

X-RAY SCATTERING IN CRYSTALS WITH EXCITON FORMATION

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Submitted to JETP editor October 13, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) 40, 913-919 (March, 1961)

A study is made of Raman scattering of x rays in crystals accompanied by the formation of excitons, i.e., "normal" electromagnetic waves in the given crystal. The plasmons (longitudinal plasma waves) in metals and dielectrics are a special case of excitons. The measurement of the energy of the scattered x-ray photons at various scattering angles may be an effective method of determining the energy of the excitons as a function of the wave vector.

1. As is well known, the excitons occurring in optical studies are nothing but the "normal" electromagnetic waves propagated in the given medium.¹⁻⁴ Hence, the determination of the exciton energy $\hbar\omega(\mathbf{k})$ as a function of the wave vector \mathbf{k} is equivalent to measuring the refractive index n of the crystal for waves of frequency ω propagated in the direction of \mathbf{k} .

However, for a number of reasons, it is difficult to work in optics with values of $n \gtrsim 10$, that is, with $k = 2\pi/\Lambda = 2\pi n/\lambda \gtrsim 10^6 \text{ cm}^{-1}$. (Here $\lambda = 2\pi c/\omega$ is the wavelength in vacuo; we assume for estimates in the optical region that $\lambda \sim 5 \times 10^{-5} \text{ cm}$; Λ is the wavelength in the given substance.) Correspondingly, it is difficult to determine one of the fundamental characteristics of excitons, the function $\omega(\mathbf{k})$, when $k \gtrsim 1 - 3 \times 10^6 \text{ cm}^{-1}$. In particular, no one has yet given by optical methods a proof at all convincing of the existence of a "new" type of waves in crystals in the vicinity of absorption lines.^{5,6} (The "new" waves merely amount to the fact that, when we take into account the spatial dispersion at the given frequency ω in the given direction, we find that not two, but a larger number of "normal" electromagnetic waves can be propagated. For further detail, see references 6 and 7.)

In view of the above, the use of non-optical methods to determine the function $\omega(\mathbf{k})$ is of great interest. If the exciton has a character essentially related to the vibrations of ions, as is the case in ionic crystals for the so-called optical vibrations,* an effective method of investigation

*Of course, a terminology in which every type of electromagnetic wave in the medium (or photon in the medium) is called an exciton may sometimes be inconvenient. We shall, however, use it here. We shall also refer to the so-called plasmons, i. e., longitudinal electromagnetic, or more precisely, "electric" waves, as excitons. For more detail on the relation between the theory of excitons and crystal electrodynamics, see reference 8.

may be the study of inelastic neutron scattering.⁹ We note that this method is especially effective in the study of acoustic lattice vibrations. However, in the case of excitons of the "electronic" type, weakly bound to the lattice vibrations, we may rely on other methods: the measurement of discrete energy losses during passage of electrons through thin films, and the study of Raman (inelastic) scattering of x rays in crystals. It is the latter phenomenon which we shall consider here.

2. Obviously, the topic here is the measurement of the frequency ω'_0 of x rays scattered at an angle θ by a crystal, with generation of an exciton. (The frequency of the incident radiation is ω_0 ; θ is the angle between the wave vectors of the scattered and incident waves \mathbf{k}'_0 and \mathbf{k}_0 .) From the conservation laws we have (neglecting the absorption of excitons, which will lead to a smearing of the pattern)

$$\omega = \omega_0 - \omega'_0, \quad \mathbf{k} = \mathbf{k}_0 - \mathbf{k}'_0,$$

$$2\Lambda \sin(\theta/2) \equiv (2\lambda/n(\omega)) \sin(\theta/2) = \lambda_0 = 2\pi c/\omega_0, \quad (1)$$

where, in deriving the latter expression, we have taken into account the fact that $n(\omega_0) \approx 1$, and $\omega \ll \omega_0$.*

Because of the crystal anisotropy, the frequency ω will depend, in general, for a given angle θ and crystal orientation, on the azimuth angle as well (i.e., on the direction of the vector \mathbf{k} for the given θ). In addition, of course, the frequencies $\omega(\mathbf{k})$ differ for excitons of differing types, e.g., of different polarization. If we assume $\lambda_0 \sim 1 - 3 \text{ \AA}$, and choose the lowest attainable angles ($\theta \sim 10'$),[†] then $\Lambda \sim (3 - 10) \times 10^{-6} \text{ cm}$; for $\theta \sim 1^\circ - 3^\circ$, we already find that $\Lambda \sim 2 \times 10^{-7} - 2 \times 10^{-6} \text{ cm}$, or $k = 2\pi n/\lambda \sim 3 \times 10^6 - 3 \times 10^7 \text{ cm}^{-1}$.

