

SOVIET PHYSICS USPEKHI

A Translation of Uspekhi Fizicheskikh Nauk

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SOVIET PHYSICS USPEKHI

(Russian Vol. 82, Nos. 3 and 4)

SEPTEMBER-OCTOBER, 1964

530.145

THE THEORY OF MOLECULAR EXCITONS

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Usp. Fiz. Nauk 82, 393-448 (March, 1964)

INTRODUCTION

IN recent years, interest in solid-state physics has grown considerably in connection with the numerous practical applications of dielectrics and semiconductors. Hence it has become necessary to understand more fully the physical phenomena taking place in solids when they interact with light, when they are irradiated by a flux of particles, when an electric current passes through them, etc. The necessity has arisen of developing the theory further.

In the development of the theory of dielectrics, the wide use of the exciton concept introduced in 1931 by Frenkel^[1] has proved especially fruitful. This concept has proved highly effective in studying energy-migration processes in solids, in certain polymers, and in biological objects. Energy migration must be studied for the development of effective luminophors, for ascertaining the possibilities of radiochemical processes in solids, and for understanding optical, photoelectric, photochemical, and biological phenomena occurring in crystals and complex molecules (polymers).

This article will discuss the theoretical description of the electronic excited states of molecular crystals and their manifestation in interaction with electromagnetic radiation. We cannot treat the latter interaction as a small one, as we can easily convince ourselves by recalling that the phase velocity of propagation of light in crystals differs by a factor of 1.5-2 from that in vacuo.

The problem of the interaction of an electromagnetic wave with a solid body of large dimensions belongs to the type of "self-consistency" problems. The light wave is governed by the values of the refractive index, which in turn depend on the interaction of this wave with the molecules of the crystal.

Owing to the linearity of Maxwell's equations and the linearity of the relation between the polarizability of the crystal and the electric field strength of the wave, the study of the passage of light through a crystal is often carried out in two stages: first one calculates the specific polarizability of the crystal produced by the external light wave, and then adjusts the parameters of the light wave to the found polarizability by means of Maxwell's equations.

In order to calculate the specific polarizability of a molecular crystal, we must know the energy spectrum and wave functions of its excited states. A knowledge of the energy spectrum and the wave functions of the excited states of a crystal is also necessary in the theoretical study of many other properties of a crystal. Here we shall limit ourselves to studying only the quantum states of a crystal and their simplest experimental manifestations, without considering in its full scope the problem of the transmission of a light wave through a crystal. The latter problem requires study of a more complex system, consisting of the crystal and the radiation.

I. EXCITON STATES IN CRYSTALS HAVING ONE MOLECULE PER UNIT CELL

Solids formed from molecules (or atoms of the inert gases) that interact by van der Waals forces are called molecular crystals. The energy of these molecular interactions is very small in comparison with the binding energy of the electrons in the molecules. Some typical molecular crystals are those formed by the aromatic anisotropic molecules anthracene, naphthalene, benzene, etc.

The theory must explain how the energy states of the free molecules are changed in the formation of the crystal, and what properties these crystals will have

with regard to interaction with electromagnetic radiation. In distinction from a gas, in the crystal the molecules are arranged in a definite order close to one another. If we could reduce the intermolecular interaction forces to zero, while maintaining the order in the arrangement of the molecules, we would obtain the model of an oriented gas, which is sometimes used to explain certain optical properties of molecular crystals. However, as we shall see, in a number of cases, even the presence of small intermolecular interactions leads to highly peculiar characteristics in the real crystal, distinguishing it from the oriented-gas model. These characteristics are essentially manifested when we study the excited states of the crystal. In the crystal, exciton states, or collective excited states can arise, and are not a simple superposition of the excited states of the free molecules.

The exciton states in a solid are not stationary. The excitation energy is partly emitted, while the rest goes over into thermal energy, i.e., it is redistributed over many degrees of freedom having low frequencies, corresponding to the vibrations of the molecules about their equilibrium positions. In order to simplify the calculations, we neglect at first the interaction of the intramolecular excitations with the vibrations of the molecules. For this purpose, we shall assume that the molecules are rigidly fixed in their equilibrium positions. This section will discuss crystals containing one molecule in each unit cell of the crystal.

The unit cell is a parallelepiped having three non-coplanar basis vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . The space lattice of the crystal is formed by periodic repetition of the unit cell in the directions of the three basis vectors. The positions of the lattice points is determined by the lattice vector

$$\mathbf{n} = \sum_{i=1}^3 n_i \mathbf{a}_i, \quad (1.1)$$

where the n_i are integers.

In crystals having one molecule per unit cell, all the molecules are alike, and have identical orientations with respect to the basis vectors. The molecules are arranged at lattice points, and hence the positions of their centers of inertia can be characterized by the lattice vectors. We assume that the crystal is a large parallelepiped with edges $N_1 \mathbf{a}_1$, $N_2 \mathbf{a}_2$, and $N_3 \mathbf{a}_3$. Then the total number of molecules in the crystal is $N = (N_1 + 1)(N_2 + 1)(N_3 + 1)$. In crystals of large dimensions, the numbers N_i can be considered to be even. The positions of the molecules (assumed rigidly fixed) in this lattice will be given by the lattice vectors [Eq. (1.1)] for the values of n_i satisfying the inequalities

$$-\frac{N_i}{2} \leq n_i \leq \frac{N_i}{2}, \quad i = 1, 2, 3. \quad (1.2)$$

In studying bulk properties in large crystals, the choice of boundary conditions at the surface of the

crystal does not play an essential role. Usually one assumes as the boundary conditions the condition of periodicity with large periods $N_i \mathbf{a}_i$.

Let $H_{\mathbf{n}}$ be the energy operator of the free molecule, and $V_{\mathbf{nm}}$ be the energy operator for the interaction of the two molecules at lattice points \mathbf{n} and \mathbf{m} . Then the total energy operator of the crystal is

$$H = \sum_{\mathbf{n}} H_{\mathbf{n}} + \frac{1}{2} \sum'_{\mathbf{n}, \mathbf{m}} V_{\mathbf{n}, \mathbf{m}}. \quad (1.3)$$

The summation in (1.3) is performed over all values of the lattice vectors \mathbf{n} and \mathbf{m} defined by Eq. (1.1) under the conditions (1.2). The prime in the second summation indicates, here and below, that terms having $\mathbf{n} = \mathbf{m}$ are omitted from the summation.

