

Interference of third-order light mixing and second-harmonic exciton generation in CuCl[†]

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The generation of the combination frequency $2\omega_1 - \omega_2$ in CuCl by two incident waves, at frequencies ω_1 and ω_2 , respectively, is measured as a function of ω_1 . When $2\omega_1$ equals the frequency of the first longitudinal-exciton resonance, a resonant dispersive behavior in the production of the intensity at $2\omega_1 - \omega_2$ is observed.

A general theory^{1,2} has recently been developed for the interference of nonresonant third-order light mixing, generating the combination frequency $\omega_3 = 2\omega_1 - \omega_2$, and two step generation via intermediate excitations at $\omega_1 - \omega_2$ and/or $2\omega_1$. Dispersive characteristics in the generation of ω_3 , while ω_3 and the incident frequencies ω_1 and ω_2 all lie in an optically transparent region, are well known³⁻⁶ when the difference frequency corresponds to a Raman-active vibrational or polariton resonance. In this note the dispersive characteristics in the generation of $\omega_3 = 2\omega_1 - \omega_2$ in CuCl are reported when the frequency $2\omega_1$ passes through the resonance of a longitudinal-exciton branch. An earlier attempt by us to observe this excitation by means of second-harmonic generation in a reflection geometry had failed. The poor physical condition of the crystal surface and the concomitant boundary effects on the exciton resonance were probably responsible.⁷ The technique presented in this paper observes the exciton in the interior bulk of the crystal and so difficulties with the condition of the crystal surface are eliminated. In addition this method also eliminates interference from rapid changes in coherence length due to the resonant behavior of the refractive index near the exciton energy that has affected previous second-harmonic generation in transmission studies.⁸ Our experimental procedure also has an advantage over two photon-absorption spectroscopy^{9,10} because the interference term in the nonlinear process observed by us permits the calibration of the exciton response in terms of the nonresonant nonlinear susceptibility $\chi_{nr}^{(3)}$.

The experimental arrangement is similar to that described by Levenson.⁵ Light from a passively Q-switched ruby laser with approximately 0.5 J per pulse was split into two beams. One beam provided a wave at the constant ruby frequency, ω_2 . The remaining beam longitudinally pumped a tunable dye laser; 3, 3'-diethyl-10-chloro 2, 2-(4, 5, 4', 5'-dibenzo) thiadiazocyanine iodine dissolved in dimethyl sulfoxide was used as the dye solution.¹¹ An etalon-type resonant reflector and a gold-coated grating with 1200

grooves/mm used in its second order in a Littrow configuration gave a measured dye-laser output linewidth of 0.3 Å over a wavelength range from 7690 to 7760 Å. This dye laser provided the tunable frequency at ω_1 .

The beams from the dye and ruby laser were focused with 40-cm-focal-length lenses to overlap inside a NaCl reference crystal and a CuCl sample crystal cooled to 15 °K. An exterior angle of 2° between the dye and ruby beams was chosen so that the coherence length for signals at ω_3 was always much greater than the thickness of the NaCl crystal. Since NaCl is transparent at ω_1 , ω_2 , $2\omega_1$, $\omega_1 - \omega_2$, and ω_3 this gave a reference signal at ω_3 proportional only to $(I_1)^2 I_2$, where I_i is the intensity of the beam at ω_i . The same exterior angle produced a coherence length l_c of about 10^{-2} cm in CuCl. Since CuCl is transparent at ω_1 , ω_2 , and ω_3 and the index of refraction is accurately known,¹ $l_c(\omega_3)$ could be calculated. The results of nonresonant generation in a geometry where excitonic-resonance effects were negligible showed a linear change of $l_c(\omega_3)$ of 30% over the range of frequency variation of ω_1 .

The coherent light rays at ω_3 emitted from the crystals passed through 870-nm spike filters and spectrometers tuned to ω_3 before being detected by RCA C31025 J photomultipliers. Their output pulses were integrated and photographed on a dual-beam oscilloscope. Calibrated filters placed in front of the photomultipliers insured that they were operated in the linear-response region. The nonresonant signal at ω_3 in the non-phase-matched CuCl corresponded to about 10^3 photons/pulse.

