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OBSERVATION OF REFLECTED LIGHT HARMONICS AT THE BOUNDARY OF PIEZOELECTRIC CRYSTALS*

J. Ducuing and N. Bloembergen
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts
(Received 2 May 1963)

The existence of harmonic light waves at the boundary of a nonlinear dielectric medium was predicted by Bloembergen and Pershan,[1] who have given a complete theoretical description for the case of cubic media. In this Letter the experimental verification of some aspects of this theory is reported. The experiments were carried out with materials which absorb both the fundamental and the second harmonic frequencies. The harmonic production was observed in reflection, created by the nonlinear polarization in the absorption depth of both frequencies. This layer is sufficiently thick—of the order of one-sixth optical wavelength—so that the observed effects have the full symmetry of the crystal lattice. They have no relation to surface effects previously reported.[2] The latter are smaller by several orders of magnitude in our case. This is evident from the fact that piezoelectric materials such as tellurium, GaAs, and InSb give signals which are at least two or three orders of magnitude larger than germanium. The signal from the latter crystal, which has bulk inversion symmetry, is not distinguishable from our experimental noise background.

The pulsed, unfocused beam of a ruby laser, Q-switched by a nitrobenzene Kerr cell, passed through an interference filter and was split by a glass plate. The intensity of the small split-off fraction was monitored by the second harmonic intensity it produced in a potassium dihydrogen phosphate crystal, which was not near the condition for phase matching. This method of calibration should give accurate relative values of nonlinearity, since uncertainties in the spatial and temporal distribution due to the multimode nature of the fundamental field are eliminated.[3] The main part of the unfocused laser beam was incident at 45° on the polished plane surface of a GaAs crystal, which could be rotated about its normal, as shown in Fig. 1. The second harmonic intensity was observed perpendicular to the fundamental beam. A Glan-Thomson prism served as an analyzer for the polarization. A diaphragm determined an aperture of about three degrees. The reflection law was accurately obeyed within this instrumental width. An interference filter centered

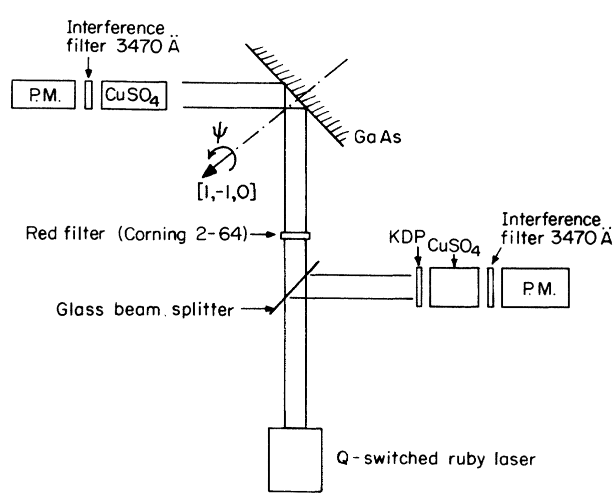

FIG. 1. Diagram of the experimental arrangement.

at the harmonic frequency with a pass band of 60 angstroms further identified the observed signal as a reflected second harmonic wave. This was confirmed by a spectrometer run from 3000 to 4000 angstroms.

The most striking confirmation comes, however, from the observed dependence of intensity and polarization of the harmonic beam on crystallographic orientation.

Consider the case that the incident laser beam is polarized normal to the plane of incidence. The electric field vector $\vec{E}(\nu)$ is then parallel to the surface which is the (1, -1, 0) plane. If the angle between $\vec{E}(\nu)$ and the [001] axis in this plane is denoted by ψ, one obtains for the second harmonic polarization normal to the plane of reflection

$$P_{\perp}^{NLS}(2\nu) = \tfrac{3}{2}\chi^{NL}E_1^{\;2}\sin^2\psi\cos\psi,$$

where $\chi^{NL} = \chi_{14} = \chi_{25} = \chi_{36}$ is the value of the nonvanishing elements of the nonlinear susceptibility tensor in the tetrahedral symmetry, E_1 is the amplitude of the fundamental electric field strength just inside the medium. The reflected intensity polarized normal to the plane of reflection, $\mathcal{I}_{\perp}(2\nu)$, is proportional to $(P_1^{NLS})^2$ according to Eq. (4.5) of BP. The experimental points agree well with the theoretical angular dependence, as shown in Fig. 2.

