SOVIET PHYSICS JETP VOLUME 18, NUMBER 2 FEBRUARY, 1964

EXCITONS IN THIN CRYSTALS

A. S. DAVYDOV

Moscow State University

Submitted to JETP editor March 14, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **45**, 723-729 (September, 1963)

It is demonstrated that at low temperatures the intensity of interaction of light with exciton states of thin crystals is a nonmonotonic function of the crystal thickness. This nonmonotonic variation is due to the discrete values of the energy and wave vector of the exciton. An interpretation is presented of the experimental data of Brodin, who observed an oscillating thickness dependence of the absorption coefficient of light in an anthracene crystal.

1. INTRODUCTION

BRODIN[1,2] observed, in investigations of the absorption of light in thin anthracene-crystal films at 20°K, an oscillating dependence of the absorption and refraction coefficients on the film thickness at 25108 cm^{-1}. These results were interpreted[3] as proving the presence in the crystal exciton absorption region of additional light waves differing from the ordinary waves only in the refractive index. The interference of two waves of identical polarization on leaving the crystal can lead to an oscillating dependence of the intensity of the transmitted light on the thickness of the plate.

For a quantitative interpretation of Brodin's experiments it became necessary to assume[2-4] for the difference in the refractive indices of these waves a value $n_+ - n_- = 6.9$. In the experiment, the refractive index ranged from 4 to 7. If we assume that $n_- = 5$, then $n_+ = 11.9$. The additional waves (with the larger refractive index) should also have large absorption coefficients, in accordance with the calculations by the author[5] and with an independent calculation[6]. For the parameters corresponding to the anthracene crystal at the frequency indicated above, the absorption coefficient of the additional waves is one order of magnitude higher than that of the ordinary waves. If we exclude the unlikely assumption that the secondary waves have an amplitude much larger than the ordinary waves, then the second wave cannot leave the crystal under the conditions of Brodin's experiments. It is therefore difficult to attribute the experimentally observed oscillations to interference.

We present here a new interpretation of Brodin's experiments. This interpretation is based on the discreteness of the energy and the wave vector of the excitons in thin films of crystals. As a consequence of this discreteness, as will be shown below, the intensity of the interaction varies with variation of crystal thickness.

2. EXCITONS IN THIN CRYSTALS

Let us consider for simplicity a cubic crystal with lattice constant a, having one isotropic molecule per unit cell. The crystal is unbounded along the x and y axes and consists of N_3 molecular layers in the z direction. We investigate the possible values of the exciton-state energies of such a crystal, assuming that the molecules are rigidly fixed in the lattice sites, identified by the lattice vector $\mathbf{m} = \Sigma m_i \mathbf{a}_i$, where m_i are integers; $\mathbf{a}_i \cdot \mathbf{a}_j = \delta_{ij}$ $(i, j = 1, 2, 3)$.

The choice of the boundary conditions in the xy plane does not play an important role in films of large area. We can therefore assume cyclicity with large periods $N_1\mathbf{a}_1$ and $N_2\mathbf{a}_2$, where $N_1, N_2 \gg N_3$. The boundary conditions along the z axis reduce to the requirement that there be no molecules for values $m_3 \le 0$ and $m_3 \ge N_3 + 1$, for which we assume the wave functions of the crystal exciton states to vanish, too. The total number of molecules in the crystal is $N = N_1N_2N_3$.

Let $\Delta\epsilon$, φ_0, and φ_f be respectively the excitation energy and the actual wave functions of the ground and excited states of an isolated molecule. Then, in the Heitler-London approximation, the crystal excitation energy operator has in the second quantization representation (see, for example, [7]) the form

$$\Delta H = (\Delta\varepsilon + D)\sum_{\mathbf{m}} B^+_{\mathbf{m}} B_{\mathbf{m}} + \sum_{\mathbf{m},\,\mathbf{n}}{}' B^+_{\mathbf{m}} B_{\mathbf{n}} M_{\mathbf{mn}}, \tag{1}$$

where D is the difference in the energy of interaction of the excited and non-excited molecule with all the remaining molecules; $M_{\mathbf{mn}}$ is the matrix element for the transfer of excitation from molecule n to molecule m (see [8]); B^+_m and B_m are the operators for the creation and annihilation of excitations in the molecule m. These operators satisfy the commutation relations $B_m B^+_n - B^+_n B_m = \delta_{mn}$; the prime at the summation sign denotes that $m \neq n$.