The total contribution to the three-wave mixing signal at ω_3 can be obtained by carrying out to third order the solution of the following three equations^{1,2}: the equation of motion of the effective exciton coordinate Q ,

$$(\ddot{Q} + \Gamma \dot{Q} + \omega_T^2 Q) = (e^*/M) E + \frac{1}{2} \beta_{eT} EE;$$

the definition of the electric polarization,

$$P = Ne^*Q + \chi^{(1)} E + N M \beta_{eT} EQ + \chi^{(2)} EE + \chi^{(3)} EEE;$$

and Maxwell's equation,

$$\nabla^2 E - \nabla(\nabla \cdot E) - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P}{\partial t^2},$$

where the vector subscripts have been suppressed; $M\beta_{eT}$ is the derivative of the transverse-exciton polarizability with respect to the normal coordinate Q , M is the reduced exciton mass, Γ is the damping rate, N is the atomic density, e^* is the effective charge, and $\chi^{(i)}$ is the i th-order susceptibility due to all transitions except those caused by the resonant exciton. Spatial dispersion of the exciton can be ignored because of its rather large total mass.^{13,14} The observed intensity at ω_3 is proportional to $|\chi_{\text{eff}}^{(3)}|^2$. General expressions for the effective coupling constant $\chi_{\text{eff}}^{(3)}$ have been given elsewhere,^{1,2} as derived from the third-order approximation to the equations for Q , P , and E .

Figure 1(a) shows one special geometry of interest in our experiments in CuCl which has $43m$ symmetry. For this geometry both light beams have their electric field vectors along the $[110]$

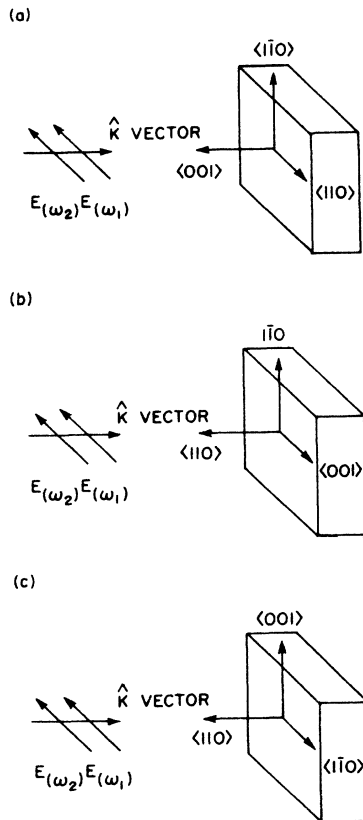


FIG. 1. Relative configuration of the crystal axes with respect to the incident-laser-propagation directions and polarizations. Three different experimental geometries are shown. In the actual experiment the laser beams are not collinear, but make an angle of about 2° in order to achieve long coherence lengths.

axis, while they propagate nearly parallel to the $[001]$ axis. In this case only the longitudinal exciton can be excited. The effective coupling coefficient for the generation of ω_3 may be written in the form

$$\chi_{\text{eff}}^{(3)} = \chi_{\text{nr}} + \frac{2NM(\beta_{eL})^2}{\omega_{eL}^2 - (2\omega_1)^2 - i2\omega_1\Gamma}. \quad (1)$$

The first term represents a nonresonant contribution; the last term is the contribution of the resonant two-step process.

First the wave at ω_1 creates a longitudinal-exciton field at $2\omega_1$ which in turn, beats with the wave at ω_2 to create a polarization at ω_3 . The longitudinal-exciton frequency is denoted by ω_{eL} , and β_{eL} is related to the coefficient β_{eT} by

$$\beta_{eL} = \beta_{eT} - 8\pi e^* \chi_{xyz}^{(2)} / M\epsilon_\infty. \quad (2)$$

Here ϵ_∞ is the dielectric constant in the uv without the excitonic contribution. Some terms in Eqs. (1) and (2) differ by a factor of 2 from corresponding terms in Ref. 1, because our resonance at $2\omega_1$ does not permit a permutation of frequencies, as occurs for a resonance at $\omega_1 - \omega_2$.

