NONLINEAR DIFFRACTION

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(Received 23 September 1968)

A periodic spatial modulation of the nonlinear susceptibility is shown theoretically and experimentally to lead to diffraction of optical harmonic radiation at angles of incidence for which Bragg's law is satisfied.

The presently known laws of nonlinear optics include nonlinear transmission, reflection, refraction, and absorption.[1-3] To this list we now add the phenomenon of nonlinear diffraction. Consider a dielectric with a spatially uniform linear susceptibility, so that no diffraction of light traversing the medium occurs, but with a periodic spatial modulation of the nonlinear susceptibility. We consider only the lowest order nonlinearity, which is responsible for frequency doubling, but an extension to higher order effects is possible. We may expect intense second-harmonic generation to occur at angles of incidence and diffraction for which the nonlinear analog of Bragg's law is satisfied. An elementary theoretical description of this effect and its experimental verification forms the subject of this Letter.

The induced nonlinear moment $P^{2\omega}$ of the lth unit cell in a cubic crystal of symmetry $\bar{4}3m$ (the system we study experimentally) is

$$P_z^{2\omega}(\vec{R}_l) = \beta_{zxy}(\vec{R}_l)E_x^{\omega}E_y^{\omega}\exp i[2\vec{k}_1\cdot\vec{R}_l-2\omega t], \tag{1}$$

where β_{zxy} is the only nonvanishing, microscopic nonlinear tensor element, $\vec{R}_l$ the position vector of the cell, $\vec{k}_1$ the wave vector of the exciting radiation, E its amplitude, and ω its frequency; local field corrections are presently irrelevant. The spatially periodic modulation of β is expanded as

$$\beta_{zxy}(\vec{R}_l) = \beta_{zxy}\sum_{a=0}^{\infty} c_a \exp(i\vec{Q}_a\cdot\vec{R}_l), \tag{2}$$

where $\vec{Q}_a$ is the wave vector of the ath Fourier component of β, and c_a the corresponding amplitude. The luminous flux (power/unit solid angle) at 2ω is then

$$I_z^{2\omega}(\vec{k}_2) = \frac{2\omega^4}{\pi c^3}F^2(\vec{k}_2\cdot\vec{p}_z^{\,2\omega})[\beta_{zxy}E_x^{\omega}E_y^{\omega}]^2\{N\sum_{a=0}^{\infty}c_a^2 + \sum_{l=1}^{N}\sum\sum_{a\neq b=0}^{\infty} c_a c_b \exp i(\vec{Q}_a-\vec{Q}_b)\cdot\vec{R}_l$$
$$+\sum_{a=0}^{\infty}\sum\sum_{l\neq m=1}^{N} c_a^2 \exp[i(\vec{k}_2-2\vec{k}_1-\vec{Q}_a)\cdot(\vec{R}_l-\vec{R}_m)]$$
$$+\sum\sum_{a\neq b=0}^{\infty}\sum\sum_{l\neq m=1}^{N} c_a c_b \exp i[(\vec{k}_2-2\vec{k}_1)\cdot(\vec{R}_l-\vec{R}_m)+\vec{Q}_a\cdot\vec{R}_l-\vec{Q}_b\cdot\vec{R}_m]\}. \tag{3}$$

Here $\vec{k}_2$ is the wave vector of the harmonic radiation, F the appropriate dipolar form factor,[4] and N the total number of irradiated particles. Nonlinear diffraction arises from the third term when

$$\vec{k}_2 = 2\vec{k}_1 + \vec{Q}_a, \tag{4}$$

with an intensity proportional to $[N+N(N-1)]c_a^2$. Equation (4) is the nonlinear analog of Bragg's law. Application of the usual boundary conditions[2,3] at each interface of the planes of the nonlinear grating results in the propagation of the free wave at 2ω along the direction required by the angular part of Eq. (4). The full amplitude of the free wave is thus available for coherent addition throughout the grating. This, of course, is implied by Eq. (3). A geometric visualization of Eq. (4) is displayed in Fig. 1. The angle of diffraction of the harmonic radiation is denoted by θ and the angle of incidence of the laser onto the ath component of the nonlinear grating by ψ_a. In most physically realizable situations the periodicity of the nonlinear grating will be imperfect. This leads to a diffuseness of the Q circle, as shown, and a range in θ and ψ over which Eq. (4)

