Nonlinear Electronic Dispersion in CuCl†

D. C. Haueisen* and Herbert Mahr
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 10 February 1971)

To determine the wavelength dependence of the nonlinear susceptibility, measurements of second-harmonic generation have been made in the region of the first exciton absorption band in CuCl at 20°K. Results show a resonance behavior in the nonlinear susceptibility which is fitted by a theoretical curve.

The efficiency of non-phase-matched second-harmonic generation (SHG) of light depends on wavelength primarily through the magnitude of the nonlinear optical susceptibility d and the linear optical constants:

$$P_{\mathrm{SHG}}/P_{\mathrm{fund}}{}^2 \propto |d|^2 l_c{}^2/n_{\mathrm{SH}}, \qquad (1)$$

where P denotes power and l_c is the coherence length given by

$$l_c = [\Delta k^2 + (\alpha/2)^2]^{-1/2},$$

$$\Delta k = k_{\mathrm{SH}} - 2k_{\mathrm{fund}},$$

α = linear absorption constant; k_{SH} and n_{SH} are the wave vector and the refractive index, respectively, at the second-harmonic wavelength. Equation (1) is restricted to the case where the condition $\alpha l_s \gg 1$ is met, l_s being the sample length.

In a region of fundamental electronic absorption, and in a system where the linear optical constants are known for that region of the spectrum, measurement of the wavelength dependence of SHG allows us to deduce the wavelength dependence of $|d|$. This Letter reports a measurement of the wavelength dependence of SHG in CuCl at 20°K. Using a tunable dye laser, the wavelength region around the first exciton absorption peak near 3.2 eV was investigated. Analysis of the data shows an *electronic* resonance behavior for $|d|$ which is fitted with a theoretical expression obtained from nonlinear exciton theory. Previously Faust and Henry[1] have reported a resonance behavior for $|d|$ in GaP near the infrared *lattice* resonance.

For the tunable dye laser, naphthalene green V in glycerin was used, pumped by a Q-switched ruby laser. Tuning was achieved with an 1800-line/mm grating as one cavity reflector. Resolution of better than $\frac{1}{2}$ Å was obtained with a telescope mounted inside the dye laser cavity which allowed illumination of the entire grating surface. Light from the dye laser (10-nsec pulses, 500 KW peak power) was focused into a CuCl sample mounted in a conduction He cryostat. The sample was oriented with the [111] direction approximately along the direction of light propagation. Second-harmonic light was detected by a monochromator-photomultiplier system, the transmission characteristics of which were calibrated using a standard lamp. The dye laser pulses were sent through a beam splitter, and second harmonic light was simultaneously collected from an ammonium dihydrogen phosphate (ADP) sample for comparison with the SHG in CuCl. The ADP sample was at room temperature and in a non-phase-matched orientation. SHG in the ADP sample showed no significant variation in efficiency in the wavelength region investigated.

Figure 1 shows the second-harmonic power from CuCl at about 20°K relative to SHG in ADP, as a function of the second-harmonic wavelength. These data are used, along with n and α, in Eq. (1) to obtain the magnitude of the nonlinear susceptibility d. Equation (1) is valid since $\alpha l_s \gtrsim 10^2$ in our experiment over the entire region. The value of n at the fundamental wavelength is

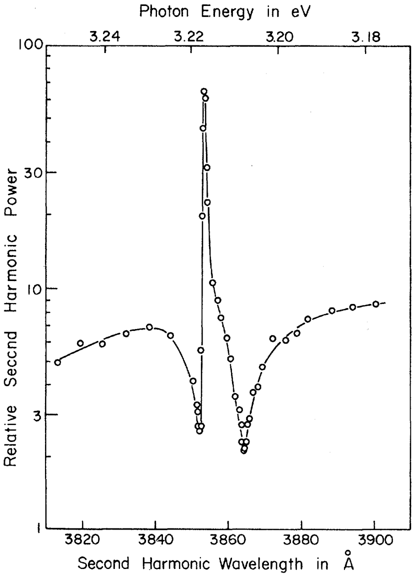

FIG. 1. Second-harmonic power from CuCl relative to ADP as a function of second-harmonic wavelength.

