restricted to pure space symmetry operations of [18,20]. The resulting point group of space transformations, which usually is just a subgroup of the classical point group characterizing the symmetry of the three-dimensional lattice, is used to calculate the nonzero tensor elements of $\chi^{(2\omega)}_{\mathrm{el}}$ in accordance with Eq. (2). For these subgroups, in contrast to the three-dimensional point groups [18,19], the tensor elements of $\chi^{(2\omega)}_{\mathrm{el}}$ have not been derived previously.

To show the predicted sensitivity of SHG to surface antiferromagnetism we restrict ourselves to the very clear-cut example of one prototypic spin structure for each of the fcc (001), (110), and (111) surfaces [21] (see Table I). In all antiferromagnetic configurations additional tensor elements compared to the paramagnetic phase appear. As a prototypic example how nonlinear magneto-optics detects antiferromagnetism unambiguously, we discuss the fcc (001) surface with spin configuration c (see Fig. 1), which is similar to the one of (001) NiO [22]. The point group describing the symmetry of this configuration consists of only one independent spatial symmetry operation,

TABLE I. Nonvanishing elements of $\chi^{(2\omega)}_{\mathrm{el}}$ for certain spin configurations of the (001), (110), and (111) surfaces of a fcc lattice. We denote χ_{ijk} by ijk.

Surface	Configuration	Point Group	Symmetry operations	Nonvanishing independent tensor elements
(001)	Para	$4mm$	$1, 2_z, \pm 4_z, \bar{2}_x, \bar{2}_y, \bar{2}_{xy}, \bar{2}_{-xy}$	$zxx = zyy, xxz = xzx = yyz = yzy, zzz$
	Ferro ($\mathbf{M} \parallel \mathbf{x}$)	$\cdots$	$1, \underline{2}_z, \bar{2}_x, \underline{\bar{2}}_y$	$xxz = xzx, zxx, yyz = yzy, zyy, zzz,$ $zzy = zyz, yzz, xxy = xyx, yxx, yyy$
	AFM			
	a)	$\cdots$	$1, \bar{2}_y$	$xxx, yyx = yxy, xyy, xxz = xzx, zxx,$ $yyz = yzy, zyy, zzx = zxz, xzz, zzz$
	b)	$\cdots$	$1, \bar{2}_x$	$xxy = xyx, yxx, yyy, xxz = xzx, zxx$ $yyz = yzy, zyy, zzy = zyz, yzz, zzz$
	c)	2	$1, 2_z$	$zxx, xxz = xzx, zyy, yyz = yzy, zzz,$ $xyz = xzy, yzx = yxz, zxy = zyx$
(110)	Para	$mm2$	$1, 2_z, \bar{2}_x, \bar{2}_y$	$zxx, xxz = xzx, zyy, yyz = yzy, zzz$
	AFM	2	$1, 2_z$	$zxx, xxz = xzx, zyy, yyz = yzy, zzz,$ $xyz = xzy, yzx = yxz, zxy = zyx$
(111) More than one monolayer	Para	$3m$	$1, \pm 3_z, 3(\bar{2}_\perp)$	$xxx = -xyy = -yyx = -yxy, zxx = zyy,$ $xxz = xzx = yyz = yzy, zzz$
	AFM	$\cdots$	$1, \bar{2}_y$	$xxx, yyx = yxy, xyy, xxz = xzx, zxx$ $yyz = yzy, zyy, zzx = zxz, xzz, zzz$
(111) Exactly one monolayer	Para	$6mm$	$1, 2_z, \pm 3_z, \pm 6_z, 6(\bar{2}_\perp)$	$zxx = zyy, xxz = xzx = yyz = yzy, zzz$
	AFM	2	$1, 2_z$	$zxx, xxz = xzx, zyy, yyz = yzy, zzz,$ $xyz = xzy, yzx = yxz, zxy = zyx$