The operator (1) is diagonalized by going from the operators B_m to new operators A(k) with the aid of the unitary transformation

$$B_m = \sum_k A(k)\, U_m(k), \tag{2}$$

where

$$U_m(k) = \sqrt{2/N}\, \sin(ak_3m_3) \exp\{i(k_1m_1 + k_2m_2)a\},$$

$$\sum_m U^*_m(k')\, U_m(k) = \delta_{kk'}.$$

U_m is a complete orthonormal system of functions satisfying the required boundary conditions at

$$k_i = 2\pi\nu_i/aN_i, \qquad -N_i/2 < \nu_i \leqslant N_i/2, \quad i = 1, 2, 3;$$

$$k_3 = \pi\nu_3/a(N_3 + 1), \qquad \nu_3 = 1, 2, \ldots, N_3. \tag{3}$$

The new operators A(k) satisfy the commutation relations

$$A(k)\, A^+(k') - A^+(k')\, A(k) = \delta_{kk'}.$$

$A^+(k)$ are the operators for the creation of exciton states with a wave vector k. The operators A(k) annihilate the corresponding exciton states.

Substituting (2) in (1) we obtain the operator for the crystal excitation energy

$$\Delta H = \sum_k \mathscr{E}(k)\, A^+(k)\, A(k); \tag{4}$$

$$\mathscr{E}(k) = \Delta\varepsilon + D + L(k),$$

$$L(k) = \sum_{m,n}{}' U_m(k)\, M_{mn} U^*_n(k). \tag{5}$$

The crystal excitation energy operator (4) is diagonal with respect to the exciton-state occupation-number operators $\hat{N}(k) = A^+(k)A(k)$. Its eigenfunctions are therefore $|\ldots N(k) \ldots\rangle$, where the quantum numbers $N(k) = 0, 1, 2, \ldots$ determine the number of exciton states. The states of the crystal with one excitation corresponding to a fixed k are characterized by the excitation energy (5). The aggregate of the excitations (5) corresponding to the values of the wave vector and satisfying conditions (3) comprises the exciton-state band. The excitation energy (5) assumes N_3 discrete values at fixed values of k_1 and k_2.

3. EXCITATION OF EXCITONS IN THIN CRYSTAL FILMS BY MEANS OF LIGHT

The interaction between a crystal and a transverse electromagnetic field of frequency ω is described in the dipole approximation by the operator

$$H_{\text{int}} = -\sum_m \mathbf{E}(m)\, \mathbf{d}(m) = we^{-i\omega t} + \text{comp. conj.} \tag{6}$$

where $\mathbf{E}(m)$ is the electric field intensity at the m-th site of the lattice and d(m) is the molecule dipole-moment operator. If $\mathbf{E}(m)$ corresponds to the external field of a plane electromagnetic wave perpendicularly incident on the surface of the crystal film, and if the thickness of the film is such ($N_3 > 100$) that the refractive index in the absorption coefficient can be regarded macroscopically, then we have inside the film, for weak absorption,

$$\mathbf{E}(m) = 2\mathbf{E}_0 \sin(aQm_3 - \omega t), \tag{7}$$

where $Q = \omega n/c$, ω is the frequency of the light, and n is the refractive index.

The interaction between the light and the crystal is a self-consistent problem. The light wave is determined by the values of the refractive index, which in turn depends on the interaction between the light wave and the crystal molecules. Owing to the linearity of Maxwell's equations and the linearity of the crystal polarizability relative to the electric field intensity, such a problem can be solved in two stages, by first calculating the crystal specific polarizability (or the polarization current density) due to the external light wave, and then using Maxwell's equations to reconcile the parameters of the light wave with the obtained specific polarization.