First we shall study the part of the operator of (1.3) not involving the interaction between molecules. This approximation corresponds to the oriented-gas model with a regular arrangement of the molecules. Let the energy operators $H_{\mathbf{n}}$ of the free molecules have a system of eigenfunctions $\varphi_{\mathbf{n}}^f(\xi_{\mathbf{n}})$ corresponding to the eigenvalues ϵ_f of the energy. The energies ϵ_f characterize the internal electronic, vibrational, or electronic-vibrational excited states of the free molecule. The symbol $\xi_{\mathbf{n}}$ denotes the set of coordinates corresponding to the internal degrees of freedom of the molecule occupying the lattice point \mathbf{n} . The symbol f denotes the set of quantum numbers of each stationary state. The ground state of the molecule corresponds to $f = 0$. Initially we shall assume for simplicity that the stationary states of the free molecules are not degenerate.

In the ground state and the excited states having an excitation energy less than the ionization energy, the wave functions of adjacent molecules in molecular crystals overlap weakly. We shall be interested only in small electronic excitations. Hence, so as to avoid considerable complications, we shall neglect the overlap functions of adjacent molecules.

The ground state of a crystal having an energy operator $H_0 = \sum_{\mathbf{n}} H_{\mathbf{n}}$ has an energy $N\epsilon_0$, and is described by the wave function

$$\psi^0 = \prod_{\mathbf{n}} \varphi_{\mathbf{n}}^0. \quad (1.4)$$

The excited states corresponding to the f -th excited state of a single molecule of the crystal have an energy of $(N-1)\epsilon_0 + \epsilon_f$. These states are N -fold degenerate, since any one of the N molecules can occur in the f -th excited state. If the molecule \mathbf{n} is excited, the corresponding wave function will have the form

$$\psi_{\mathbf{n}}^f = \varphi_{\mathbf{n}}^f \prod_{\mathbf{m}} \varphi_{\mathbf{m}}^0, \quad \mathbf{m} \neq \mathbf{n}. \quad (1.5)$$

All of the molecules in the crystal are identical, and hence, instead of the function (1.5), which specifies the site of the excited molecule in the crystal, we can introduce N new orthonormalized functions

$$|kf\rangle = \frac{1}{\sqrt{N}} \sum_n \psi_n^f e^{ikn}, \quad (1.6)$$

These differ in the values of the wave vector \mathbf{k} , which is defined by the relations

$$\mathbf{k} = \sum_{i=1}^3 \frac{2\pi}{N_i} v_i \mathbf{b}_i, \quad -\frac{N_i}{2} \leq v_i \leq \frac{N_i}{2}, \quad (1.7)$$

where the \mathbf{b}_i are the basis vectors of the reciprocal lattice, which are related to the basis vectors of the direct lattice by the equations $\mathbf{b}_i \cdot \mathbf{a}_j = \delta_{ij}$. The set of all vectors (1.7) forms the first Brillouin zone in \mathbf{k} -space. The functions

$$N^{-1/2} e^{i\mathbf{k}\mathbf{n}} \equiv \Omega(\mathbf{k}\mathbf{n})$$

constitute a complete system of functions, satisfying the relations

$$\sum_{\mathbf{k}} \Omega(\mathbf{k}\mathbf{n}) \Omega^*(\mathbf{k}\mathbf{m}) = \delta_{nm}, \quad \sum_{\mathbf{n}} \Omega(\mathbf{k}\mathbf{n}) \Omega^*(\mathbf{k}'\mathbf{n}) = \delta_{\mathbf{k}'\mathbf{k}}.$$

The transformation (1.6) can be considered to be a unitary transformation to a new representation of the wave functions.

In a system having the operator H_0 , all the states (1.6) differing in the values of the wave vector \mathbf{k} have identical energies. This degeneracy is removed when we take into account the interactions between the molecules. In molecular crystals, the interaction between molecules is small. Hence, in the first-order perturbation theory, the energy of the crystal is equal to the mean value of the operator (1.3) over the states corresponding to the wave functions (1.4) and (1.5) of the zero-order approximation. Thus we obtain the energy of the ground state and that of the excited states of the crystal corresponding to the functions (1.6). By taking their differences, we can find the excitation energy of the crystal in a transition from the ground state (1.4) to the excited state (1.6):

$$E^f(\mathbf{k}) = \Delta\epsilon_f + D_f + L_f(\mathbf{k}), \quad (1.8)$$

where $\Delta\epsilon_f$ is the excitation energy of the free molecule,

$$D_f = \sum_{\mathbf{m}} \left\{ \int |\varphi_n^f|^2 V_{nm} |\varphi_m^0|^2 d\tau - \int |\varphi_n^0|^2 V_{nm} |\varphi_m^0|^2 d\tau \right\} \quad (1.9)$$

is the change in the interaction energy of a single molecule with all the adjacent molecules upon transition to the f -th excited state, and

$$L_f(\mathbf{k}) = \sum_{\mathbf{m}}' M_{mn}^f \exp\{i\mathbf{k}(\mathbf{n} - \mathbf{m})\} \quad (1.10)$$

is an addition term to the excitation energy depending on the wave vector \mathbf{k} of the excited state. The matrix element

$$M_{nm}^f = \int \varphi_n^0 \varphi_m^* V_{nm} \varphi_m^0 \varphi_n^f d\tau \quad (1.11)$$

governs the transfer of the f -th excited state from molecule \mathbf{n} to molecule \mathbf{m} .

Usually an excited molecule interacts more strongly than an unexcited one with the adjacent molecules.

Hence, the correction (1.9) to the excitation energy of the crystal is negative in sign, leading to a decrease in the excitation energy of the crystal. The third term in (1.10) depends on the N values of the wave vector \mathbf{k} . Thus, in the crystal N different excited states correspond to a non-degenerate excited state of the free molecule. In crystals of large dimensions, the consecutive values of \mathbf{k} differ little from one another. Hence, the N values of the excitation energy (1.8) form a quasicontinuous band of excited states of the crystal, consisting of N sublevels. Each of these excited states, pertaining to a definite value of the wave vector \mathbf{k} , is a collective excited state of the whole crystal. Such elementary excitations were first discussed by Frenkel^[1] and termed excitons.

The exciton states of the crystal are characterized by the quasimomentum $\mathbf{p} = \hbar\mathbf{k}$ and the energy (1.8). The wave function of an exciton, taking into account its time-dependence, can be written in the form

$$\Phi_{kf}(\dots \xi_n \dots) = \frac{1}{\sqrt{N}} \sum_n \psi_n^f(\xi_n) (\exp\{i[\mathbf{k}\mathbf{n} - \omega_f(\mathbf{k})t]\}), \quad (1.12)$$

where $\omega_f(\mathbf{k}) = E_f(\mathbf{k})/\hbar$. The form of the function (1.12) implies that all the molecules in the crystal play the same role in the formation of the exciton state. In other words, the excitation of the crystal corresponding to the exciton state (1.12) is distributed throughout the crystal, rather than concentrated in one molecule.