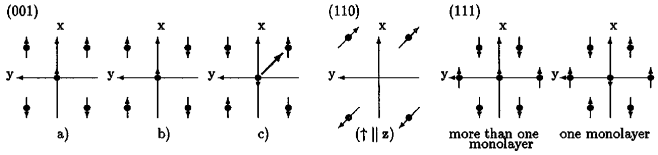

FIG. 1. Antiferromagnetic spin configurations of low index surfaces of NiO.

i.e., the 180° rotation about the z axis 2_z (z axis perpendicular to the surface, x and y axes in the surface plane), which transforms $(x, y, z) \rightarrow (-x, -y, z)$ and causes the spin moments, parallel or antiparallel to the x direction, to flip. But this spin flip, corresponding to time-reversal R, can be replaced by a translation T about half the negative x-y diagonal of the square unit cell indicated by the arrow. So $2_z T$ and RT are symmetry elements of the space group. Consequently, 2_z and R turn out to be symmetry elements of the corresponding magnetic point group obtained by setting T equal to unity. (Other symmetry operations, for example, reflection at the x-z or y-z plane, are not allowed for this configuration, since under these transformations single spins change sign, whereas others stay invariant. So the spin structure changes and cannot be restored by time reversal or a translation.) Dropping R in classifying a dynamical process the remaining point group is the classical monoclinic group **2** which consists of the elements 1 and 2_z. Hence, as can be seen from Table I, this spin configuration is especially suited for the detection of antiferromagnetism by nonlinear magneto-optics: The tensor elements $xyz = xzy$, $yzx = yxz$, and $zxy = zyx$ appear in the antiferromagnetic phase only. Both in the paramagnetic and in the ferromagnetic state ($\mathbf{M} \parallel \mathbf{x}$) they are zero. On the other hand, there are tensor elements, for example, yyy, yxx, and yzz, which occur exclusively in the ferromagnetic state.

Having completed now the symmetry analysis of the susceptibility tensor the various tensor elements can be singled out in the SHG response by varying the light polarization [3,5]: Using the appropriate boundary conditions for the electromagnetic fields and the inhomogenous wave equation the reflected light at frequency 2ω for surfaces is given by [23]

$$E^{(2\omega)}(\Phi, \phi) = 2i\left(\frac{\omega}{c}\right)|E_0^{(\omega)}|^2 \begin{pmatrix} A_p F_c \cos\Phi \\ A_s \sin\Phi \\ A_p N^2 F_s \cos\Phi \end{pmatrix} \chi_{\mathrm{el}}^{(2\omega)} \times \begin{pmatrix} f_c^2 t_p^2 \cos^2\varphi \\ t_s^2 \sin^2\varphi \\ f_s^2 t_p^2 \cos^2\varphi \\ 2 f_s t_p t_s \cos\varphi \sin\varphi \\ 2 f_c f_s t_p^2 \cos^2\varphi \\ 2 f_c t_p t_s \cos\varphi \sin\varphi \end{pmatrix}, \quad (4)$$

where $\chi_{\mathrm{el}}^{(2\omega)}$ is the susceptibility tensor for the respective surface configurations, Φ, φ are the angles of polarization for the reflected second harmonic and fundamental light, $N(2\omega)$ is the index of refraction at frequency 2ω, $F_{c,s}, f_{c,s}$ are the corresponding Fresnel coefficients, $T_{s,p}, t_{s,p}$ the linear transmission coefficients, and A_p, A_s the amplitude factors of s- and p-polarized light. It becomes obvious how by varying the light polarization different elements of χ_{ijk} enter. To discriminate optically the antiferromagnetic spin configuration of the (001) surface from the paramagnetic or ferromagnetic one it is sufficient to measure the s-polarized SHG output as a function of the polarization of the fundamental light. Table II shows the resulting SHG fields obtained by Eq. (4) with the characteristic tensor elements for the three phases and different incoming light polarizations. Obviously the difference between the polarized SHG signals of the states is caused by the appearance of the yyy element in the ferromagnetic phase in contrast to the paramagnetic and antiferromagnetic ones ($s \rightarrow s$) and by the appearance of the yzx element in the antiferromagnetic state in contrast to the paramagnetic one ($p \rightarrow s$). Figure 2 schematically illustrates the differences between the phases in dependence on the polarization of incident fundamental and reflected SHG light: In the paramagnetic state the s-SHG signal vanishes for both s- and p-polarized incoming light, in the antiferromagnetic state it vanishes only for s-polarized

TABLE II. Reflected SHG signal for different polarizations of the fundamental light for the (001) surface of a fcc crystal.