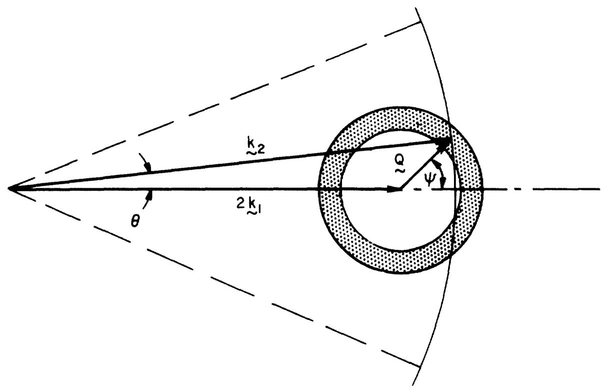

FIG. 1. Wave vectors discussed in the text. $\vec{k}_1$ and $\vec{k}_2$ are the wave vectors of the laser and its harmonic, respectively. $\vec{Q}$ is the wave vector of the nonlinear grating. θ is the angle of diffraction and ψ the angle of incidence. The diffuseness of the Q circle displays the effects of dispersion in the grating spacing.

may be satisfied. For such an imperfect structure we cannot expect the very intense, coherent generation of optical harmonics predicted by Eq. (3) but must be satisfied with an enhancement in intensity at angles for which Eq. (4) is satisfied.

A natural realization of Eq. (2) may be found in multidomain materials in which the domain structure takes the form of a stack of sheets of more or less equal thicknesses, and in which β alternates sign from sheet to sheet (180° domains), or is zero in every other sheet (90° domains). For 180° domains $c_0 = 0$ ($\vec{Q} \equiv 0$), $c_a = 2(-1)^{a-1}/\pi(2a-1)$, and $|Q_a| = 2\pi(2a-1)/2s$, where s is the thickness of a sheet; for 90° domains $c_0 = \frac{1}{2}$, and $c_a = (-1)^{a-1}/\pi(2a-1)$. In both instances only odd components are present. If s is sufficiently large ($|\vec{Q}_1| < |\vec{k}_2| - 2|\vec{k}_1|$), the fundamental Q_1 circle everywhere falls within the k_2 circle, while for very small s ($|\vec{Q}_1| > 2|\vec{k}_1| + |\vec{k}_2|$) the k_2 circle lies completely within the Q_1 circle; in the former instance wave-vector matching may be possible for some of the higher components.

A special case of the phenomenon described here, in which all the vectors in Fig. 1 are parallel, was demonstrated several years ago by Miller, who observed an enhancement of second-harmonic generation in multidomain ferroelectric $BaTiO_3$ and triglycine sulfate over single-domain material.[5] Our own experiments in which the general phenomenon was discovered were performed on a crystal of cubic NH_4Cl (symmetry $\bar{4}3m$) below its λ-point transition temperature of ~242.5°K.[6] In this material the nature of the transition is such that 180° domains may be expected, and we interpret the apparent periodic modulation found for β in terms of such domains. The experimental apparatus is sketched in Fig. 2(a). Both the quartz (QTZ) and the NH_4Cl are polished, plane-parallel slabs; the NH_4Cl crystal is very nearly a (110) section. The function of the quartz standard is to locate conveniently zero angle and to provide a measure of the divergence of the laser beam. Note that the harmonic radiation from the quartz passes through the NH_4Cl crystal. The far-field pattern recorded on the film with a single firing of the laser and with the crystal at ~200°K is shown in Fig. 2(b). The angular scale is corrected for refraction and is measured inside the crystal. The small central spot at zero angle is from the quartz standard and disappears in its absence; the diffuse spot off to the side is the nonlinearly diffracted radiation from the NH_4Cl. Very careful photoelectric measurements yielded an angle of diffraction, $\theta = 9.8 \pm 0.5$ mrad, and also (with the quartz removed)

