Spatial dispersion of two-photon absorption

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The feasibility of observing angular dispersion of two-photon absorption in the exciton region of a CdS crystal is discussed. A formula (7) is derived, which expresses the two-photon absorption coefficient β in terms of quadratic polarizability χ and polariton mean free path α^{-1}. An estimate of β yielded the value 0.2 cm/GW. A plot is presented of the expected dependence of the maximal absorption coefficient ω_1 on the angle θ between the wave vector of the signal $\mathbf{k}_1$ and the pumping wave vector $\mathbf{k}_2$. It follows from the plot that $\omega_1/2\pi c$ changes by approximately 15 cm^{-1} when θ changes from 0 to 180°.

Recently, Fröhlich et al.[1] demonstrated a new method of measuring the dielectric constant $\epsilon(\omega)$ of non-centrally-symmetric crystals in the exciton region of the spectrum. This method is based on the observation of the additional absorption experienced by light of frequency ω_1 and wave vector $\mathbf{k}_1$ (signal) in the presence of the intense pumping wave ω_2, $\mathbf{k}_2$. The frequencies ω_1 and ω_2 are chosen such that the summary frequency $\omega = \omega_1 + \omega_2$ lies in the exciton region of the spectrum. This induced (two-photon) absorption depends on the angle θ between $\mathbf{k}_1$ and $\mathbf{k}_2$ according to the principle of spatial synchronism

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}, \tag{1}$$

where $\mathbf{k}$ is the wave vector of the polariton (light exciton) with frequency ω. By recording the frequency-angle relation $\theta(\omega_1)$ we can calculate the dispersion $k(\omega)$ (and $\epsilon(\omega)$) in the region of the upper polariton branch of the exciton resonance. The measured dispersion relations $\mathbf{k}(\omega)$ or $\epsilon(\omega)$ can be further connected with the properties of the excitons.

A similar method, described by Hauisen and Mahr[2], is based on the observation of the light of frequency ω emitted by the crystal. Note that the relation $k = \omega \operatorname{Re}\sqrt{\epsilon}/c$, which defines the proper polariton wavelength, does hold in general (cf. the analogous situation in the interpretation of experiments on light scattering by ionic polaritons[3,4]). Here, however, we are considering the case $\epsilon'' \ll \epsilon'$, where it is possible to use that relation.

This paper gives a phenomenological description of two-photon absorption in terms of the nonlinear polarizability of the crystal (a description of many-photon resonance processes in molecular crystals which does not employ Maxwell's macroscopie equations was developed by Ovander and Agranovich in[5]). This description yields a rough estimate of the absorption for CdS crystals on the basis of experiments[6,7] on doubling of the light frequency. We present also a plot of the expected $\omega_1(\theta)$ dependence calculated with the help of Eq. (1) and the published parameters of the exciton lines in CdS.

1. We estimate the two-photon absorption coefficient within the framework of the following one-dimensional model. Let the sample be a plane-parallel infinite layer, while the signal and pump are plane monochromatic waves with real wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ and intensities S_1 and S_2. We define β_{12} by the following equation

$$|\cos\vartheta_1|\frac{dS_1}{dz} = -(\alpha_1 + \beta_{12}S_2)S_1 \equiv -\tilde{\alpha}_1 S_1, \tag{2}$$

where α_1 is the linear absorption coefficient and ϑ_1 is the angle between $\mathbf{k}_1$ and the normal to the layer. The pump intensity S_2 is assumed to be constant.

We express $\tilde{\alpha}_1$ in terms of the phenomenological polarizabilities determined by expanding the polarization of the sample in powers of the macrofield[8]:

$$P = \frac{\varepsilon - 1}{4\pi}E + \hat{\chi}E^2 + \hat{\eta}E^3, \tag{3}$$

where $\hat{\chi}$ and $\hat{\eta}$ are the quadratic and cubic polarizability tensors, respectively. Usually[8] only $\hat{\eta}$ is used to describe two-photon absorption, but for non-centrally-symmetric crystals $\hat{\chi}$ must be taken into account as well. Substituting (3) in Maxwell's macroscopic equations for an infinite homogeneous medium one can determine without difficulty the correction $\Delta\hat{\epsilon}_1$ to $\hat{\epsilon}_1$, which is due to the pump field (note that an analogous expression describes the spontaneous and stimulated scattering by ionic polaritons[4]):

$$\Delta\hat{\varepsilon}(\omega_1, \mathbf{k}_1) = \left(4\pi\hat{\tilde{\eta}} + \frac{16\pi^2\hat{\chi}^2}{n^2\cos^2\rho - \tilde{\varepsilon}}\right)E_2^2, \tag{4}$$

$$n \equiv |\mathbf{k}_1 + \mathbf{k}_2|c/\omega. \tag{5}$$

It is assumed that the crystal is not transparent at the polariton frequency ω. Here ρ is the anisotropy angle and $\tilde{\epsilon}$, $\hat{\tilde{\chi}}$, and $\hat{\tilde{\eta}}$ are the contractions of the tensors from (3) with the corresponding polarization unit vectors, which are considered real.