In the representation of the occupation numbers corresponding to the operator $B^+_m B_m$ the molecule dipole moment operator is of the form

$$\mathbf{d}(m) = \langle\varphi_f|e\mathbf{r}|\varphi_0\rangle\,(B^+_m + B_m). \tag{8}$$

Substituting this expression and (7) in (6) and using the canonical transformation (2) we obtain the value of w in the operator (6) in the representation of the occupation numbers of the exciton states:

$$w = \mathbf{E}_0 \langle\varphi_f|e\mathbf{r}|\varphi_0\rangle \sqrt{N/2} \sum_k (A^+(k) + A(k))\, \delta_{k_10}\delta_{k_20}\Delta(k_3 - Q), \tag{9}$$

$$\Delta(x - y) = \frac{\cos[{}^1\!/_2\, a(N_3 + 1)(x - y)]\, \sin[{}^1\!/_2\, aN_3(x - y)]}{N_3 \sin[{}^1\!/_2\, a(x - y)]}. \tag{10}$$

$\Delta(x - y)$ is equal to unity when $x = y$ and vanishes when $|x - y| = 2\pi/aN_3$. With further increase of $|x - y|$, the function (10) increases periodically and reaches values of the order of N_3^{-1}. As $N_3 \to \infty$ this function reduces to the Kronecker symbol δ_{xy}.

It follows from (9) that for a fixed frequency and wave-vector direction the light wave interacts only with the excitons characterized by values $k_1 = k_2 = 0$ and

$$k_3 \equiv \pi\nu_3/a\,(N_3+1) \approx Q = \omega n/c, \tag{11}$$

In the general case, owing to the discreteness of k_3, Eq. (11) is not satisfied for fixed values of N_3 and Q. For example, for radiation of frequency 25,000 cm^{-1} and $n = 4.5$, Eq. (11) is satisfied for $\nu_3 = 1$ only if the crystal thickness is $a(N_3+1) = L_0 = 0.044\,\mu$. When the thickness of the crystal deviates slightly[1] from this value, w decreases sharply, but when the thickness of the crystal reaches values that are a multiple of L_0, the value of w is again maximal. Indeed, if $a(N_3+1) = \nu_3 L_0$ ($\nu_3 = 2, 3, \ldots$), Eq. (11) is again satisfied. For large crystal thicknesses, the spacing between the neighboring discrete permissible values of k_3 increases, and (11) is satisfied in practice for any crystal thickness.

To investigate the volume properties of a crystal it is sufficient to know its complex polarizability. To determine the polarizability it is necessary to calculate the average value of the specific electric moment produced under the influence of the external wave.

If $|0\rangle$ is the wave function of the crystal without the excitons, then the wave function of the crystal in the presence of a wave (7), having a frequency close to the exciton-excitation frequency $\Omega(k_3) = \mathscr{E}(k_3)/\hbar$ is, in first order perturbation theory,

$$\psi = |0\rangle + \frac{1}{\hbar}\sum_{k_3}\frac{we^{-i\omega t}}{\Omega(k_3) - \omega - {}^1\!/_2\, i\gamma(k_3)}A^+(k_3)\,|0\rangle,$$

where $\hbar\gamma(k_3)$ characterizes the exciton-state width due to the interaction between the excitons and the vibrations of the molecules in the lattice. $\gamma(k_3)$ increases with temperature.

If v is the volume of the crystal unit cell, then the average value of the polarization vector per unit crystal volume in the state ψ, at the place occupied by the site **m**, is determined by the equation

$$\mathbf{P}(\mathbf{m}) = v^{-1}\langle\psi\,|\,\mathbf{d}(\mathbf{m})\,|\,\psi\rangle.$$

Substituting (8), (9), and (2) in this expression and separating the complex polarizability $\alpha(\omega)$, we obtain

$$\alpha(\omega) = \frac{\langle\varphi_f\,|\,e\mathbf{r}\,|\,\varphi_0\rangle^2}{\hbar v}\sum_{k_3}\frac{\Delta(k_3 - Q)}{\Omega(k_3) - \omega - {}^1\!/_2\, i\gamma(k_3)}.$$

