THE INFLUENCE OF EXCITON CONCENTRATIONS ON THE DIELECTRIC PROPERTIES OF MOLECULAR CRYSTALS

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The refraction and absorption properties of molecular crystals for low as well as for high exciton concentrations were analysed in the present paper. It was shown that high exciton concentrations cause high absorption in long-wave range while in short-wave range they lead to high transparency of the crystal.

I. INTRODUCTION

The object of this paper are the investigations of dielectric properties of molecular crystals at low as well as at high concentrations of excitons. Such analyses are very complicated mathematically, lengthy and time consuming. Fortunately, there exist three papers [1—3] where the problems of low as well as high concentrations were analysed with all necessary details. The methodologies of these papers will be used here without quoting the details since the reader can find them in the mentioned papers.

Using the mentioned procedures we shall demonstrate here that the increase of exciton concentration drastically changes the refraction index and absorption coefficient of molecular crystals.

1. Low Exciton Concentrations

In this Section we shall follow the methodology of paper [1]. The dielectric permeability tensor will be analysed in the isotropic approximation. The spatial dispersion will be neglected. In this case the general formula from [4] reduces to the following one:

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$$\varepsilon^{-1}(\omega) = 1 + S \sum_i \frac{2\pi}{i}[\Gamma(\omega) + \Gamma(-\omega)]; \quad S = \frac{\tau_0 E_0^2}{8\pi\hbar}. \quad (1.1)$$

In this formula ε is the dielectric constant, τ_0 is the elementary cell volume in a simple lattice, E_0 is electrical field per elementary cell and $\Gamma(\omega)$ is the Fourier component of Green's exciton function

$$\Gamma_{nm}(t) = \langle\langle P_n(t)|P_m^+(0)\rangle\rangle, \quad (1.2)$$

with neglected dependence on the wave vector k. In the formula (1.2) $P_n(t)$ are the Pauli operators annihilating excitons. It means that the two-level exciton scheme is considered here.

The Hamiltonian of the system is given by [5, 6]:

$$H = \Delta \sum_n P_n^+ P_n + \sum_{n,m} X_{nm} P_n^+ P_m + \sum_{n,m} Y_{nm} P_n^+ P_n P_m^+ P_{m'} \quad (1.3)$$

In this expression for H, the excitation energy of an isolated molecule is denoted by Δ, while X and Y represent the matrix elements of dipole–dipole interaction.

The higher order Green's functions of a type $\langle\langle P^+PP|P^+\rangle\rangle$ appear in the equation for the Green's function $\langle\langle P|P^+\rangle\rangle$. Following the approach from [1] we substitute in the higher order Green's functions Pauli operators by Bose operator forms (see [7]):

$$P \approx B - B^+BB. \quad (1.4)$$

In the decoupling procedure the terms proportional to exciton concentrations are neglected, so that this procedure schematically can be expressed as follows:

$$\langle\langle P_a^+P_bP_c|P_d^+\rangle\rangle \approx \langle\langle B_a^+B_bB_c|B_d^+\rangle\rangle$$
$$\approx -2\langle\langle B_a^+|B_d\rangle\rangle\langle\langle B_b|B_d^+\rangle\rangle - \langle\langle B_a^+B_bB_c|B_d^+B_dB_d\rangle\rangle \approx . \quad (1.5)$$

Using the mentioned approximations in finding Γ and formula (1.1) we obtain the expression for $\varepsilon(\omega)$. The refraction index n_1 and absorption coefficient K_1 are connected with ε by the well-known relation $n + i K = \varepsilon^{1/2}$. We quote here the final expressions for n and K, only. These expressions are:

$$n_1(\xi) = \frac{1}{\sqrt{2}}\left[\frac{\sqrt{p^2(\xi) + q^2(\xi)} + p(\xi)}{p^2(\xi) + q^2(\xi)}\right]^{1/2};$$

$$K_1(\xi) = \frac{1}{2}\left[\frac{\sqrt{p^2(\xi) + q^2(\xi)} - p(\xi)}{p^2(\xi) + q^2(\xi)}\right]^{1/2};$$

$$p(\xi) = 1 + \frac{2\gamma_0}{\xi^2 - 1}; \quad q(\xi) = \frac{\gamma_0}{\xi - 1}\frac{3\pi}{32}\left(1 - \frac{\pi^2}{12}\right); \quad (1.6)$$

$$\gamma_0 = \frac{S}{\Omega_\Delta}, \quad \xi = \frac{\omega}{\Omega_\Delta}, \quad \Omega_\Delta = \frac{\Delta}{\hbar}.$$

It should be noticed here that in (1.6) the frequencies $\Omega_x = \frac{X}{\hbar}$ and $\Omega_y = Y/\hbar$ were neglected with respect to Ω_Δ because they are for two orders of magnitude less than Ω_Δ.