We restrict ourselves to the frequency region in which $\epsilon'' \ll \epsilon'$. In this region the first term in (4) may be neglected; the second term, however, has a resonant character, and $\Delta\epsilon_1$ increases sharply when conditions (1) and (5) are fulfilled simultaneously. In this way, stimulated (two-photon) absorption in piezocrystals has spatial dispersion even if the polarizabilities $\epsilon - 1$, χ, and η are independent of $\mathbf{k}$. This circumstance is well known in the case when ω is in the transparency band, and then the stimulated absorption is due to the loss to the synchronous generation at the summary frequency. In the extreme opposite case, where ω lies in the intrinsic absorption band, the synchronism (1) is impossible ($\mathbf{k} \gg \mathbf{k}_1 + \mathbf{k}_2$) and ordinary interband two-photon absorption independent of $\mathbf{k}_1$ and $\mathbf{k}_2$ is observed.

Thus, at synchronism the induced dielectric constant is, according to (4) and (5),

$$\Delta\hat{\varepsilon}_1 = 16i\pi^2\hat{\tilde{\chi}}^2 E_2/\varepsilon'', \tag{6}$$

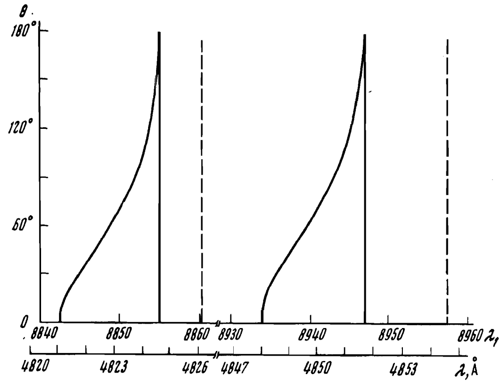
where ϵ'' can be expressed in terms of the polariton mean free path α^{-1} ($\epsilon'' = \alpha nc \cos\rho/\omega$) or in terms of the induced-absorption width $\Delta\omega$ and the group velocity of the polariton u($a \approx \Delta\omega/u$ when $u \ll u_1$), from which it follows that

$$\beta_{12}=\frac{(2\pi)^3\omega\omega_1\chi_{\mathrm{eff}}^2}{c^3nn_1n_2\cos\rho\cos\rho_1\cos\rho_2}\frac{4}{\alpha}\approx\frac{128\pi^4\nu_1^2}{c^2n_1^2}\frac{u\chi_{\mathrm{eff}}^2}{n\Delta\nu},$$
$$\chi_{\mathrm{eff}}=\hat{\chi}ee_1e_2,\quad \nu_1\equiv\omega_1/2\pi c\approx\nu/2. \tag{7}$$

Formula (7) with $n\alpha\cos\rho$ substituted for $\omega_l\epsilon''(\omega_l)/c$ determines the coefficient of the two-photon absorption due to purely longitudinal excitons of frequency ω_l.

Let us estimate β_{12} for a CdS crystal. Substituting in (7) $\chi_{\mathrm{eff}} = 10^{-7}$ abs. units (with $\nu_1 = \nu_2 = 1/1.06\ \mu$)[6,7,9], $\Delta\nu = 4\ \mathrm{cm}^{-1}$[10], c/u = 500, and n = 2 (for $\theta = 0$), we get $\beta_{12} = 0.2$ cm/GW, which is two orders of magnitude less than the analogous quantity for interband two-photon absorption[11]. This estimate does not take into account nonlinear-polarizability dispersion and is in all probability rather low (at certain frequencies, however, it is possible to have mutual cancellation of the resonance and "background" nonlinearities, an effect which has been observed in polariton-scattering spectra[4].

2. We consider now the $\omega_1(\theta)$ dependence determined by the synchronism condition for a CdS crystal of hexagonal modification. Its birefringence in the transparency region is negligible, and synchronism is possible only in the upper polariton branches (as in the case of cubic CuCl crystals[1,2]). Let the pump be a neodymium laser ($\nu_2 = 0.943\ \mu^{-1}$), and let the signal be extraordinary but the pumping and polariton ordinary (then we have both types of exciton—A and B). To determine n we employ the equation of Thomas and Hopfield[12], adding terms corresponding to the exciton resonances. The results obtained by solving (1) for $\lambda_1(\theta)$, using data from[12] for the refractive index in the visible region, are shown in the figure.



Predicted angle-frequency spectra of two-photon absorption by excitons in CdS. The ordinates are the angles between the pump and signal beams inside the crystal, while the abscissas are the signal and optical-exciton wavelengths. The solid vertical lines correspond to "longitudinal" exciton frequencies ($\epsilon = 0$) and the dashed lines correspond to "transverse" exciton frequencies ($\epsilon = \infty$).

In conclusion, we are confident that the effect in question will find extensive use in the investigation of the properties of electronic excitons in piezocrystals with small values of **k** (e.g., to observe the effects of spatial dispersion[3]), in analogy with the use of polariton scattering to study lattice-vibration spectra.

Note added in proof (November 21, 1972). We have recently become acquainted with the material in [13,14]. β was calculated by Bogget and Loudon using a simple two-oscillator model. Pradere and Mysyrovicz measured directly the two-photon absorption coefficient for CdS, equal to 0.7 cm/GW for A-excitons. Calculation of β with formula (7) under the experimental value can be traced to the neglect of the dispersion of χ in the calculations.

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