*With regard to radiation scattered in the vicinity of a Bragg maximum, see below.

[†]The authors are grateful to V. V. Shmidt for information on the experimental limitations.

Typical energy values for excitons lie within the limits $\hbar\omega \sim 0.1 - 10$ eV. We may point out for comparison that in scattering by free electrons $\hbar\omega \approx (\hbar\omega_0/2mc^2) \theta^2 \hbar\omega_0$. Thus, if $\theta = 1^\circ$ and $\lambda_0 \sim 3$ Å, then the energy loss of the x-ray photon $\hbar\omega \sim 4 \times 10^{-3}$ eV. The resolving power of x-ray spectroscopic apparatus in energy terms is at most only ~ 0.3 eV (at $\lambda_0 \sim 3$ Å); this limits considerably the possibilities of the method, but still, when $\hbar\omega \gtrsim 0.5 - 1$ eV, we may hope to obtain valuable information on the function $\omega(\mathbf{k})$, provided that the intensity of the Raman scattering is sufficient.*

3. The physical picture is especially clear in the limiting case in which the frequency of the x-rays is large in comparison with all characteristic frequencies of the medium. In this case, as is known (see, e.g., reference 11), the effective coherent-scattering cross-section for unpolarized radiation is given by the formula

$$d\sigma = r_0^2 \frac{1 + \cos^2 \theta}{2} \left| \int N_0(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} d\mathbf{r} \right|^2 d\Omega, \quad (2)$$

where $N_0(\mathbf{r})$ is the time-average electron density, $r_0 = e^2/mc^2$, and $d\Omega = \sin \theta d\theta d\varphi$.

We may obtain this result by the quantum-mechanical approach by taking the expression $(e^2/2mc^2) N_0(\mathbf{r}) \mathbf{A}^2(\mathbf{r})$ for the interaction energy in the Hamiltonian in this problem. Here, \mathbf{A} is the vector potential of the radiation field.

In the study of Raman scattering with the participation of an electromagnetic wave in the medium (an exciton), we can no longer consider the concentration $N(\mathbf{r})$ to be fixed, and we write

$$N(\mathbf{r}) = N_0(\mathbf{r}) + N'(\mathbf{r});$$

$$4\pi e N'(\mathbf{r}) = \text{div } \mathbf{E}_j = -i(\mathbf{k}j) E_j^0 \exp[i(\omega_j t - \mathbf{k}\mathbf{r})]. \quad (3)$$

Here $\mathbf{E}_j(\mathbf{r}) = jE_j^0 \exp[i(\omega_j t - \mathbf{k}\cdot\mathbf{r})]$ is the electric field in the "normal" wave (exciton) of type j being studied (the unit vector j defines the polarization of the wave).† The energy of this wave can

*From the quantum viewpoint, the well-known thermal diffuse scattering of x-rays is Raman (inelastic, incoherent) scattering involving phonons. Raman scattering involving the lattice (or the ions) will not be considered below. For excitons having $\hbar\omega < 0.1$ eV, the frequency shift may be measured by means of the Mössbauer effect.¹⁰

†The "normal" waves used here, with $E_j^0 = \text{const}$, are the solutions of the field equations in which the dielectric-constant tensor $\epsilon_{ij}(\omega, \mathbf{k})$ is introduced. For wavelengths comparable with the lattice parameter of the crystal, such a treatment is no longer accurate, since for the "normal" waves in the crystal, the amplitudes E_j^0 are periodic functions of \mathbf{r} .

be represented in the form of the energy of an oscillator

$$a_j(\mathbf{k}) E_j^* E_j V = (p_j^* p_j + \omega_j^2 q_j^* q_j) = 2\omega_j^2 q_j^* q_j = \hbar\omega_j l, \quad (4)$$

where the last result is obtained by quantization ($l = 0, 1, 2, \dots$); V is the volume of the crystal, and the coefficient $a(\mathbf{k})$ can be calculated from a consideration of the energy of the system.