Configuration	$P_{\text{incoming light}}$	$P_{\text{SHG light}}$	SHG wave $E^{(\omega)}$
Para	s	s	0
	p	s	0
	Mix(45°)	s	$2i(\frac{\omega}{c})\,|E_0^{(\omega)}|^2 A_s f_s t_p t_s xxz$
Ferro	s	s	$2i(\frac{\omega}{c})\,|E_0^{(\omega)}|^2 A_s t_s^2 yyy$
($\mathbf{M} \parallel \mathbf{x}$)	p	s	$2i(\frac{\omega}{c})\,|E_0^{(\omega)}|^2 A_s t_p^2 (f_c^2 yxx + f_s^2 yzz)$
	Mix(45°)	s	$2i(\frac{\omega}{c})\,|E_0^{(\omega)}|^2 A_s (\frac{1}{2} f_c^2 f_p^2 yxx + \frac{1}{2} t_s^2 yyy + \frac{1}{2} f_s^2 t_p^2 yzz + f_s t_p t_s yyz)$
AFM	s	s	0
	p	s	$2i(\frac{\omega}{c})\,|E_0^{(\omega)}|^2 A_s t_p^2 2 f_c f_s yzx$
	Mix(45°)	s	$2i(\frac{\omega}{c})\,|E_0^{(\omega)}|^2 A_s (f_s t_p t_s yyz + f_c f_s t_p^2 yzx)$

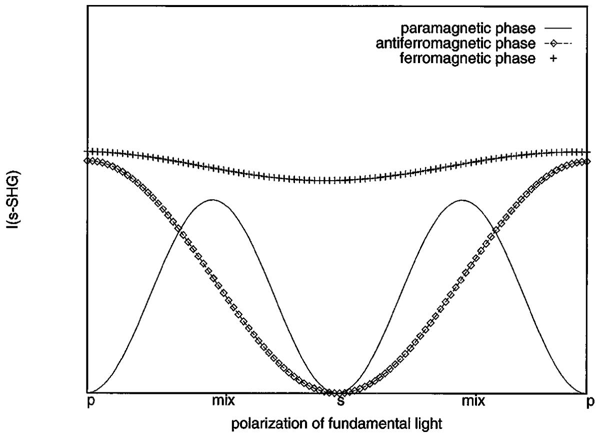

FIG. 2. Dependence of the s-polarized SHG signal on the polarization of the incoming light.

incoming light, and in the ferromagnetic state a pronounced s-SHG signal occurs for all three polarizations of the fundamental light. Thus, performing measurements with s-, p-, or mixed polarized incoming light allows one to sort out the antiferromagnetic state unambiguously. Moreover, using appropriate polarizations of incident and SHG light one can directly observe the transition between the antiferromagnetic and paramagnetic states upon varying the temperature: The characteristic SHG signal for the antiferromagnetic phase disappears upon crossing the Néel point.

In conclusion, our analysis shows that nonlinear optics provides a very sensitive optical probe for antiferromagnetically ordered surfaces. The time-inversion symmetry of these surfaces needs not to be broken either [24]. This could be important for the observation of surfaces of oxidized transition metals and oxides like NiO, which often exhibit the above mentioned symmetry. Our analysis of antiferromagnetic spin configurations can be extended to interfaces such as Fe/Cr and offers a possibility for the imaging of an ensemble of *ferromagnetic* domains. An interesting application is also the determination of spin waves via time-resolved SHG spectroscopy.

[1] Ru-Pin Pan, H. D. Wei, and Y. R. Shen, Phys. Rev. B **39**, 1229 (1989).

[2] J. Reif *et al.*, Phys. Rev. Lett. **67**, 2878 (1991).

[3] K. Böhmer, Ph.D. thesis, Freie Universität Berlin, 1994.