The component of the nonlinear polarization in the plane of reflection is also parallel to the surface. Its magnitude is given by

$$P_{\parallel}^{NLS} = \tfrac{1}{2}\chi^{NL}E_1^{\;2}\sin\psi(1 - 3\cos^2\psi).$$

The harmonic intensity polarized in the plane of reflection, $\mathcal{I}_{\parallel}(2\nu)$, is proportional to $(P_{\parallel}^{NLS})^2$ according to Eq. (4.13) of BP.[4] The agreement between theory and experiment is shown in Fig. 3. The harmonic intensity is always zero, if E_1 is along [0, 0, 1]. If E_1 is along [1, 1, 1], the harmonic wave is polarized normal to the plane of reflection, and if E_1 is along [1, 1, 0], the polarization is in the plane of reflection.

If the laser beam is polarized in the plane of incidence, the electric field $E_1(\nu)$ after refraction will have a component normal to the surface. This component is quite small, however, due to the large index of refraction of GaAs. P^{NLS} is therefore approximately the same as in the preceding case, except for a 90° rotation of ψ. This qualitative behavior was verified.

The symmetry of the effect precludes an appreciable contribution due to carrier plasma.[2,5] The absence of an observable effect in germanium confirms this. InSb gives results roughly comparable to GaAs.

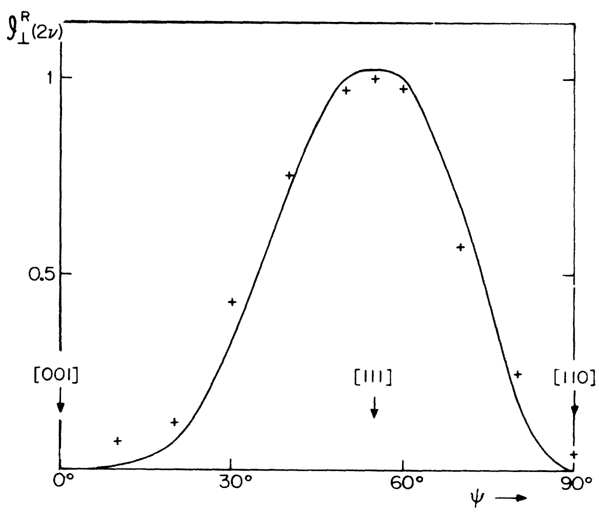

FIG. 2. Reflected second harmonic intensity from GaAs, polarized normal to the plane of reflection, as a function of the angle (90°-ψ) between the [001] axis and the plane of incidence.

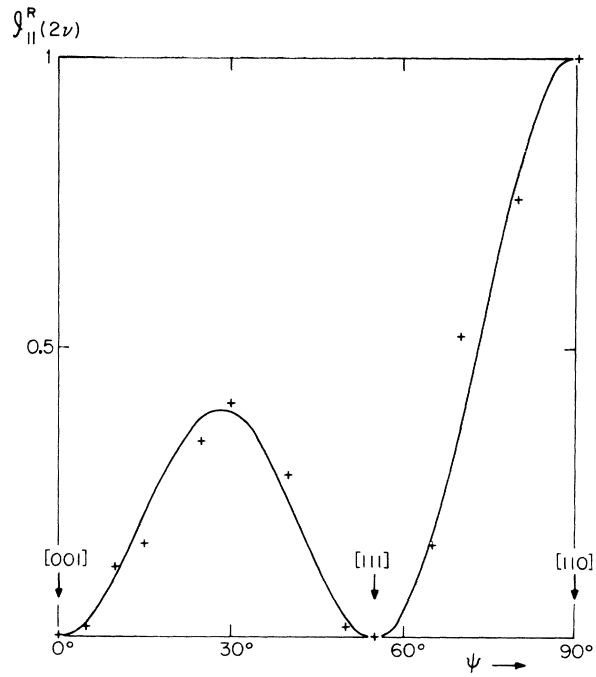

FIG. 3. Reflected second harmonic intensity from GaAs polarized in the plane of reflection, as a function of the angle between the [001] axis and the plane of incidence.