The states of the crystal corresponding to the excitation of some region of the crystal are represented by wave packets, i.e., linear combinations of functions (1.12), for example

$$\Psi = \sum_{\mathbf{k}} w(\mathbf{k}) \Phi_{kf}, \quad (1.13)$$

where $w(\mathbf{k})$ differs from zero only for values of \mathbf{k} satisfying the conditions $k_x^0 - \Delta k \leq k_x \leq k_x^0 + \Delta k$, $k_y = k_y^0$, $k_z = k_z^0$.

The excited states described by the wave packets (1.13) do not have a definite energy and a definite value of the wave vector. The smaller the region of excitation Δx is, the greater the uncertainty in the values of Δk ,

$$\Delta x \Delta k \approx 2\pi. \quad (1.14)$$

When electromagnetic radiation acts on a crystal, the excited region in the crystal has linear dimensions of the order of the wavelength of the radiation. For visible and ultraviolet radiation, the wavelength is considerably larger than the lattice constant. Hence the resultant excited state of the crystal will be described by a wave packet having a very small range of values of wave vectors \mathbf{k} . To a good degree of approximation, such excited states can be treated as the idealized ex-

citon states of (1.12) corresponding to a definite value of \mathbf{k} .

The explicit relation of the energy of the exciton states of the crystal to the wave vector is determined by the summation in (1.10). Section 5 will indicate the methods of calculating these summations. In the region of small values of \mathbf{k} , for each given direction, which we shall denote by the unit vector \mathbf{s} , the excitation energy (1.8) is a quadratic function of the absolute value of \mathbf{k} :

$$E(\mathbf{s}k) = E(\mathbf{s}0) + \frac{\hbar^2 \mathbf{k}^2}{2m^*(\mathbf{s})}. \quad (1.15)$$

Hence, for small \mathbf{k} values, the relation of the energy of the exciton states to the quasimomentum $\hbar \mathbf{k}$ is the same as for some particle having a mass $m^*(\mathbf{s})$. The quantity $m^*(\mathbf{s})$ is called the effective mass of the exciton. In general it depends on its direction of motion and can be either positive or negative.

An excitation encompassing some region of the crystal and described by a wave packet (1.13), in which $w(\mathbf{k})$ differs from zero only when \mathbf{k} is parallel to \mathbf{s} and has an absolute magnitude in some small interval about k_0 , moves through the crystal in the direction of \mathbf{s} with a group velocity

$$v(\mathbf{s}k_0) = \left(\frac{d\omega_f(\mathbf{s}k)}{d\mathbf{k}} \right)_{k=k_0} = -\frac{\hbar k_0}{m^*(\mathbf{s})} \mathbf{s}. \quad (1.16)$$

In order to estimate roughly the quantities cited above, we can consider a crystal whose unit cell is formed by three mutually perpendicular basis vectors \mathbf{a}_i . If we limit ourselves in calculating (1.11) to taking into account the matrix elements M_i for transfer of excitation between molecules adjacent in the directions \mathbf{a}_i , then

$$L(\mathbf{k}) \approx 2 \sum_{i=1}^3 M_i \cos(\mathbf{k} \mathbf{a}_i).$$

In this approximation the effective mass of an exciton moving along \mathbf{a}_i is

$$m_i^* = -\frac{\hbar^2}{2M_i a_i^2}, \quad (1.17)$$

and the group velocity is

$$v_i = 2\hbar^{-1} |M_i| a_i^2 \mathbf{k}. \quad (1.18)$$

The time for transfer of the excitation to the adjacent molecule in the \mathbf{a}_i direction is

$$\tau = \frac{a_i}{v_i} = \frac{\hbar}{2|M_i| k a_i}. \quad (1.19)$$

In the approximation used here, the width of the exciton band is

$$\Delta L_i \equiv \left| L(0) - L\left(\frac{\pi}{a_i}\right) \right| = 4|M_i|.$$

Hence, the absolute value of the effective mass of the exciton can be expressed in terms of the width of the exciton band:

$$|m_i^*| = \frac{2\hbar^2}{a_i^2 \Delta L_i}. \quad (1.20)$$

2. EXCITON STATES IN CRYSTALS HAVING SEVERAL MOLECULES PER UNIT CELL

Let the crystal contain σ molecules per unit cell. Then the positions of the molecules in the crystal are determined by the vectors

$$\mathbf{R}_{n\alpha} = \mathbf{n} + \mathbf{e}_\alpha, \quad \alpha = 1, 2, \dots, \sigma, \quad (2.1)$$

where the lattice vector \mathbf{n} indicates the location of the unit cell, while the vector \mathbf{e}_α indicates the position of molecule number α in the unit cell. We shall assume that a specification of the index α characterizes the orientation of the molecule at the same time. The molecules having the same indices α can be superposed by translations having the lattice periodicity; hence they are called translationally-equivalent.

The energy operator of a crystal with fixed molecules can be written in the form

$$H = \sum_{n\alpha} H_{n\alpha} + \frac{1}{2} \sum'_{n\alpha, m\beta} V_{n\alpha, m\beta}. \quad (2.2)$$

The summation in (2.2) is performed over all of the σN molecules of the crystal. The prime in the second summation indicates that the terms for which simultaneously $\mathbf{n} = \mathbf{m}$ and $\alpha = \beta$ are omitted from the summation.

If all the molecules of the crystal are identical, and the eigenvalues ϵ_f and the eigenfunctions $\varphi_{\mathbf{n}\alpha}^f$ correspond to the energy operators $H_{n\alpha}$, then the wave function of the ground state of the crystal in the zero-order approximation will have the form

$$\Psi^0 = \prod_{n\alpha} \varphi_{n\alpha}^0. \quad (2.3)$$

The energy of this state in the first-order approximation is

$$\mathcal{E}_0 = N\sigma\epsilon_0 + \frac{1}{2} \sum' \int |\varphi_{n\alpha}^0|^2 V_{n\alpha, m\beta} |\varphi_{m\beta}^0|^2 d\tau. \quad (2.4)$$

The states of the crystal in which only the single molecule $n\alpha$ is excited are represented in the zero-order approximation by the wave function

$$\Psi_{n\alpha}^f = \varphi_{n\alpha}^f \prod_{m\beta} \varphi_{m\beta}^0, \quad m\beta \neq n\alpha. \quad (2.3a)$$

Instead of the system of functions (2.3a), it is more convenient to consider another system of orthonormalized functions,

$$\Psi_\alpha^f(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \varphi_{n\alpha}^f e^{i\mathbf{k}\cdot\mathbf{n}}, \quad (2.5)$$

where the wave vector is defined by (1.7).