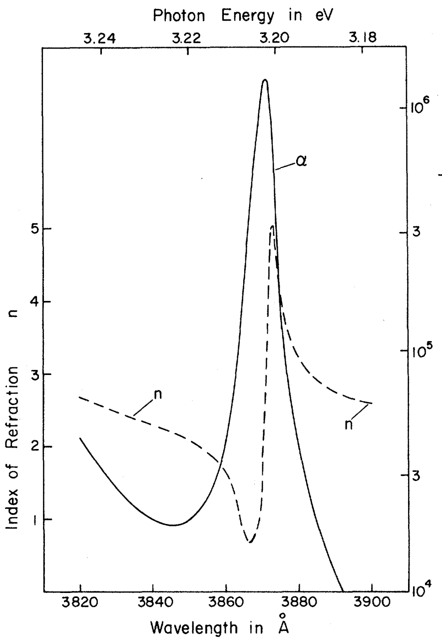

FIG. 2. Linear optical constants calculated from a Lorentz model fitted to Kramers-Kronig analysis of reflectivity by Staude.

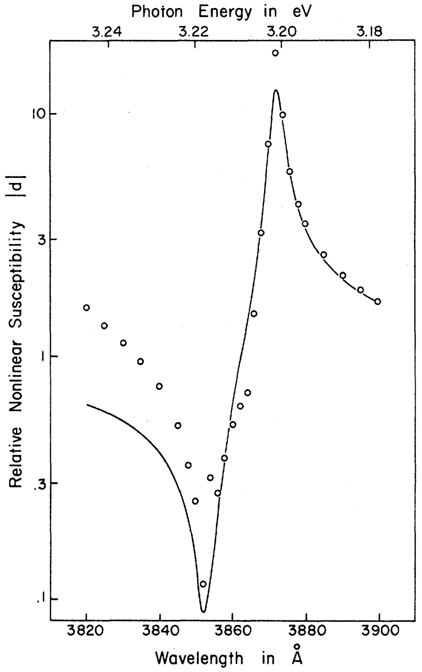

FIG. 3. Experimentally determined nonlinear optical susceptibility of CuCl at 20°K (circles) and the anharmonic oscillator model fit.

taken[2] as 1.95. However, there are difficulties in obtaining good values for the linear optical constants n and α at the second-harmonic wavelength, as demonstrated by the work of various authors[3,4] as well as our own failures in attempting to measure absorption in thin CuCl samples at low temperatures. The simplest approach is to use the Lorentz model of a classical oscillator, recognizing that in reality the exciton certainly is not a classical oscillator but a quasiparticle with some effective mass. However, using this simple model, a fit was made to a Kramers-Kronig analysis of reflectivity data by Staude.[5] These values for n and α were used in calculating $|d|$ and are plotted in Fig. 2. Finally, the result showing $|d|$ is given by the circles in Fig. 3. A reflectivity correction to the data of Fig. 1 is included in the calculation. The solid curve in Fig. 3 is a theoretical calculation of $|d|$ fitted to the experimental result. The model used is a simple anharmonic oscillator, where $|d|$ has the form[6]

$$|d| = \left[1 + \frac{A^2 + 2A(1-X^2)}{(1-X^2)^2 + \Gamma^2 X^2}\right]^{1/2},$$

$$X = \omega/\omega_0 = \lambda_0/\lambda.$$

The theoretical curve has been normalized to 1 at large frequencies. In Fig. 3, the parameters have the values $A = 0.010$, $\Gamma = 0.0008$,[7] and $\lambda_0 = 3872$ Å. The deviation of the experimental data at the short-wavelength end is most likely due to the second exciton absorption peak around 3770 Å which is expected to cause another resonance in $|d|$. For this reason the experimental data in that region were ignored in making the theoretical fit.

Although the above analysis appears to attain overall consistency, one might expect that the classical model of Lorentz oscillators would fail to describe, in finer details, the behavior of excitons. This suspicion is borne out by comparison with an additional experiment, which consisted of measuring the luminescence from the CuCl sample while the dye laser was tuned through the exciton band, just as done in the SHG measurements. Following absorption in the exciton band, CuCl emits luminescence into a broad band around 3950-4150 Å. Luminescence in this band was measured and a narrow ($\lesssim 0.8$ Å), strong peak was found for a second-harmonic excitation wavelength of 3864 Å. This result has been confirmed by direct two-photon absorption measurements.[8] However, from the classical oscillator model considered above, the luminescence should peak for second-harmonic excitation at 3871 Å, the peak in the one-photon absorption spectrum. We take this discrepancy as an indication of the failure of the classical model.