A single crystal of tellurium, a piezoelectric element with the same symmetry, 32, as quartz, also yields boundary harmonics of the same order of magnitude as GaAs. A characteristic variation of $\mathscr{I}(2\nu)$ is obtained for rotation about the normal, which coincides with the trigonal axis. When the incident field $E_1(\nu)$ is perpendicular to the axis, one polarization of the reflected harmonic beam has zeros at $\psi=0$ and π, the other polarization at $\psi=\frac{1}{2}\pi$ and $\frac{3}{2}\pi$.

A program is planned to determine the dispersion of the nonlinear index of refraction of many III-V and II-VI compounds with $\bar{4}3m$ symmetry. This new method will give additional information about the structure of the optical absorption bands in these materials. Many other features of the BP theory will also be subjected to experimental verification.

The assistance of Dr. J. A. Armstrong in building the experimental arrangement is gratefully acknowledged. The crystal of tellurium was kindly given to us by Professor Aigrain and Dr. Rigaux of the University of Paris, Paris, France.

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Cl nmr IN ANTIFERROMAGNETIC $CuCl_2 \cdot 2H_2O$

W. J. O'Sullivan, W. W. Simmons, and W. A. Robinson
Space Technology Laboratories, Incorporated, Redondo Beach, California
(Received 22 April 1963)

While $CuCl_2 \cdot 2H_2O$ qualifies as the most frequently studied antiferromagnet, only the proton nmr[1-3] has been observed below T_N (4.32°K). In contrast with the protons which are coupled to the magnetic system through long-range dipolar interactions, the Cl^- valence electron distributions are modified by the formation of a partial covalent bond with neighboring Cu^{++} ions. Hence, the chlorine nmr will be importantly influenced by short-range magnetic interactions dominated by the effective hyperfine coupling with nearest-neighbor copper ions.

In this Letter we wish to report the preliminary results of observations of the Cl^{35} and Cl^{37} zero external field nmr in $CuCl_2 \cdot 2H_2O$ within the temperature range 1.3°K-4.24°K. Initial theoretical analysis of the observed nmr frequencies predicts an internal magnetic field of 28.00 ± 0.50 kG at a chlorine nuclear site in $CuCl_2 \cdot 2H_2O$ at 0°K. The temperature dependence of the departure of the internal field from the estimated saturation value displays a T^4 dependence within the temperature range $1.4°K \leq T \leq 3.8°K$, in agreement with the zero-field proton nmr measurements of Poulis et al.[3]

$CuCl_2 \cdot 2H_2O$ has an orthorhombic unit cell, space group $D_{2h}{}^7$. The b axis is a common principal axis for both the Cl site and the electric field gradient (EFG) and effective hyperfine interaction tensors. There are two distinguishable chlorine sites per unit cell, related by symmetry operations in such a way that their EFG are equivalent in the general sense (principal axis systems identical but rotated relative to each other). Below 4.32°K, $CuCl_2 \cdot 2H_2O$ orders antiferromagnetically with the sublattice magnetization vectors lying in ac planes, either along the a axis[2] or canted slightly from the a axis.[4]

The resonances were studied in a single-crystal sample ($\simeq 0.1$ cm^3) using externally quenched superregenerative detectors and sine-wave magnetic field modulation. The frequency range 2.5 Mc/sec-40 Mc/sec was covered. Attempts to detect the Cl nmr with marginal oscillator or pulse techniques proved unsuccessful. While it was not possible to determine an accurate value for the linewidth from the rather complicated recorder tracings of the resonances (the total pattern width $\simeq 140$ kc/sec), the estimated linewidth is $\simeq 40$ kc/sec for all the observed transitions with no detectable temperature variation through the range $1.3°K < T < 5.1°K$ and at $T = 77°K$. It was