The excited states of the crystal are determined by the energy operator

$$\Delta H = H - \mathcal{E}_0,$$

where H is given by Eq. (2.2). As represented in terms of the wave functions (2.5), the operator ΔH has the form of a matrix with matrix elements

$$\mathcal{L}_{\alpha\beta}(\mathbf{k}) \equiv \langle \alpha | \Delta H | \beta \rangle = (\Delta \varepsilon_f + D_f) \delta_{\alpha\beta} + L_{\alpha\beta}^f(\mathbf{k}), \quad (2.6)$$

where

$$D_f = \sum'_{n\alpha} \left\{ \int |\varphi_{m\beta}^f|^2 V_{n\alpha, m\beta} |\varphi_{n\alpha}|^2 d\tau - \int |\varphi_{m\beta}^0|^2 V_{n\alpha, m\beta} |\varphi_{n\alpha}^0|^2 d\tau \right\}$$

$$L_{\alpha\beta}^f(\mathbf{k}) = \sum'_{\mathbf{n}} M_{m\beta, n\alpha}^f \exp\{i\mathbf{k}(\mathbf{n} - \mathbf{m})\}. \quad (2.7)$$

In Eq. (2.7),

$$M_{m\beta, n\alpha}^f = \int \varphi_{n\alpha}^0 \varphi_{m\beta}^{f*} V_{n\alpha, m\beta} \varphi_{m\beta}^f \varphi_{n\alpha}^0 d\tau \quad (2.8)$$

are the matrix elements for transfer of the excitation f from the molecule $n\alpha$ to the molecule $m\beta$. These elements are real and symmetric with respect to the indices $n\alpha$ and $m\beta$. In crystals having a center of symmetry, the matrix elements are real functions of \mathbf{k} , symmetric with respect to the indices α and β . We shall call the matrix formed from the matrix elements (2.7) the resonance-interaction matrix, since its matrix elements essentially depend on (2.8), which governs the transfer of excitation from one molecule to another.

The eigenvalues of the operator ΔH having the matrix elements (2.6) determine the energy of the exciton states in the crystal. To ascertain these eigenvalues, we must transform from the basis functions (2.5) to new basis functions $\Phi_\mu^f(\mathbf{k})$, for which the operator ΔH is diagonal. This transformation is carried out using the unitary transformation

$$\psi_\alpha^f(\mathbf{k}) = \sum_{\mu=1}^{\sigma} u_{\alpha\mu} \Phi_\mu^f(\mathbf{k}), \quad (2.9)$$

$$\sum_{\alpha=1}^{\sigma} u_{\alpha\mu}^* u_{\alpha\nu} = \delta_{\mu\nu}. \quad (2.9a)$$

The coefficients of the unitary transformation (2.9) are determined from the equations

$$\sum_{\alpha, \beta} u_{\alpha\nu}^* \mathcal{L}_{\alpha\beta}^f(\mathbf{k}) u_{\beta\mu} = E_\mu^f(\mathbf{k}) \delta_{\nu\mu} \quad (2.10)$$

or the equivalent ones

$$\sum_{\beta=1}^{\sigma} \mathcal{L}_{\alpha\beta}^f(\mathbf{k}) u_{\beta\mu} = E_\mu^f(\mathbf{k}) u_{\alpha\mu}. \quad (2.10a)$$

Equation (2.10a) implies that the σ coefficients $u_{\alpha\mu}$ for fixed μ form the eigenfunctions of the matrix Hermitian operator (2.6) for the eigenvalues $E_\mu^f(\mathbf{k})$. In order to determine these eigenvalues and eigenfunctions, we must solve the system of σ homogeneous equations

$$\sum_{\beta=1}^{\sigma} \mathcal{L}_{\alpha\beta}(\mathbf{k}) u_\beta = E^f(\mathbf{k}) u_\alpha.$$

The condition that this system shall have a nontrivial solution amounts to an equation of degree σ with respect to $E^f(\mathbf{k})$. Since (2.6) is Hermitian, all the roots of this equation $E_\mu^f(\mathbf{k})$, $\mu = 1, 2, 3, \dots, \sigma$, are real. They define σ bands of quasicontinuous excited states of the crystal for each excited state of the free mole-

cule. The μ -th root corresponds to the μ -th column of matrix elements in the matrix $(u_{\alpha\mu})$, and (according to (2.9)), the wave function is

$$\Phi_\mu^f(\mathbf{k}) = \sum_{\alpha} \psi_\alpha^f(\mathbf{k}) u_{\alpha\mu}^*. \quad (2.11)$$

In general, the different bands of excited states can overlap. The greatest and least values of $E_\mu^f(\mathbf{k})$ for a given μ are called the limits of the band. As will be shown below, the spectroscopic properties of the crystal are basically determined only by the regions of the bands corresponding to $\mathbf{k} \approx 0$. If the crystal has a center of symmetry, the following equations hold:

$$E_\mu^f(\mathbf{k}) = E_\mu^f(-\mathbf{k}), \quad \Phi_\mu^f(\mathbf{k}) = \Phi_\mu^f(-\mathbf{k}).$$

To illustrate the relations given above, we shall consider monoclinic crystals of the type of anthracene, naphthalene, etc., which contain two identical molecules per unit cell. The matrix elements of the operator (2.6) for such crystals form a second-order square matrix

$$\begin{pmatrix} \Delta \varepsilon_f + D_f + L_{11}(\mathbf{k}), & L_{12}(\mathbf{k}) \\ L_{21}(\mathbf{k}), & \Delta \varepsilon_f + D_f + L_{22}(\mathbf{k}) \end{pmatrix}, \quad (2.12)$$

where $L_{12} = L_{21}$.

As will be shown in Sec. 4, when the wave vector is perpendicular or parallel to the plane of symmetry of the crystal, the following equations hold:

$$L_{11}(\mathbf{k}) = L_{22}(\mathbf{k}).$$

In this case, the excitation-energy matrix (2.12) can be diagonalized by the transformation matrix

$$u_{\alpha\mu} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1, & 1 \\ 1, & -1 \end{pmatrix}, \quad (2.13)$$

which is independent of the vector \mathbf{k} .