The result (1.6) for $\gamma_0 = 0.5$; 1 and 2 are graphically expressed in Fig. 1.
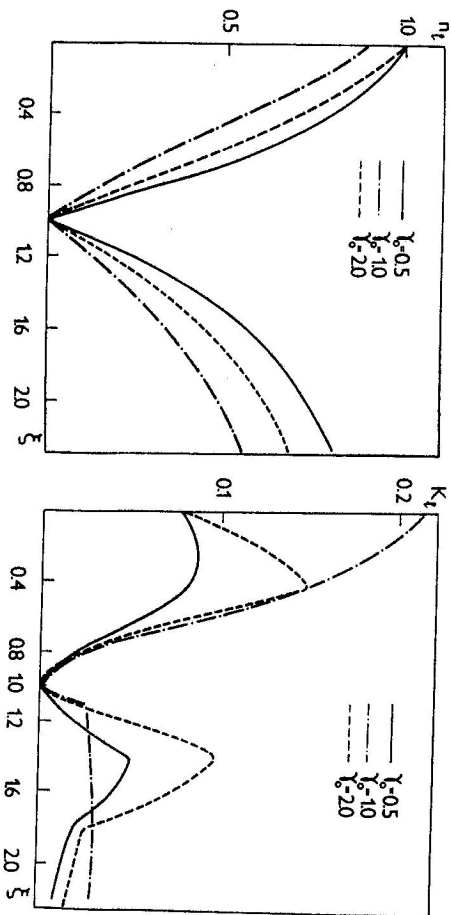
Fig. 1.

2. The high exciton concentration

The evaluation of the refraction index as well as the absorption coefficient at high exciton concentrations require an essentially new approach in the calculation of Green's function Γ. In this case the exact formulae from [7] have to be used, i.e. the Pauli operators are expressed in terms of the Bose operators in the following way:

$$\hat{P} = \hat{f}^{1/2}B; \quad P^+ = B^+\hat{f}^{1/2}, \quad \hat{f} = \sum_{v=0}^{\infty}\frac{(-2)^v}{(1+v)!}B^{+v}B^v. \quad (2.1)$$

The coefficients of the operator function $\hat{f}$ are very complicated so that the direct evaluation of Green's function $\langle\langle P|P^+\rangle\rangle$ is practically impossible. Following the ideas from [3] we shall calculate the auxiliary Green's function of the form

$$L_{nm}(t) = \langle\langle\sqrt{1 + B_n^+(t)B_n(t)}\,P_n(t)|P_m^+(0)\sqrt{1 + B_m^+(0)B_m(0)}\rangle\rangle \quad (2.2)$$

where P and P^+ are given by (2.1). It turns out that the evaluation of this function is not so complicated as the evaluation of the function $\langle\langle P | P^+ \rangle\rangle$. For detailed explanation see [2, 3]. The function L contains all powers of exciton concentrations $\bar{n} = \langle B^+ B \rangle$ but not all possible products of the boson Green's functions. During the calculation of L all terms containing products of four etc. Green's functions are neglected. Such an approximation enables us to obtain the expression for L in a finite form (for details see [2, 3]).

The functions Γ and L can be described by the following relation:

$$\Gamma_{nm}(t) = (1 + 2\bar{n})^{-1} L_{nm}(t).$$ (2.3)

The relation is approximate but can be considered as satisfactory at high exciton concentrations.