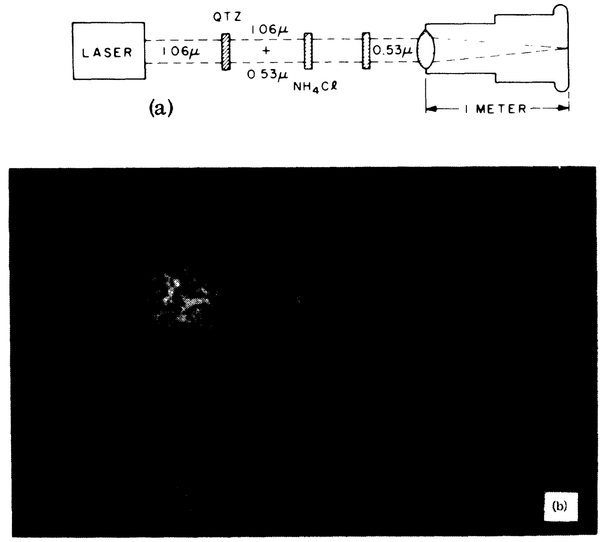

FIG. 2. (a) Experimental apparatus. The laser emits ~5-10 MW. Both the quartz (QTZ) and NH_4Cl are plane parallel slabs. The filter (Schott Model No. KG-3) absorbs the laser but transmits its harmonic. The camera records the far-field pattern of the harmonic radiation from the quartz and NH_4Cl on the film (Polaroid 410). The NH_4Cl crystal is very nearly a (110) section, oriented with the z axis in the plane of the figure. (b) Nonlinear diffraction pattern of the harmonic radiation from NH_4Cl (diffuse, off-center spot). The small central spot at zero angle is from the quartz. The deflection of the harmonic radiation from the NH_4Cl is the plane of (a).

revealed a peak at zero angle and another weaker one at ~−10 mrad. The intensities of these are, respectively, ~$\frac{1}{3}$ and ~$\frac{1}{4}$ the intensity of the 9.8-mrad peak.

The measured value of θ determines, together with Eq. (4), a value of $\psi = 31° \pm 3°$. This, combined with an accurate determination of the crystal orientation via backscattered Laue diffraction, identifies the domain walls as crystallographic (111) planes, for which we compute $\psi = 33.2°$.[7] The effective domain thickness s is found to be approximately 8 μ.

Rotation of the crystal by 180° about an axis perpendicular to $\vec{k}_1$, but in the plane of $\vec{k}_1$ and $\vec{k}_2$, switches the deflection of the spot in Fig. 2(b) to the right of center—in accord with the symmetry properties of a grating. Rotation by 180° about an axis perpendicular to the plane of $\vec{k}_1$ and $\vec{k}_2$ does not change the deflection of the harmonic radiation—again in accord with the symmetry properties of a grating. A prism, however, would change its direction of deflection under such a rotation, but not under the one considered first. The deflection of the harmonic radiation from the NH_4Cl is, as expected, also switched under rotation by 180° about $\vec{k}_1$.

Table I summarizes the important parameters of this experiment. We include also a comparison with normal Bragg diffraction at $\lambda = 5300$ Å. The qualitatively different tuning characteristics arise solely from the dispersion in the refractive index. Variation of ψ by about 15° indicates that the effective dispersion in s is a few microns and confirms that θ is indeed a very insensitive function of ψ.