Substituting (2.13) into (2.10) and (2.11), we find that the molecular excitation $\Delta \varepsilon_f$ corresponds in the crystal to a band of excited states

$$E_1^f(\mathbf{k}) = \Delta \varepsilon_f + D_f + L_{11}(\mathbf{k}) + L_{12}(\mathbf{k}) \quad (2.14)$$

having the wave functions

$$\Phi_1^f(\mathbf{k}) = \frac{1}{\sqrt{2}} \{\psi_1^f(\mathbf{k}) + \psi_2^f(\mathbf{k})\} \quad (2.15)$$

and a band of excited states

$$E_2^f(\mathbf{k}) = \Delta \varepsilon_f + D_f + L_{11}(\mathbf{k}) - L_{12}(\mathbf{k}) \quad (2.16)$$

having the wave functions

$$\Phi_2^f(\mathbf{k}) = \frac{1}{\sqrt{2}} \{\psi_1^f(\mathbf{k}) - \psi_2^f(\mathbf{k})\}. \quad (2.17)$$

In the general case,^[2] the matrix elements L_{11} and L_{12} are not analytical functions of \mathbf{k} in the region $\mathbf{k} \approx 0$, and we cannot expand them in series in the neighborhood of this point. However, we can carry out this expansion for a fixed direction of \mathbf{k} . Let \mathbf{s} be a unit vector defining one of the directions for which (2.14) and (2.16) are valid. Then $\mathbf{k} = \mathbf{s}k$, and in the region

of small \mathbf{k} , we can write

$$E_1(s\mathbf{k}) = E_1(s_0) + \frac{\hbar^2 \mathbf{k}^2}{2m_1^*(s)}, \quad E_2(s\mathbf{k}) = E_2(s_0) + \frac{\hbar^2 \mathbf{k}^2}{2m_2^*(s)},$$

where $m_1^*(\mathbf{s})$ and $m_2^*(\mathbf{s})$ are the effective masses of the exciton states in the direction of \mathbf{s} , as determined by the equations

$$\frac{1}{m_1^*(\mathbf{s})} = \hbar^2 \left\{ \frac{\partial^2}{\partial k^2} [L_{11}(s\mathbf{k}) + L_{12}(s\mathbf{k})] \right\}_{\hbar=0},$$

$$\frac{1}{m_2^*(\mathbf{s})} = \hbar^2 \left\{ \frac{\partial^2}{\partial k^2} [L_{11}(s\mathbf{k}) - L_{12}(s\mathbf{k})] \right\}_{\hbar=0}.$$

In general, the effective mass of an exciton depends on its direction of motion and on which exciton band it belongs to. If the following inequality is satisfied:

$$\left| \left\{ \frac{\partial^2}{\partial k^2} L_{11}(s\mathbf{k}) \right\}_{\hbar=0} \right| < \left| \left\{ \frac{\partial^2}{\partial k^2} L_{12}(s\mathbf{k}) \right\}_{\hbar=0} \right|,$$

the effective masses of the excitons in the two bands will be of opposite signs in the region of $\mathbf{k} \approx 0$. If the converse inequality holds, the two effective masses will have the same sign.

If the unit cell of the crystal contains two unlike molecules, or the direction of the wave vector is not perpendicular to the symmetry plane, nor lie in this plane, then $L_{11}(\mathbf{k})$ can differ from $L_{22}(\mathbf{k})$. In this case, upon solving the system of equations (2.10a), we obtain

$$E_\mu(\mathbf{k}) = \Delta\varepsilon_f + D_f + \frac{L_{11} + L_{22}}{2} + \frac{(-1)^\mu}{2} \sqrt{(L_{11} - L_{22})^2 + 4L_{12}^2},$$

$$(u_{\alpha\mu}) = \begin{pmatrix} \cos \frac{\gamma}{2} & \sin \frac{\gamma}{2} \\ \sin \frac{\gamma}{2} & -\cos \frac{\gamma}{2} \end{pmatrix}, \quad (2.18)$$

where γ is given by the equation

$$\tan \gamma = \frac{2L_{12}}{L_{11} - L_{22}}.$$

Using (2.11), we find the wave functions of the exciton states corresponding to the excitation energies (2.18):

$$\Phi_1(\mathbf{k}) = \psi_1(\mathbf{k}) \cos \frac{\gamma}{2} + \psi_2(\mathbf{k}) \sin \frac{\gamma}{2},$$

$$\Phi_2(\mathbf{k}) = \psi_1(\mathbf{k}) \sin \frac{\gamma}{2} - \psi_2(\mathbf{k}) \cos \frac{\gamma}{2}.$$

When $|L_{11} - L_{22}| \gg |L_{12}|$, the value of $\gamma \sim 0$, and the functions $\Phi_1(\mathbf{k}) \approx \psi_1(\mathbf{k})$ and $\Phi_2(\mathbf{k}) \approx -\psi_2(\mathbf{k})$ correspond to states having excitation energies

$$E_1 = \Delta\varepsilon + D + L_{11}(\mathbf{k}), \quad E_2 = \Delta\varepsilon + D + L_{22}(\mathbf{k}).$$

In this case, the molecules of orientation (or type) 1 take part in the formation of the excited state independently of the molecules of orientation (or type) 2. If the following inequality holds:

$$|L_{11} - L_{22}| \ll |L_{12}|,$$

then $\gamma \approx \pi/2$, and the wave functions and excitation energies will differ little from the corresponding values determined by Eqs. (2.14)–(2.17).

Thus, in crystals containing two molecules per unit cell, one non-degenerate state of the free molecule

corresponds to two bands of excited states, rather than one. This splitting was first discussed by Davydov, [3–5] and is usually called [2,6–12] Davydov splitting to distinguish it from the splitting effect studied by Bethe, [13] or Bethe splitting, in degenerate energy levels of atoms and molecules in crystals under the influence of the internal electric fields of the crystal.

When the energy of the excited states of the crystal is determined by (2.14) and (2.15), the absolute size of the splitting for a fixed value of the wave vector is

$$|\Delta E(\mathbf{k})| \equiv |E_1(\mathbf{k}) - E_2(\mathbf{k})| = 2|L_{12}(\mathbf{k})|. \quad (2.19)$$