The energy of interaction with the x rays is now equal to [see Eqs. (3) and (4)]:

$$\frac{e^2}{2mc^2} [N_0(\mathbf{r}) + N'(\mathbf{r})] \mathbf{A}^2(\mathbf{r}) = \frac{e^2}{2mc^2} \left\{ N_0(\mathbf{r}) - \frac{i(\mathbf{k}j) q_j \omega_j \sqrt{2}}{4\pi e \sqrt{V} a_j} e^{i(\omega_j t - \mathbf{k}\mathbf{r})} \right\} \mathbf{A}^2(\mathbf{r}). \quad (5)$$

If $l \gg 1$, the problem becomes classical, and is reduced to the scattering of transverse electromagnetic waves (x rays) by waves having a longitudinal field component (e.g., in an isotropic plasma only plasma waves are of interest, whereas in a magnetoactive plasma all waves are in general responsible for the scattering^{7,12}). Crystals in an initial equilibrium state contain practically no excitons, and thus, we must consider the transition from the state $l = 0$ to the state $l = 1$ [see Eq. (4)]. The matrix element for such a transition is

$$(0 | q_j e^{i\omega_j t} | 1) = \sqrt{\hbar/2\omega_j}.$$

Here we need not solve the x-ray scattering problem anew, since by starting with Eq. (5) with $q_j = 0$, we can derive Eq. (2), while the calculation with $q_j \neq 0$ is essentially the same.

Thus by using Eqs. (2) and (5) together, we find the cross section for the Raman scattering:

$$d\sigma_R = r_0^2 \frac{1 + \cos^2 \theta}{2} (\mathbf{k}j)^2 \frac{V \hbar \omega_j}{(4\pi e)^2 a_j} d\Omega = r_0^2 \frac{1 + \cos^2 \theta}{2} (\mathbf{k}j)^2 \frac{\hbar \omega_j \bar{N}_0 V}{4\pi a_j m \omega_p^2} d\Omega, \quad (6)$$

where $\omega_p^2 = (4\pi e^2/m) \bar{N}_0$ is the "plasma frequency," and \bar{N}_0 is the mean electron density.

For incoherent scattering by free electrons, we have in Eq. (2):

(with the period of the lattice). By writing the field in the "normal" wave in the form

$$\mathbf{E}_j = \mathbf{E}_{j\mathbf{k}}^0(\mathbf{r}) \exp[i(\omega_j t - \mathbf{k}\mathbf{r})],$$

where $\mathbf{E}_{j\mathbf{k}}^0(\mathbf{r})$ is a periodic function of \mathbf{r} (with the lattice periodicity), we can calculate the Raman scattering in a way analogous to that used in the body of this article. The very important qualitative difference which arises here is the appearance of Raman scattering with $\mathbf{k}_0 - \mathbf{k}'_0 = \mathbf{k} + \mathbf{b}$, where \mathbf{b} is an integer reciprocal-lattice vector. The authors are grateful to L. V. Keldysh for a discussion of this question.

$$\left| \int N_0(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \right|^2 = \bar{N}_0 V,$$

since $N(\mathbf{r}) = \sum_{\mathbf{k}} \delta(\mathbf{r} - \mathbf{r}_1)$. Hence, the ratio of the cross-section in Eq. (6) to the cross-section for scattering by free-electrons $d\sigma_0$ is equal to

$$\frac{d\sigma_k}{d\sigma_0} = \frac{(\mathbf{k}\mathbf{j})^2 \hbar\omega_j}{4\pi a_j m\omega_p^2} = \left(\frac{\hbar\omega_0}{mc^2} \right) \left(\frac{\omega_0 \omega_j}{\omega_p^2} \right) \frac{\sin^2(\theta/2) \cos^2\psi}{\pi a_j}, \quad (7)$$

where ψ is the angle between \mathbf{k} and \mathbf{j} , and Eq. (1) has been used:

$$k^2 = (2\omega_0/c)^2 \sin^2(\theta/2).$$

In the propagation of waves along corresponding symmetry axes, or in any direction in cubic crystals (neglecting spatial dispersion⁶), the "normal" waves are divided into transverse and longitudinal waves. For transverse waves, $\mathbf{k} \cdot \mathbf{j} = 0$, and thus in the present approximation, no Raman scattering will arise [see Eqs. (6) – (7)].