The details of the calculations will not be quoted here because the reader can find them in [2, 3]. Here the expression for $\Gamma(\omega)$ will be given by the use of the exposed approach as follows:

$$\Gamma(\omega) = \frac{i}{2\pi}(1 + 2\bar{n})^{-5}\left[\frac{A(\bar{n}) - iB(\bar{n})}{\omega - \Omega_A}\right];$$

$$A(\bar{n}) = 1 + 4\bar{n} + 8\bar{n}^2 + 8\bar{n}^3 + 4\bar{n}^4 + \frac{1}{2}(1 + 2\bar{n})^{-2}$$ (2.4)

$$B^{-1}(\bar{n}) = \frac{64}{3\pi}(1 + 2\bar{n})^2.$$

Introducing (2.4) into (1.1) and calculating the refraction index n_h as well as the absorption coefficient K_h we obtain the following result:

$$n_h(\xi) = \frac{1}{\sqrt{2}}\left[\frac{\sqrt{P^2(\xi) + Q^2(\xi)} + P(\xi)}{P^2(\xi) + Q^2(\xi)}\right]^{1/2};$$

$$K_h(\xi) = \frac{1}{\sqrt{2}}\left[\frac{\sqrt{P^2(\xi) + Q^2(\xi)} - P(\xi)}{P^2(\xi) + Q^2(\xi)}\right]^{1/2};$$

$$Q(\xi) = \frac{\chi_0}{\xi^2 - 1}\frac{3\pi}{32(1 + 2\bar{n})};$$ (2.5)

$$P(\xi) = 1 + 2\frac{\chi_0}{\xi^2 - 1}\frac{A(\bar{n})}{[1 + 2\bar{n}]^5}.$$

Taking extremely high exciton concentrations for the values $\chi_0 = 0.5; 1$ and 2 (the same as in the previous Section) we obtain the following curves for n_h and K_h (see Fig. 2).
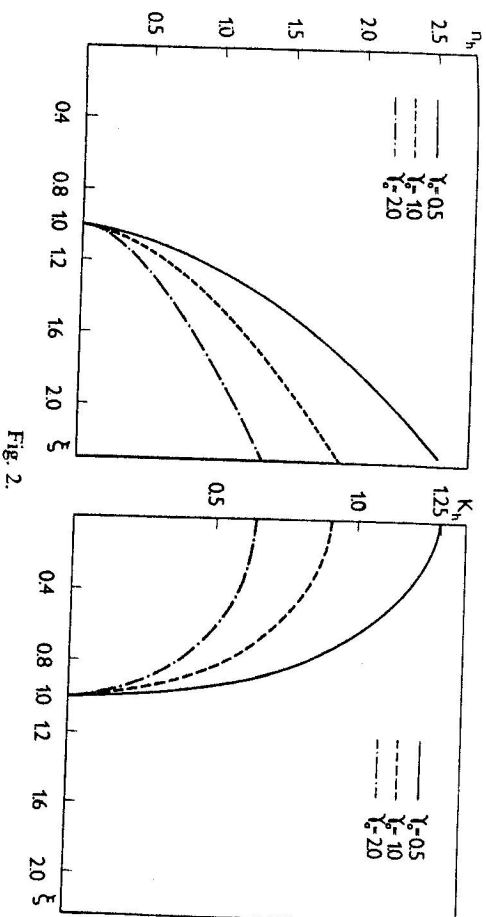
Fig. 2.

Comparing Fig. 1 with Fig. 2 we immediately conclude that the increase of exciton concentration drastically changes the refraction and the absorption properties of the exciton system.

It is seen from Fig. 2 that in the long wavelength region ($\omega < \Omega_A$) $n_h \approx 0$ since K_h has relatively high values. It means that all the electromagnetic energy is practically absorbed in this region. On the other hand for $\omega > \Omega_A$ the absorption coefficient is negligible while the refraction index has relatively high values. It means that in the short wave region the molecular crystal is practically transparent.

3. CONCLUSION

The results of this paper can be summarized as follows: a) At low exciton concentrations the absorption as well as the refraction phenomena are present for all wavelengths. It is interesting to note that the exciton-exciton interaction causes the appearance of a wide peak in the absorption coefficient in the long-wave region. b) At high concentrations the absorption phenomena are dominant in the long-wave region while the refraction is practically negligible. In the short-wave region absorption practically disappears and the molecular crystal becomes transparent for light beams.

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ВЛИЯНИЕ ПЛОТНОСТЕЙ ЭКСИТОНОВ НА ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА МОЛЕКУЛЯРНЫХ КРИСТАЛЛОВ

В работе приведен анализ свойств молекулярных кристаллов по отношению к преломлению и поглощению света для малых и больших плотностей экситонов. Показано, что большие плотности экситонов являются причиной интенсивного поглощения в длинноволновой области, в то время как в коротковолновой области большие плотности экситонов приводят к высокой прозрачности кристалла.