If the unit cell of the crystal contains σ molecules, the excitation energy of the crystal will be broken down into σ bands of excited states, whose energies and wave functions (2.11) are determined by solving the system of σ homogeneous equations (2.10) for each value of the wave vector \mathbf{k} . In the general case, such computations are complicated. However, they become considerably simpler in special cases. For example, in crystals consisting of identical molecules, the diagonal matrix elements $\mathcal{L}_{\alpha\alpha}(\mathbf{k})$ of the operator (2.6) are the same (see Sec. 4) for all values of α for all directions of the wave vector \mathbf{k} perpendicular to or lying in the symmetry planes of the crystal. In this case, all the matrix elements of the unitary matrix ($u_{\alpha\mu}$) are independent of \mathbf{k} , and have the same absolute value, i.e.,

$$|u_{\alpha\mu}|^2 = \text{const}. \quad (2.20)$$

In centrosymmetric crystals, the operators $L_{\alpha\beta}(\mathbf{k})$ are real, since they are Hermitian and symmetric. Hence, the coefficients $u_{\alpha\mu}$, being the solutions of Eqs. (2.10a), can also be chosen as being real. In such cases, for the wave-vector directions indicated above, the conditions of unitarity (2.9a) and the conditions (2.20) are reduced to the equations

$$\sum_{\alpha} u_{\alpha\mu} u_{\alpha\nu} = \delta_{\nu\mu}, \quad u_{\alpha\mu}^2 = \text{const}, \quad (2.21)$$

which unambiguously determine all the values of $u_{\alpha\mu}$. For example, in crystals having a center of symmetry and containing four identical molecules per unit cell, we find from the conditions (2.20)

$$(u_{\alpha\mu}) = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & -1 & -1 \end{pmatrix}.$$

3. THE SPECIFIC ELECTRIC MOMENT OF TRANSITION FROM THE GROUND STATE OF THE CRYSTAL TO THE EXCITON STATE

The exciton states are manifested in the absorption of light by the crystal, and in certain other ways of excitation of crystals. In line with the fact that the wavelength of light exceeds the lattice constant by a factor of thousands or hundreds, at low temperatures light mainly excites excitons having wave vectors $\mathbf{k} \approx 0$.

If the molecules and the crystal have a center of symmetry, then in the ground and excited states, their specific electric moment will be zero. A transition to an excited state of the exciton type is characterized by the specific electric moment of the transition. The direction of the electric moment of the transition determines the electric field direction of the light wave that brings about the transition. Hence we must calculate the specific electric moment of the transition to the exciton state in studying theoretically the absorption of polarized light by the crystal.

The operator for the specific electric dipole moment of the unit cell of the crystal can be given in the coordinate representation by the expression

$$\mathbf{p}_n = \frac{e}{v} \sum_{\alpha=1}^{\sigma} \mathbf{r}(\mathbf{n}\alpha), \quad (3.1)$$

where $v = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ is the volume of the unit cell, and $\mathbf{er}(\mathbf{n}\alpha)$ is the operator for the electric dipole moment of the molecule located in the n -th cell at the site α .

According to (2.11) and (2.5), the excitation energy $E_{\mu}(\mathbf{k})$ of an exciton having a wave vector \mathbf{k} corresponds to the wave function

$$\Phi_{\mu}(\mathbf{k}) = N^{-1/2} \sum_{\mathbf{m}} e^{i\mathbf{k}\mathbf{m}} \sum_{\alpha} \psi_{\mathbf{m}\alpha} u_{\alpha\mu}^*. \quad (3.2)$$

The ground state of the crystal is characterized by the function (2.3). Consequently, the specific electric moment of the transition between these states is

$$\langle \Phi_{\mu}(\mathbf{k}) | \mathbf{p}_n | \psi^0 \rangle = \frac{e^{i\mathbf{k}\mathbf{n}}}{v \sqrt{N}} \sum_{\alpha} \mathbf{d}_{\alpha} u_{\alpha\mu}^*, \quad (3.3)$$

where

$$\mathbf{d}_{\alpha} = \int \varphi_{n\alpha}^* \mathbf{er}(\mathbf{n}\alpha) \varphi_{n\alpha}^0 d\tau$$

is the electric dipole moment of the transition in the molecule α .

If we know the coefficients $u_{\alpha\mu}$ and the direction of the transition dipole moment in each molecule in the unit cell, we can calculate (3.3). Since in optical transitions states having $\mathbf{k} \approx 0$ are excited, we must know the value of (3.3) for $\mathbf{k}_{\alpha\mu} = 0$.

In crystals having two identical molecules in the unit cell, the coefficients $u_{\alpha\mu}$ form the matrix (2.13) for all directions of the exciton wave vector lying in the symmetry plane of the crystal or normal to it. In this case,

$$v \sqrt{2N} \langle \Phi_{\mu}(0) | \mathbf{p}_n | \psi^0 \rangle = \begin{cases} \mathbf{d}_1 + \mathbf{d}_2, & \text{if } \mu = 1, \\ \mathbf{d}_1 - \mathbf{d}_2, & \text{if } \mu = 2. \end{cases}$$

Hence, the moments of the transitions to the exciton bands $\mu = 1$ and $\mu = 2$ are mutually perpendicular. Thus the excitations corresponding to the different bands of exciton states have not only differing energies, but also differing polarizations, although they belong to one energetically non-degenerate state in the

free molecule. This polarization is characterized by the symmetry properties of the crystal, and emphasizes the collective nature of the exciton states, which are due to the interactions between molecules. If a molecular crystal were a simple assemblage of oriented anisotropic molecules (the oriented-gas model), the polarization mentioned above would not occur.

Figure 1 illustrates this statement schematically. The left side of the diagram covers the case corresponding to the oriented-gas model. In this case, the directions of the transition dipole moments of the individual molecules are independent, and correspond to a single frequency ω_0 . The intensity of absorption and emission of light of frequency ω_0 will vary little with change in polarization. The right side of Fig. 1 shows the case closer to reality. Both molecules participate in the absorption and emission of light. The frequency ω_1 corresponds to a collective excitation in which the dipole moment of the unit cell of the crystal (solid arrow) is formed by addition of the transition dipole moments of the molecules (dotted arrows).

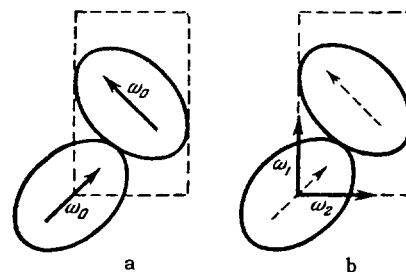


FIG. 1. Dipole moments of the quantum transitions in the crystal. a) Oriented-gas model; b) real crystal.

The frequency ω_2 corresponds to a collective excitation in which the dipole moment of the unit cell of the crystal is the difference of the transition dipole moments of the molecules. Consequently, the frequencies ω_1 and ω_2 will be manifested in the different components of the polarized light.