Longitudinal waves (for which $d\sigma_k \neq 0$) are commonly called plasma waves (plasmons), since they are analogous to the longitudinal waves in an isotropic plasma. For plasma waves in a gas of free electrons, neglecting spatial dispersion (this means that $\omega_p^2 \gg v_0^2 k^2$, where v_0 is some mean electron velocity), $\omega_j = \omega_p$, and $a_j = \frac{1}{2}\pi$ (see, e.g., reference 7). However, in the case of any given optically-isotropic medium (metals, dielectrics) having sufficiently weak absorption in the given frequency range, we find for long longitudinal (plasma) waves

$$\epsilon(\omega_j) = 0, \quad a_j = (\omega_j/4\pi) (d\epsilon/d\omega) \omega_j,$$

where $\epsilon(\omega)$ is the dielectric constant of the medium, and $d\epsilon/d\omega$ is evaluated for $\omega = \omega_j$ (for free electrons, $\epsilon = 1 - \omega_p^2/\omega^2$).

In the case of free electrons, we have

$$d\sigma_{k,p}/d\sigma_0 = \hbar k^2/2m\omega_p = 2(\hbar\omega_0/mc^2) (\omega_0/\omega_p) \sin^2(\theta/2). \quad (8)$$

Equation (8) is equivalent to the corresponding formula derived in the classical calculation of scattering by a plasma wave $N' \exp[i(\omega_p t - \mathbf{k} \cdot \mathbf{r})]$ having an amplitude

$$|N'| = \sqrt{\hbar k^2 \bar{N}_0 / 2m\omega_p} V.$$

The wave amplitude has this value if we set $E^*EV/2\pi = \hbar\omega_p$.

If $\theta \sim 3^\circ$, $\hbar\omega_0 \sim 5 \times 10^3$ eV ($\lambda_0 \sim 3$ Å), and $\hbar\omega_p \sim 10$ eV, the ratio $d\sigma_{k,p}/d\sigma_0 \sim 10^{-2}$. Obviously, it follows that the intensity of the Raman scattering is sufficient for reliable measurement, provided that the actual values of the coefficients $1/a_j$ and $\cos^2\psi$ in Eq. (7) are not much smaller than the

values used in deriving Eq. (8): $1/a_j = 2\pi$, and $\cos^2\psi = 1$.

4. In order to take into account the role of bound electrons and to specify the type of exciton considered, we shall study the model of a molecular crystal. In this case, the operator H' for the interaction with the radiation field can be written as a sum⁴

$$H' = H^{(1)} + H^{(2)}, \quad (9)$$

$$H^{(1)} = -\frac{e}{mc} \sum_{n\alpha, i_{n\alpha}} \mathbf{A}(r_{n\alpha}^i) \mathbf{p}_{n\alpha}^i, \quad (9a)$$

$$H^{(2)} = \frac{e^2}{2mc^2} \sum_{n\alpha, i_{n\alpha}} \mathbf{A}^2(r_{n\alpha}^i). \quad (9b)$$

In Eqs. (9a) and (9b) $\mathbf{r}_{n\alpha}^i$ is the radius vector of the i -th electron belonging to the $n\alpha$ -th molecule, $\mathbf{p}_{n\alpha}^i$ is its momentum (\mathbf{n} is an integral lattice vector, and α is the number of the molecule in the unit cell, $\alpha = 1, 2, \dots, \sigma$).

The operator $H^{(1)}$ gives the contribution to the intensity of Raman scattering of x-ray photons with formation of excitons only via transitions between intermediate states. It is easily seen that in calculating this contribution, the only appreciable interaction can be that of the x-ray photons with the strongly-bound electrons, whose binding energies are of the order of the x-ray photon energy.