[4] B. Koopmans *et al.*, Appl. Phys. A **60**, 103 (1995).

[5] W. Hübner and K. H. Bennemann, Phys. Rev. B **52**, 13 411 (1995).

[6] J. Reif, C. Rau, and E. Matthias, Phys. Rev. Lett. **71**, 1931 (1993).

[7] M. Straub, R. Vollmer, and J. Kirschner, Phys. Rev. Lett. **77**, 743 (1996).

[8] B. Koopmans *et al.*, Phys. Rev. Lett. **74**, 3692 (1995).

[9] H. A. Wierenga *et al.*, Phys. Rev. Lett. **74**, 1462 (1995).

[10] T. A. Luce, W. Hübner, and K. H. Bennemann, Phys. Rev. Lett. **77**, 2810 (1996).

[11] Th. Rasing (to be published).

[12] J. Hohlfeld (private communication).

[13] For an analysis of antiferromagnetic *bulk* structures, see, for example, V. V. Eremenko and N. F. Kharchenko, Phys. Rep. **155**, 379 (1987); R. Zawodny and S. Kielich, Phys. Rev. A **38**, 3504 (1988); I. Dzyaloshinskii, Sov. Phys. JETP **5**, 1259 (1957); S. B. Borisov *et al.*, Sov. Phys. Solid State **32**, 2127 (1990); N. N. Akhmedeiev *et al.*, Sov. Phys. Solid State **27**, 650 (1985); B. B. Krichetsov *et al.*, J. Phys. Condens. Matter **5**, 8233 (1993).

[14] M. Fiebig *et al.*, Phys. Rev. Lett. **73**, 2127 (1994).

[15] M. Fiebig *et al.*, Appl. Phys. Lett. **66**, 2906 (1995).

[16] Note for ferromagnets a similar interference of the odd and even elements of the electric susceptibility tensor $\chi_{\mathrm{el}}^{(2\omega)}$ is required for the observation of the nonlinear Kerr effect.

[17] V. N. Muthukumar, R. Valentí, and C. Gros, Phys. Rev. Lett. **75**, 2766 (1995).

[18] R. R. Birss, *Symmetry and Magnetism* (North-Holland, Amsterdam, 1964).

[19] S. Bhagavantam, *Crystal Symmetry and Physical Properties* (Academic Press, London, 1966).

[20] Nevertheless, classifying $\chi_{\mathrm{el}}^{(2\omega)}$ from ferromagnetic surfaces, Pan *et al.* [1] used time inversion in combination with space symmetry operations. This is not allowed, since SHG is a dynamical process. Without using R as a symmetry element additional nonvanishing elements of $\chi_{\mathrm{el}}^{(2\omega)}$ should occur. Since, however, for our configurations R never appears in combination with any space transformation but always as an independent symmetry element, this problem does not affect our symmetry analysis: If R is an allowed operation for examining $\chi_{\mathrm{el}}^{(2\omega)}$, according to Eq. (3) all the nonzero tensor elements must be invariant under time inversion. (Thus, they have to be even in the antiferromagnetic order parameter.) Whereas leaving R out of the symmetry analysis, they may be of i *or* c character, where i refers to invariance and c to change of sign under time reversal.

[21] The complete symmetry classification will be given in a forthcoming publication.

[22] Since bulk NiO has NaCl structure, i.e., it consists of two staggered fcc lattices, the unit cell of the (001) surface is a square which contains two nickel ions carrying the spin moments and two oxygen ions.

[23] J. E. Sipe, D. J. Moss, and H. M. van Driel, Phys. Rev. B **35**, 1129 (1987).

[24] Domain imaging in the way performed by Fiebig *et al.* [14,15] on Cr_2O_3 is impossible for this symmetry. To get the necessary effect of interference there had to exist 180° spin domains in the surface which could not be brought to identity by a translation. As a consequence, time-inversion symmetry R of the surface had to be broken. Although this is not the case for our regular lattices, we point out that small distortions, caused by surface reconstruction and observed in experiments on NiO, for example, could easily induce an appropriate structure.