It must be pointed out that Eqs. (1) and (2), which are based on Refs. 1 and 2, do not take into account a local-field correction factor which was recently obtained by Bedeaux and Bloembergen.¹⁵ Their Eqs. (3.21) and (3.22) show the correct relation between $\chi_{\text{eff}}^{(3)}$ and $(\chi^{(2)})^2$. For longitudinal excitation the propagator F_ϵ in these equations should be taken as $4\pi\epsilon^{-1}(2\omega)$. If both the local field acting on the excitons and the local field acting on the nonresonant valence electrons are taken as Lorentz local fields at points with cubic symmetry, then the last term in our Eq. (1) would need a correction factor $1 + \epsilon(2\omega)/4\pi[\epsilon(2\omega) + 2]$. If both the exciton orbits and the valence-electron orbitals are spread out uniformly over the unit cell, the appropriate correction factor would be $1 + \epsilon(2\omega)/12\pi$. In reality, the correction factors may be expected to lie somewhere between these expressions. Fortunately, these corrections are relatively modest even for the large variations in $\epsilon(2\omega)$ occurring near the exciton resonance. In the following evaluation of the experimental results, the correction factor has rather arbitrarily been taken as unity. It is estimated that the systematic error introduced by this procedure is less than 25%.

The experimental results for the geometry of Fig. 1(a), exhibiting the longitudinal exciton resonance, are shown in Fig. 2. The solid curve is a theoretical best fit using Eq. (1) in which an additional background term has been added to the intensity. This term is probably due to scattering inside the crystal. The deviation in the data from

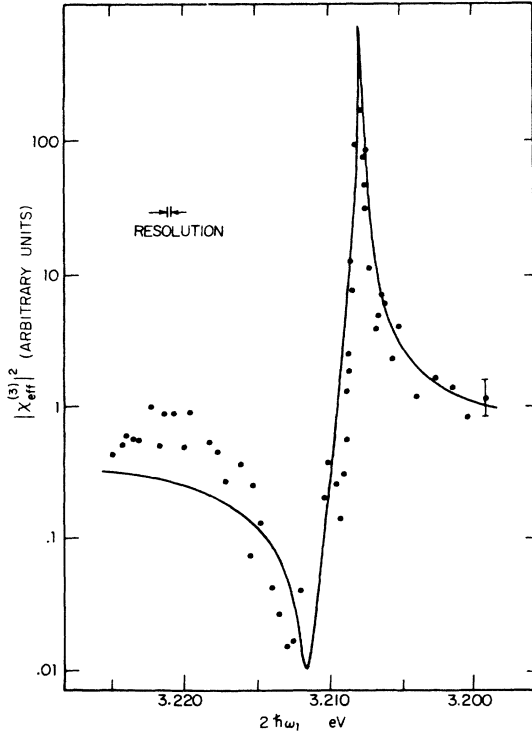


FIG. 2. The dispersion of $|\chi_{\text{eff}}^{(3)}|^2$ in CuCl at 15°K for the orientation of Fig. 1a. The intensity of the light generated at $2\omega_1 - \omega_2$ is plotted as the frequency ω_1 is varied, while ω_2 is the fixed ruby-laser frequency. A resonance occurs when $2\omega_1$ is tuned past the longitudinal exciton frequency.

the fitted curve at higher energies may be the result of interference from the next-higher-lying exciton at 3.29 eV which was not included in this simple theory.

The data can be fitted by Eq. (1) with the following values: $\hbar\omega_{eL} = 3.2077 \pm 0.0003$ eV; $\hbar\Gamma \leq 2 \times 10^{-4}$ eV; and $2NM\beta_{eL}^2 \hbar^2 / \chi_{nr} = 0.024 \pm 0.001$ eV². The value of χ_{nr} was calibrated in terms of the value of $\chi_{xxxx}^{(3)}$ in diamond,⁵ by replacing the CuCl sample in the cryostat with a diamond. The result of this determination, when the experimental value $M = 0.406m_e$ ¹⁴ is used and the frequency dispersion of the nonlinearity in diamond is ignored, yields

$$\chi_{nr} = (30 \pm 13)\chi_{xxxx}^{(3)}(\text{diamond}) = (3.3 \pm 2.0) \times 10^{-12} \text{ cm}^3/\text{erg}.$$