The process of Raman scattering of x-ray quanta by individual atoms with production of plasmons has already been studied by Sobel'man and Feinberg,¹³ who took into account the intermediate states of the K electrons.* It follows from the formula for the ratio $\sigma_{k,p}/\sigma_0$ given in reference 13 that intermediate states of the K electrons may contribute appreciably to the Raman-scattering cross section only in case that the energy of the x-ray photon is very near to the binding energy $|\epsilon_0|$ of the K electron. In this energy range, however, difficulties may arise in the observation of Raman scattering, owing to the nearness of the absorption edge. However, if $|\hbar\omega_0 - |\epsilon_0|| \sim \hbar\omega_0$ the contribution to the cross section calculated in reference 13 turns out to be small ($\sigma_{k,p}/\sigma_0 \lesssim 10^{-7}$) in comparison with the contribution due to direct transitions effected by the perturbation $H^{(2)}$. [Thus, it follows from Eq. (8) given above that $\sigma_{k,p}/\sigma_0 \sim 1$.] Hence, we shall limit ourselves below to calculating this fundamen-

*We note that reference 13 also considers the excitation of a plasmon upon absorption of an x-ray quantum. Of course, such a process may also involve the generation of an exciton of a more general type. However, in studies of x-ray absorption there is practically no opportunity to distinguish the excitons in terms of their momenta.

tal contribution, in complete agreement with the calculations given in Sec. 3, having in mind an energy range of x ray quanta sufficiently distant from the absorption edge.

The vector potential of the x ray radiation field has the following form:¹⁴

$$A(\mathbf{r}) = \sum_{\mathbf{q}j} \sqrt{\frac{2\pi c^2 \hbar}{V \rho c}} \mathbf{l}_{\mathbf{q}j} (a_{\mathbf{q}j} e^{i\mathbf{q}\mathbf{r}} + a_{\mathbf{q}j}^+ e^{-i\mathbf{q}\mathbf{r}}), \quad (10)$$

where $\mathbf{l}_{\mathbf{q}j}$ ($j = 1, 2$) are unit vectors defining the transverse polarization of the photons ($\mathbf{q}j$), and $a_{\mathbf{q}j}^+$ and $a_{\mathbf{q}j}$ are operators for the production and destruction of the photons ($\mathbf{q}j$). Substitution of Eq. (10) into (9b) leads to a quadratic form with respect to the operators for production and destruction of photons. However, in this expression only the terms proportional to $a_{\mathbf{k}_0 j}^+ a_{\mathbf{k}'_0 j'}$ give non-zero contributions to the cross section of the process being studied. If j and j' denote the polarization of the x-ray quantum before and after scattering, the perturbation operator which we must take into account is:

$$H^{(2)}(\mathbf{k}_0 j, \mathbf{k}'_0 j') = \frac{2e^2 \pi \hbar}{mcV} \sum_{\mathbf{n}\alpha} a_{\mathbf{k}_0 j} a_{\mathbf{k}'_0 j'}^+ \frac{\mathbf{l}_{\mathbf{k}_0 j} \mathbf{l}_{\mathbf{k}'_0 j'}}{(\mathbf{k}_0 \mathbf{k}'_0)^{1/2}} \exp\{i(\mathbf{k}_0 - \mathbf{k}'_0, \mathbf{r}_{\mathbf{n}\alpha})\} F(\mathbf{n}, \alpha). \quad (11)$$

The function

$$F(\mathbf{n}, \alpha) = \sum_{i\mathbf{n}\alpha} \exp\{i(\mathbf{k}_0 - \mathbf{k}'_0, \mathbf{r}_i)\} \quad (12)$$

depends on the coordinates of the electrons of the molecule ($\mathbf{n}\alpha$) with respect to the lattice point at which this molecule is situated.

In order to calculate the value of the cross section, we must know the wave function of the electrons of the crystal in the ground state as well as in the excited state accompanying the presence of the exciton. Neglecting retardation, which is not very substantial here,* these wave functions have the following form in the Heitler-London approximation (the weak effect of intermolecular exchange of electrons is not taken into account below):

$$\Phi_0 = \prod_{\mathbf{n}\alpha} \Phi_{\mathbf{n}\alpha}^0, \quad \Phi_{\mu}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}\alpha} B_{\alpha\mu}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{r}_{\mathbf{n}\alpha}) \Phi_{\mathbf{n}\alpha}^f; \quad (13)$$

$$\Phi_{\mathbf{n}\alpha}^f = \Phi_{\mathbf{n}\alpha}^f \prod_{\mathbf{m}\beta \neq \mathbf{n}\alpha} \Phi_{\mathbf{m}\beta}^0.$$

Here, μ is the number of the exciton band, \mathbf{k} is the wave vector of the exciton, and Φ^0 and Φ^f are

*Exciton states corresponding to sufficiently high quasi-momentum values (see Sec. 1) exhibit basically the expected properties of excitons derived without taking retardation into account.¹⁻⁴

the wave functions of the molecules in the ground state and in the f -th excited state (for more detail, see reference 15).