If ϵ_0 is the dielectric constant due to all other electron states of the crystal, then it follows from Maxwell's equations that the refractive index and the absorption coefficient κ of a monochromatic wave of frequency ω are defined by $(n + i\kappa)^2 = \epsilon_0 + 4\pi\alpha(\omega)$, from which it follows that

$$n^2 = \tfrac{1}{2}\left\{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1\right\}, \qquad \varkappa^2 = \tfrac{1}{2}\left\{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1\right\},$$

where

$$\varepsilon_1 = \varepsilon_0 + \frac{4\pi\langle\varphi_f\,|\,e\mathbf{r}\,|\,\varphi_0\rangle^2}{\hbar v}\sum_{k_3}\frac{[\Omega(k_3) - \omega]\,\Delta(k_3 - Q)}{[\Omega(k_3) - \omega]^2 + {}^1\!/_4\gamma^2(k_3)},$$

$$\varepsilon_2 = \frac{2\pi\langle\varphi_f\,|\,e\mathbf{r}\,|\,\varphi_0\rangle^2}{\hbar v}\sum_{k_3}\frac{\gamma(k_3)\,\Delta(k_3 - Q)}{[\Omega(k_3) - \omega]^2 + {}^1\!/_4\gamma^2(k_3)}. \tag{12}$$

Let us assume that for some value $k_3^0 = (\pi\nu_3^0/a) \times (N_3+1)$ the following two equations are simultaneously satisfied:

$$\omega = \Omega(k_3^0), \qquad k_3^0 = \omega n/c. \tag{13}$$

Then only the terms $k_3 = k_3^0$ for which $\Delta(k_3^0 - Q) = 1$ make a noticeable contribution to the sums in (12). When $\omega = \Omega(k_3^0)$ the imaginary part of the dielectric constant and the absorption coefficient reach their maximum values

$$\varkappa^2_{max} = \tfrac{1}{2}\{\sqrt{\varepsilon^2 + \Gamma^2} - \varepsilon\},$$

$$(\varepsilon_2)_{max} = 8\pi\langle\varphi_f\,|\,e\mathbf{r}\,|\,\varphi_0\rangle^2/\hbar v\gamma(k_3^0) \equiv \Gamma. \tag{14}$$

Then the value of n in (13) is given by

$$n^2 = \tfrac{1}{2}\{\sqrt{\varepsilon^2 + \Gamma^2} + \varepsilon\}, \tag{15}$$

and ϵ is obtained from ϵ_1 (12) by eliminating the values of k_3^0 from the sum over k_3.

The refractive index has a maximum when the following two conditions are satisfied simultaneously

$$|\,\Omega(k_3^0) - \omega\,| = \tfrac{1}{2}\gamma(k_3^0), \qquad k_3^0 = \omega n_{max}/c. \tag{16}$$

In this case

$$(\varepsilon_1)_{max} = \varepsilon + \tfrac{1}{2}\Gamma, \qquad \varepsilon_2 \approx \tfrac{1}{2}\Gamma,$$

$$n^2_{max} = \tfrac{1}{2}\left\{\sqrt{\varepsilon^2 + \varepsilon\Gamma + \Gamma^2/2} + \varepsilon + \tfrac{1}{2}\Gamma\right\},$$

where Γ is defined by (14).

Generally speaking, conditions (13) and (16) are satisfied for different crystal thicknesses. For small $\gamma(k_3^0)$ the refractive index given in (13) and (15) differs little from n_{max}, so that conditions (13) are more important.

Substituting in (13) the value of k_3^0 we can verify that these conditions are satisfied for crystal thicknesses

---

[1] Strictly speaking, for a fixed value of N_3 the crystal thickness is $l = (N_3 - 1)a$. Consequently, $L_0 \equiv (N_3 + 1)a = l + 2a$.

$$L \equiv a(N_3+1) = \pi c\nu_3/\omega n, \qquad \nu_3 = 1, 2, 3, \ldots \tag{17}$$

Let us assume that this equation is satisfied for

$$L_0 = \pi c\nu_3^0/\omega n. \tag{18}$$

Then (17) and (13) are satisfied also for crystal thicknesses that are multiples of L_0 (if n is constant).

The foregoing results pertain to the case of weak absorption, when the decrease in the amplitude of the light wave passing through the crystal can be neglected. An account of the light-wave attenuation leads to an uncertainty in the value of the wave vector inside the crystal. This uncertainty is of the order of $\omega\kappa/c$, where κ is the absorption coefficient. In this connection, condition (13) can be satisfied accurate to $\omega\kappa/c$. To obtain discrete values of k_3 it is necessary to satisfy the inequality

$$\Delta k_3 \equiv \pi/(N_3+1)\,a > \omega\kappa/c. \tag{19}$$

For energy resonances to occur it is necessary that the distances between the exciton-state levels pertaining to different values of k_3 exceed the corresponding value of γ. The order of magnitude of this distance is M/N_3, where M is the width of the exciton band of a thick crystal. Consequently, the following inequality must be satisfied

$$M/N_3 > \gamma. \tag{20}$$

Inequalities (19) and (20) are easier to satisfy if N_3 is small. However, at very small values of N_3 the sharp maximum of the function (10), which determines the resonance in the wave numbers, becomes smoothed out and n or κ is no longer macroscopic.