4. APPLICATION OF GROUP THEORY FOR QUALITATIVE INTERPRETATION OF THE PROPERTIES OF EXCITON STATES

The preceding sections have discussed exciton states corresponding to non-degenerate excited states of the free molecule. In such cases, the calculation of the energy and wave functions of the excitons has been reduced to solving the system of equations (2.10a). If the molecule has degenerate excited states and the crystal has a complex symmetry, such calculations become unwieldy even for specified directions of the wave vector. However, we can establish a number of qualitative properties of the exciton states in crystals without resorting to explicit calculation of the wave functions of the crystal. Rather, we can take into ac-

count the symmetry properties of the crystal and the molecule by using the methods of group theory. The application of group theory considerably simplifies the direct calculations as well. For qualitative interpretation of the properties of exciton states, group theory has been applied by Davydov,^[4] Winston,^[6] and Lubchenko and Rashba.^[14]

The wave functions $\varphi_{n\alpha}$ of the stationary states of a single molecule belong to the different irreducible representations of the symmetry group of the molecule as it occurs in the crystal. Generally, this symmetry group can differ from the symmetry group of the free molecule. It is difficult to calculate the small distortions in the shape of the molecule in the crystal. We shall assume that the functions $\varphi_{n\alpha}$ already take these distortions into account, and we shall study the role of the collective effects arising from the regular arrangement of molecules in the crystal and their resonance interaction. Winston^[6] has proposed that the symmetry group of a molecule as it occurs in a crystal be called the site group, i.e., the symmetry group of the site in the crystal occupied by the molecule.

The application of group theory in studying exciton states in crystals is essentially involved with taking their symmetries into account. The basic symmetry elements of crystals of infinite dimensions include: parallel translations in certain directions by definite distances, rotations about certain directions by definite angles, and mirror reflections. The set of all symmetry elements forms the space group. The space group has a translation subgroup formed by all the lattice vectors $\mathbf{n} = \sum_i n_i \mathbf{a}_i$. The set of all symmetry elements transforming any vector of the translation subgroup into any vector of the same subgroup forms the factor group.

According to the general rules of quantum mechanics,^[15,16] the wave functions of the stationary states of a quantum system are bases for the irreducible representations of the group of symmetry operations which leave the Hamiltonian operator of the system invariant. Hence, the wave functions (2.11) of the exciton states of a crystal must form bases for the separate irreducible representations of the space group of the symmetry of the crystal. This requirement imposes rather rigid limitations on the possible forms of the eigenfunctions.

The wave function (2.3) of the ground state of the crystal usually belongs to the totally-symmetric representation of the space group of the crystal, since the wave functions of the ground states of almost all molecules belong to the totally-symmetric representation. The wave function (2.3a) corresponding to the state of the crystal in which only one molecule is in the excited state forms a basis for some irreducible representation Γ_f of the symmetry group of the molecule (or more exactly, the site group). If the irreducible representation is one-dimensional, then the

molecular level f is non-degenerate, and the exciton states of the crystal, according to (2.11), are represented by the functions

$$\Phi_{\mu}^f(\mathbf{k}) = \sum_{\alpha} \psi_{\alpha}^f(\mathbf{k}) u_{\alpha\mu}^*, \quad (4.1)$$

where

$$\psi_{\alpha}^f(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \psi_{n\alpha}^f e^{i\mathbf{k}\mathbf{n}}. \quad (4.2)$$

If the excited state of the molecule belongs to an irreducible representation Γ_f of dimension s , then the molecular level f corresponds to s wave functions $\psi_{n\alpha}^{f\gamma}$, which we shall distinguish by the second superscript γ . In this case, the exciton states in the crystal are represented by the functions

$$\Phi_{\mu}^f(\mathbf{k}) = \sum_{\alpha, \gamma} \psi_{\alpha}^{f\gamma}(\mathbf{k}) u_{\alpha\mu}^{*\gamma}, \quad (4.3)$$

where

$$\psi_{\alpha}^{f\gamma}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \psi_{n\alpha}^{f\gamma} e^{i\mathbf{k}\mathbf{n}}, \quad (4.4)$$

$$\psi_{n\alpha}^{f\gamma} = \varphi_{n\alpha}^{f\gamma} \prod_{m\beta} \varphi_{m\beta}^0, \quad m\beta \neq n\alpha. \quad (4.5)$$

The exciton functions (4.1) and (4.4) are defined for each value of the wave vector \mathbf{k} in the first Brillouin zone. The wave vector \mathbf{k} characterizes the corresponding irreducible representation of the translation subgroup. Since the symmetry elements of the translation subgroup commute, all of its irreducible representations are one-dimensional. Each wave vector \mathbf{k} can be related to a certain number of vectors \mathbf{k}_i that transform into one another upon application of the symmetry operations of the factor group of the crystal. The set of all such vectors is usually called the \mathbf{k} -representation star.^[17] Each vector of the \mathbf{k} -representation star is transformed by any symmetry element of the space group of the crystal into a vector also belonging to the star.

For illustration, we shall consider a crystal of the monoclinic system having the point-group symmetry C_{2h} . This group contains three symmetry elements besides the identity element: inversion, 180° rotation about the monoclinic axis, and reflection in a plane normal to the monoclinic axis. Hence, the \mathbf{k} -representation star for such a crystal will generally consist of four vectors: \mathbf{k}_1 , \mathbf{k}_2 , $-\mathbf{k}_1$, and $-\mathbf{k}_2$, where \mathbf{k}_2 is obtained from \mathbf{k}_1 by a 180° rotation about the monoclinic axis. The \mathbf{k} -representation star corresponding to a wave vector \mathbf{k} lying along the monoclinic axis or in the plane normal to it will consist of only two vectors, \mathbf{k} and $-\mathbf{k}$.

Owing to the equivalence (with respect to the symmetry properties of the potential field of the crystal) of the wave vectors belonging to a single \mathbf{k} -representation star, the wave functions (4.1) and (4.3) maintain their form for all vectors \mathbf{k}_i of the given star. In

crystals having a symmetry center, $\Phi_\mu(\mathbf{k}) = \Phi_\mu(-\mathbf{k})$. Hence, for all \mathbf{k} -representations containing only two vectors, \mathbf{k} and $-\mathbf{k}$, the functions (4.3) coincide identically for the two vectors of the star.