The matrix element of operator (11), as constructed from the functions of the initial and final states, is equal to

$$\langle \mathbf{k}_0 j; 0 | H^{(2)} | \mathbf{k}'_0 j'; \mu \mathbf{k} \rangle = \frac{2e^2 \pi \hbar (\mathbf{l}_{\mathbf{k}_0 j} \mathbf{l}_{\mathbf{k}'_0 j'})}{mcV \sqrt{V \overline{k_0 k'_0}}} \sum_{\mathbf{n}\alpha, \mathbf{m}\beta} B_{\alpha\mu}^*(\mathbf{k}) F_{\mathbf{m}\beta}(\mathbf{n}, \alpha) \exp\{i(\mathbf{k}_0 - \mathbf{k}'_0, \mathbf{r}_{\mathbf{n}\alpha}) - i\mathbf{k}\mathbf{r}_{\mathbf{m}\beta}\}, \quad (14)$$

where

$$F_{\mathbf{m}\beta}(\mathbf{n}, \alpha) = \langle \Phi_0 | F(\mathbf{n}, \alpha) | \Phi_{\mathbf{m}\beta}^f \rangle. \quad (15)$$

However, since [see Eq. (13)],

$$F_{\mathbf{m}\beta}(\mathbf{n}, \alpha) = \langle \Phi_{\mathbf{n}\alpha}^0 | F(\mathbf{n}, \alpha) | \Phi_{\mathbf{n}\alpha}^f \rangle \delta_{\mathbf{n}\alpha, \mathbf{m}\beta} \equiv F_{\alpha} \delta_{\mathbf{n}\alpha, \mathbf{m}\beta}, \quad (16)$$

(here $\delta_{\mathbf{x}, \mathbf{y}} = 0$ if $\mathbf{x} \neq \mathbf{y}$, and $\delta_{\mathbf{x}, \mathbf{y}} = 1$ if $\mathbf{x} = \mathbf{y}$), we find that

$$\langle \mathbf{k}_0 j; 0 | H^{(2)} | \mathbf{k}'_0 j'; \mu, \mathbf{k} \rangle = \frac{2e^2 \pi \hbar (\mathbf{l}_{\mathbf{k}_0 j} \mathbf{l}_{\mathbf{k}'_0 j'})}{mcV \sqrt{k_0 k'_0}} \sqrt{N} \sum_{\alpha} B_{\alpha\mu}^*(\mathbf{k}) F_{\alpha} \delta_{\mathbf{k}_0 - \mathbf{k}'_0, \mathbf{k} + \mathbf{b}}, \quad (17)$$

where \mathbf{b} is an integer reciprocal-lattice vector.

The Raman-scattering cross section has the form (see reference 14):

$$d\sigma_h = (2\pi V / \hbar c) |\langle \mathbf{k}_0 j; 0 | H^{(2)} | \mathbf{k}'_0 j'; \mu, \mathbf{k}_0 - \mathbf{k}'_0 \rangle|^2 \rho_{\epsilon'}, \quad (18)$$

where the number of final states per unit energy interval is

$$\rho_{\epsilon'} = (k'_0)^2 (2\pi)^{-3} V (dk'_0/d\epsilon') d\Omega = (k'_0)^2 (2\pi)^{-3} (V/\hbar c) d\Omega;$$

Here we have taken into account the fact that $\epsilon' = \hbar k'_0 c = \hbar \omega'_0$. Hence, upon substituting Eq. (17) into (18), summing over the polarization j' , and averaging over the polarization j , we find that

$$d\sigma_h = r_0^2 \left(\frac{k'_0}{k_0}\right) \frac{1 + \cos^2 \theta}{2} N \left| \sum_{\alpha} B_{\alpha\mu}^*(\mathbf{k}) F_{\alpha} \right|^2 d\Omega. \quad (19)$$

If the wavelength of the exciton is large in comparison with the molecular dimensions, then for $\mathbf{b} = 0$.*