This gives

$$|\beta_{eL}| = (1.8 \pm 0.5) \times 10^{11} \text{ cm}^4/\text{erg sec}^2.$$

Miller *et al.*¹⁶ have shown that $\chi_{xyz}^{(2)}$ is negative. The data of Mahr⁸ show, furthermore, that β_{eT} must have the same sign as $\chi_{xyz}^{(2)}$. In Eq. (2) $e^* = -0.07|e|$ is also a negative quantity. Consistency can only be obtained, if we choose $\beta_{eL} < 0$. With

this choice and with^{16,17} $\chi_{xyz}^{(2)} = -6 \times 10^{-6} (\text{cm}^3/\text{erg})^{1/2}$, Eq. (2) yields $\beta_{eT} = -(1.4 \pm 0.7) \times 10^{11} \text{ cm}^4/\text{erg sec}^2$. This method probably determines the exciton damping and nonlinear coupling coefficients more precisely than the second-harmonic-generation (SHG) experiments^{8,18} which depend critically on linear-refraction data. The value of Γ is to be considered an upper limit set by the present width of the dye laser. Experiments to measure this quantity more precisely as a function of temperature are in progress. The value of $\hbar\omega_{eL}$ agrees closely with previous data from two-photon absorption experiments.^{9,13} Although the coupling coefficient β_{eL} also describes two-photon absorption, the direct comparison of β_{eL} with $\chi_{nr}^{(3)}$ by our present method provides a more accurate determination of β_{eL} than could be obtained from two-photon absorption experiments.¹⁶ Unfortunately, the published data obtained in these experiments and those with the SHG method lack the necessary information about the intensity of the laser field or the specification of the geometry, so that no quantitative values of β_{eL} or β_{eT} can be extracted from them for a direct comparison with our data.

Fig. 1(b) shows an orientation with the electric fields aligned along a cubic axis of CuCl. In this geometry no two-step contributions occur, and $\chi_{nr} = 3\chi_{xxxx}^{(3)}$ (CuCl). In agreement with this prediction neither a longitudinal- nor a transverse-exciton resonance was observed experimentally. The observed nonresonant signal is consistent with a value $\chi_{xxxx}^{(3)}$ (CuCl) = $(5 \pm 2.5)\chi_{xxxx}^{(3)}$ (diamond), and a nonresonant anisotropy ratio $\chi_{xyy}^{(3)}$ (CuCl)/ $\chi_{xxxx}^{(3)}$ (CuCl) = 0.4 ± 0.2 .

Fig. 1(c) shows a configuration in which only the transverse exciton could be excited. Experimentally, no resonance peak was seen. The reason is that the two-step transverse exciton contribution to $\chi_{\text{eff}}^{(3)}$ in this orientation is proportional to

$$[\epsilon(2\omega_1) - \epsilon(\omega_1)]^{-1} [\omega_{eT}^2 - (2\omega_1)^2 - 2i\omega_1\Gamma]^{-1}$$

where ω_{eT} is the transverse-exciton frequency and $\epsilon(\omega)$ is the dielectric constant at the frequency ω . Therefore, the minimum in the resonant denominator for $2\omega_1 = \omega_{eT}$ is largely compensated by the maximum in $\epsilon(\omega_{eT})$. What happens is that the phase matching between the wave at ω_1 and its second harmonic is weak when the driving force due to the transverse exciton for the production of the second-harmonic wave is strong. The compensation of the two effects in the configuration used in this experiment was nearly complete. It should nevertheless be possible to observe the transverse-exciton resonance by choosing different directions for the two incident waves at ω_1 and for the one wave at ω_2 . This would eliminate the large nonresonant back-

ground term in the orientation of Fig. 1(c) which obscured the small transverse-exciton resonant peak.

While this note has been limited to the case of a single beam at ω_1 , the theory is easily extended to the case where two beams at ω_1 intersect at a nonzero angle. By varying this angle it should be possible to study the line shape of the excitonic polariton at various points on its dispersion curve.

It is concluded that third-order light mixing is a useful technique to study excitons in noncentrosymmetric crystals. It augments the information obtainable from SHG and two-photon-absorption measurements.

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