A better model would take into account the finite effective mass of the exciton, i.e., the effects of spatial dispersion.[8,9] This considerably complicates the problem in that with spatial dispersion, two waves with different damping can propagate in the crystal at the same frequency. Also, the improved model should allow the damping term Γ to be a function of wave vector since absorption of the mixed-state particle, a polariton, arises from scattering processes.[10,11] It is hoped that this more complete model will accurately describe both SHG and the nonlinear susceptibility as well as the luminescence results.

We wish to thank Professor Dietmar Fröhlich for providing CuCl samples and the unpublished reflectivity data of Staude as well as his helpful discussions. We would like to thank Dr. E. Schoenherr, for growing the crystal used in these experiments.

---

†Work supported by the U. S. Office of Naval Research under Contract No. NONR-401(47), Technical Report No. 36 and by the Advanced Research Projects Agency through the Materials Science Center at Cornell University, MSC Report No. 1513.

*National Science Foundation Graduate Fellow.

[1] W. L. Faust and C. H. Henry, Phys. Rev. Lett. 17, 1265 (1966); W. L. Faust, C. H. Henry, and R. H. Eick, Phys. Rev. 173, 781 (1968).

[2] A. Feldman and D. Horowitz, J. Opt. Soc. Amer. 59, 1406 (1969).

[3] R. Reiss and S. Nikitine, C. R. Acad. Sci. 250, 2862 (1960).

[4] J. Ringeissen, thesis, University of Strasbourg, 1967 (unpublished); C. Jung, J. Ringeissen, and S. Nikitine, Opt. Commun. 1, 25 (1969).

[5] W. Staude, Phys. Lett. 29A, 228 (1969). Data used for the Lorentz-model fit were the computer output of the Kramers-Kronig calculation done by Staude for zero magnetic field in his magnetoreflection study.

[6] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).

[7] The value of 0.0008 for Γ in the nonlinear susceptibility compares with 0.000 61 for the linear susceptibility, the value used to fit the Kramers-Kronig analysis of reflectivity by Staude.

[8] Private communication by Professor Dietmar Fröhlich, Frankfurt, Germany.

[9] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).

[10] V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Interscience, New York 1966).

[11] J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

[12] W. C. Tait and R. L. Weiher, Phys. Rev. 166, 769 (1968).

Splitting of the π Bands in Graphite

B. Feuerbacher and B. Fitton
Surface Physics Division, European Space Research Organisation, Noordwijk, Holland

(Received 25 January 1971)

The splitting of the π bands in graphite due to multilayer interaction has been observed directly for the first time for the valence-band states at P and Q on the vertical face of the Brillouin zone, using photoemission techniques. The splitting is found to be 0.8 ± 0.1 eV for both P and Q, giving a value of 0.42 eV for the parameter γ_1, in agreement with other experiments.

The splitting of the π bands in graphite due to multiple-layer interaction has been thoroughly investigated both theoretically[1] and experimentally[2] along the vertical edge of the Brillouin zone. Recently three-dimensional band-structure calculations have been performed for the vertical face of the Brillouin zone by Greenaway *et al.*[3] and by Doni and Pastori Parravicini,[4] using an experimentally adjusted tight-binding scheme. These authors showed that the order of even and odd states at Q and Γ (using the notation of Refs. 3 and 4) is reversed in the valence and conduction bands. Selection rules[5] allow transitions only between even and odd states at Q. The energy difference for the two allowed π-π optical transitions at Q is of the order of 0.1 eV, although the splitting of the bands is predicted to be 0.3 to 0.4 eV. Because of this small difference in the optical transition energies, a doublet structure at 4.8 eV is not observed in the optical experiments of Taft and Philipp,[6] Ergun and McCartney,[7] and Greenaway *et al.*[3] This inversion of the order of states was also found by Painter and Ellis[8] in an *ab initio* variational band-structure calculation. The pseudopotential calculation by van Haeringen and Junginger[9] yielded values which are too low for the transition energy at Q. A theoretical determination of the dielectric function calculated