*Processes with $\mathbf{b} \neq 0$ and $k \ll b$ will give rise to inelastically scattered photons concentrated in the neighborhoods of the Bragg maxima (of course, it is assumed that the crystal is properly oriented). However, since in such cases the change in the wave vector of the photons is great, the quantities $|F_{\alpha}|$ [see Eqs. (12) and (16)] will be considerably lower than in the case $\mathbf{b} = 0$. In addition, since the quantities $|F_{\alpha}|$ decrease with increasing $|\mathbf{b}|$, the largest cross section will be found in the neighborhood of the first Bragg maximum (the smallest value of $|\mathbf{b}|$). From the standpoint of observing scattering near the Bragg maxima, "loosely-packed" crystals, in which the lattice parameter is considerably greater than the dimensions of the molecules, are of interest.

$$F_{\alpha} \approx i(\mathbf{P}_{\mu}(\mathbf{k}) \cdot \mathbf{k}) / e; \quad (20)$$

Here

$$\mathbf{P}_{\mu}(\mathbf{k}) = \sum_{\alpha} B_{\alpha\mu}^*(\mathbf{k}) \mathbf{P}_{\alpha}^{of}$$

is the amplitude of the dipole moment corresponding to the exciton state $\mu\mathbf{k}$, and

$$\mathbf{P}_{\alpha}^{of} = \int \varphi_{n\alpha}^{*0} \mathbf{P}_{n\alpha} \varphi_{n\alpha}^i d\tau,$$

where $\mathbf{P}_{n\alpha}$ is the dipole-moment operator of the molecule $n\alpha$.

Thus,

$$d\sigma_k = (r_0^2 / 2e^2 \Delta) (k'_0 / k_0) (1 + \cos^2 \theta) V |\mathbf{P}_{\mu}(\mathbf{k})|^2 k^2 \cos^2 \Psi d\Omega, \quad (21)$$

where Δ is the unit-cell volume, and Ψ is the angle between the vectors $\mathbf{P}_{\mu}(\mathbf{k})$ and \mathbf{k} .

Upon applying Eq. (21) as before, we find that

$$\frac{d\sigma_k}{d\sigma_0} = 16\pi \left(\frac{k'_0}{k_0} \right) \left(\frac{\omega_0^2}{\omega_p^2} \right) \left(\frac{|\mathbf{P}_{\mu}(\mathbf{k})|^2}{mc^2 \Delta} \right) \sin^2 \frac{\theta}{2} \cos^2 \Psi,$$

$$d\sigma_0 = \frac{1}{2} r_0^2 (1 + \cos^2 \theta) \bar{N}_0 V d\Omega, \quad \omega_p^2 = 4\pi e^2 \bar{N}_0 / m. \quad (22)$$

It follows from Eqs. (21) and (22) that the calculated cross-section is proportional to the oscillator strength of the transition in the molecule. Among molecular crystals, the most intense dipole transitions are exhibited by anthracene (the second electronic transition¹⁶), for which $|\mathbf{P}_{\mu}|/e \approx 3 \times 10^{-8}$ cm. In this case, assuming that $\Delta \approx 125 \times 10^{-24}$ cm³, $\theta \approx 3^\circ$, $\cos^2 \Psi \approx 1/3$, $k'_0/k_0 \approx 1$, and $\omega_0/\omega_p \approx 5 \times 10^2$, we find that $d\sigma_k/d\sigma_0 \approx 4 \times 10^{-3}$. At $\theta \approx 30^\circ$, the ratio $d\sigma_k/d\sigma_0 \approx 4 \times 10^{-1}$.

It follows from a comparison of Eqs. (22) and (7) that for Frenkel' excitons the quantity a_j [see also Eq. (4)] is inversely proportional to the square of the matrix element of the dipole-moment operator. Also, a_j becomes infinite for those excitons which cannot be excited by light in the dipole approximation. In the latter case, according to Eq. (6), $d\sigma_k \rightarrow 0$; in the present approximation this is due to the vanishing of the amplitude of the electric field [see Eq. (4) for $a_j \rightarrow \infty$].

Of course, Eq. (22) can be derived by first finding the dielectric-constant tensor $\epsilon_{ij}(\omega, \mathbf{k})$ for our model and then calculating the coefficient a_j entering into Eqs. (4) and (6).

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Translated by M. V. King