At low temperatures (small γ) we can hope to observe a change in the values of n and κ with variation of crystal thickness in the region of exciton bands with $M \sim 10^3\ \text{cm}^{-1}$, for crystals containing several hundred molecular layers.

In the cited experiments by Brodin, variations of κ and n were observed at 20°K in anthracene crystals at 25,108 cm^{-1}, with the crystal thickness varying from 0.07 to 0.3 μ (variation of N_3 from 74 to 310). This frequency corresponds to an exciton band several thousand cm^{-1} thick. For $a(N_3 + 1) = 0.1\,\mu$ the measured value of κ is 0.96. Consequently, $\pi/a(N_3 + 1) = 3.14 \times 10^5\ \text{cm}^{-1}$, and $\omega\kappa/c = 1.5 \times 10^5\ \text{cm}^{-1}$. Thus, inequality (19) is still satisfied. At thicknesses above 0.3 μ (19) is not satisfied.

The maximum values of the absorption coefficient were observed by Brodin at crystal thicknesses 0.105, 0.168, and 0.223 μ. We can therefore assume $L_0 \approx 0.059\,\mu$. According to (18) this can correspond to n = 3.38 for $\nu_3 = 1$ or n = 6.76 for $\nu_3 = 2$. In Brodin's experiments the refractive index reached 6.8. Consequently, the second variant (n = 6.76 and $\nu_3 = 2$) is in good agreement with experiment. Our simplified theory cannot claim better agreement. It is important that comparison of the theoretical estimates with experiment does not call for additional (unmeasured) parameters to be introduced. We recall that the interpretation of Brodin's experiments on the basis of the notion of second waves[2-4] calls for these waves to have a refractive index ~ 12 and a low absorption coefficient. Since the measured values of n do not exceed 7, it is still necessary to explain why no values n ~ 12 are observed in experiment, although it is assumed that the second waves pass through the crystal.

Thus, small crystal thicknesses lead to discreteness of the possible values of the wave vector and exciton energy. At low temperatures and for not very thin crystals this discreteness can manifest itself in a nonmonotonic thickness dependence of the interaction between the crystal and the light. With increasing temperature, the value of γ increases because of the increase in the intensity of the interaction between the excitons and the phonons, and because of violation of the selection rules in k_3 (11) when the excitons and phonons interact. Under these conditions, the discreteness of the levels of the exciton band disappears. At 77°K and at room temperature, no oscillations are observed in Brodin's experiments.

The author is grateful to M. S. Brodin for supplying the experimental data and to V. M. Agranovich for a discussion of the results.

---

[1] M. S. Brodin and A. F. Prikhot'ko, Optika i spektroskopiya **7**, 132 (1959).

[2] M. S. Brodin and S. I. Pekar, JETP **38**, 74 (1960), Soviet Phys. JETP **11**, 55 (1960).

[3] S. I. Pekar, UFN **77**, 309 (1962), Soviet Phys. Uspekhi **5**, 515 (1962).

[4] M. S. Brodin and S. I. Pekar, JETP **38**, 1910 (1960), Soviet Phys. JETP **11**, 1373 (1960).

[5] A. S. Davydov, JETP **43**, 1832 (1962), Soviet Phys. JETP **16**, 1293 (1963).

[6] V. M. Agranovich and V. L. Ginzburg, UFN **77**, 663 (1962), Soviet Phys. Uspekhi **5**, 675 (1963).

[7] V. M. Agranovich, JETP **37**, 430 (1959), Soviet Phys. JETP **10**, 307 (1960).

[8] A. S. Davydov, Teoriya pogloshcheniya sveta v molekulyarnykh kristallakh (Theory of Light Absorption in Molecular Crystals), AN UkrSSR, 1951.

Translated by J. G. Adashko
120