There is an a priori equal probability for the occurrence of $(11\bar{1})$ domains and nonlinear diffraction from these should be observable. This was also found after a small rotation of the crystal. For the radiation from a ruby laser $n_2 - n_1 = 0.056$, and the fundamental Q_1 circle is too small to satisfy Eq. (4) at any orientation of the crystal. This was confirmed by experiments with a ruby laser in which a very narrow 2ω peak at zero angle was observed, together with a much weaker one at $\theta \approx 18$ mrad. This corresponds to matching to the tail of Q_3 and yields a value of $s \lesssim 3 \times 3.2\ \mu = 9.6\ \mu$. Matching to Q_3 can occur at $\psi = 56°$ and $\theta = 33$ mrad, but our present apparatus does not permit such a large value of ψ. For the same reason, matching to Q_3 for a Nd laser is not attainable; in this instance $\psi = 75°$, and $\theta = 56$ mrad.

Table I. Summary of the important experimental parameters and comparison with normal Bragg diffraction at $\lambda = 5300$ Å.

	Nonlinear diffraction $n_2 - n_1 = 0.027$	Normal Bragg diffraction $n_2 \equiv n_1$
θ(expt) (mrad)	9.8 ± 0.5	9.8 ± 0.5
ψ	$31° \pm 3°$	89.7°
s (μ)	8.4 ± 1	16.5 ± 2
$d\psi/ds$ (mrad/μ)	200	0.3
$d\theta/d\psi$ (mrad/rad)	23	2000
$d\theta/ds$ (mrad/μ)	4.5	0.6

Nonlinear diffraction should generally be observable in other substances and provides a new means for probing their structures.

I am pleased to acknowledge several early discussions with D. A. Kleinman on theoretical matters and numerous helpful comments and suggestions by J. A. Giordmaine and S. K. Kurtz. Many of the experiments described here were performed by L. Kopf; his technical assistance has been invaluable.

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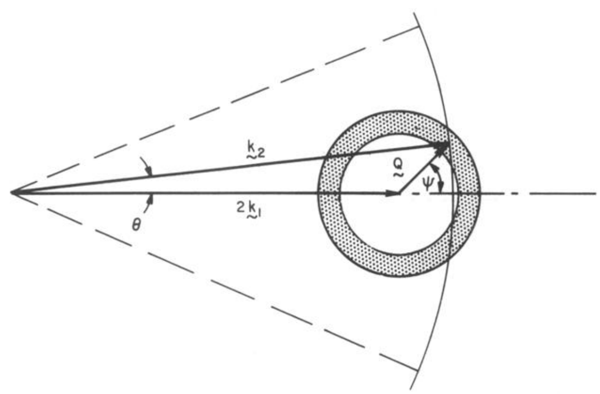
[7]The existence of (111) domains in NH_4Cl has been independently discovered by P. D. Lazay (Massachusetts Institute of Technology), who has also very kindly supplied me with the single crystals used in this work.



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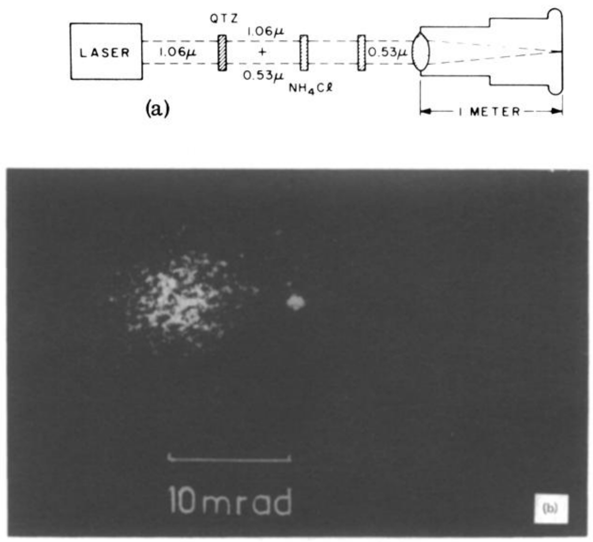

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