Let \mathbf{k} in (4.3) be one of the vectors of a \mathbf{k} -representation star; then the coefficients $u_{\alpha\mu}^\gamma$ must be the eigenfunctions of a Hermitian operator having matrix elements

$$\mathcal{L}_{\alpha\beta}^{\gamma}(\mathbf{k}) = (\Delta\varepsilon_f + D_f) \delta_{\alpha\beta} + L_{\alpha\beta}^{\gamma}(\mathbf{k}),$$

where \mathbf{k} is one of the vectors of the same star. Owing to the symmetry properties of the crystal, only the designations of the elements change in this matrix as we go from one vector in the star to another. For example, in the monoclinic system with two identical molecules per unit cell, two vectors \mathbf{k}_1 and \mathbf{k}_2 that transform into one another upon application of the operation of 180° rotation about the monoclinic axis correspond to two matrices satisfying the equation

$$\begin{pmatrix} \Delta\varepsilon + D + L_{11}(\mathbf{k}_1), & L_{12}(\mathbf{k}_1) \\ L_{21}(\mathbf{k}_1), & \Delta\varepsilon + D + L_{22}(\mathbf{k}_1) \end{pmatrix} = \begin{pmatrix} \Delta\varepsilon + D + L_{22}(\mathbf{k}_2), & L_{21}(\mathbf{k}_2) \\ L_{12}(\mathbf{k}_2), & \Delta\varepsilon + D + L_{11}(\mathbf{k}_2) \end{pmatrix}. \quad (4.6)$$

Equation (4.6) implies that for all \mathbf{k} directions belonging to vectors \mathbf{k} lying in the symmetry plane of the crystal or normal to it (when $\mathbf{k}_1 = \mathbf{k}_2$), the following equations hold:

$$L_{12}(\mathbf{k}) = L_{21}(\mathbf{k}), \quad L_{11}(\mathbf{k}) = L_{22}(\mathbf{k}). \quad (4.7)$$

Exciton states having wave vectors \mathbf{k} for which Eqs. (4.7) hold are characterized by wave functions (4.3) with coefficients $u_{\alpha\mu}^\gamma$ independent of the value of \mathbf{k} . These coefficients are determined directly by group-theory methods from the condition that the functions Φ_μ^f should form bases for the irreducible representations of the space group of the crystal.

In experimental studies, one usually uses thin crystal plates having their plane of development normal to the symmetry plane of the crystal. One studies the transmission of light incident normal to these plates. Under these conditions, the light wave excites excitons having wave vectors lying in the symmetry plane. As was shown above, for the wave functions of these excitons, the coefficients $u_{\alpha\mu}^\gamma$ do not depend on the wave vector. Bearing in mind the fact that in the absorption of light by crystals (at low temperatures) only excitons with small values of the wave vector will have appreciable values, we should consider only functions of the form

$$\Phi_\mu^f(0) = \sum_{\alpha} \psi_{\alpha}^{\gamma} u_{\alpha\mu}^{\gamma}. \quad (4.8)$$

These functions form a basis for the irreducible representations of the factor group of the crystal.

For a qualitative analysis of the possible alterations in the energy states of the molecules when they form a crystal, we need not calculate the explicit form of the functions (4.8). It is sufficient to ascertain the nature of the irreducible representations of the factor

group to which the functions (4.8) corresponding to each energy excitation of the molecule belong.

We shall assume that the f -th excited state of the molecule is characterized by a wave function belonging to the irreducible representation Γ_f of the symmetry group of the molecule (the local group), and we know (see, e.g., [15,16]) the characters $X_f(R_m)$ of this representation for each symmetry element R_m . We shall denote by the letter R one of the symmetry operations of the factor group of the crystal. If the symmetry operation R does not coincide with any of the symmetry elements of the molecule, then the action of R will interchange the molecules in the crystal. Hence, the corresponding representation of the factor group will be given by a matrix without diagonal elements, and the character of this representation will be zero. If the symmetry operation R coincides with one of the operations R_m of the symmetry group of the molecule, then the action of R will not displace the molecules, and the corresponding representation of the factor group will be given by a diagonal matrix, and the character of this representation will be the sum of the characters of the corresponding representations of the molecule. Thus the character of a representation of the factor group corresponding to a molecular term of the irreducible representation Γ_f can be obtained for each symmetry element of the factor group by the rule

$$\chi(R) = \sum_{R_m} X_f(R_m) \delta_{R,R_m}, \quad (4.9)$$

where δ_{ij} is the Kronecker delta.

In the general case, the calculated characters refer to a reducible representation of the factor group. They can be expressed in terms of the characters χ_l of the irreducible representations of this group:

$$\chi(R) = \sum_l n_l \chi_l(R), \quad (4.10)$$

where the coefficients n_l are given by the formula

$$n_l = \frac{1}{\sigma h} \sum_R \chi_l^*(R) \chi(R). \quad (4.11)$$

Here h is the number of symmetry operations in the group of the molecule, and σ is the number of molecules per unit cell.

As an example, we shall consider the application of the relations derived above to the anthracene crystal. This crystal belongs to the monoclinic system with basis vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} , with $\mathbf{a} \perp \mathbf{b}$. There are two molecules in the unit cell. The basis vector \mathbf{b} determines the direction of the monoclinic axis. Experimentally, one uses light incident to the \mathbf{ab} plane of the crystal. The factor group is isomorphic to the point group C_{2h} . The characters of the irreducible representations of this group are given in Table I. The first column of Table I gives the symbols for the irreducible representations. The last column gives the projections x , y , and z of an arbitrary vector \mathbf{r} on the axes of a

Table I. Characters of the group C_{2h}

	E	C_2^b	i	σ^b	
A_g	1	1	1	1	
A_u	1	1	-1	-1	z
B_g	1	-1	1	-1	
B_u	1	-1	-1	1	x, y

Cartesian system in which the z axis lies along the monoclinic axis of the crystal.

The anthracene molecule has a symmetry corresponding to the point group D_{2h} . The characters of the irreducible representations of this group are given in Table II. The last column of Table II gives the projections of the vector \mathbf{r} on the axes ξ , η , and ζ of the coordinate system associated with the molecule. To get a rough approximation, we can represent the anthracene molecule as a triaxial ellipsoid. We shall assume that the coordinate axis ζ lies along the long axis, and the ξ axis along the shortest axis of the molecule.

Table II. Characters of the group D_{2h}

	E	C_2^ξ	C_2^η	C_2^ζ	i	σ^ξ	σ^η	σ^ζ	
A_{1g}	1	1	1	1	1	1	1	1	
B_{1g}	1	-1	-1	1	1	-1	-1	1	
A_{2g}	1	1	-1	-1	1	1	-1	-1	
B_{2g}	1	-1	1	-1	1	-1	1	-1	
A_{1u}	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	-1	-1	1	-1	1	1	-1	
A_{2u}	1	1	-1	-1	-1	-1	1	1	
B_{2u}	1	-1	1	-1	-1	1	-1	1	ξ, η, ζ

We shall consider an energy term of the molecule belonging to the irreducible representation B_{2u} . The excitation B_{2u} corresponds to a transition electric dipole moment lying along the intermediate axis of the molecule. The group C_{2h} and the symmetry group of the molecule have only two coinciding symmetry elements, E and i . Using Eq. (4.9) and the values of the characters of the irreducible representation B_{2u} of Table II, we find the characters:

$$\chi(E) = 2X_{B_{2u}}(E) = 2, \quad \chi(C_2^b) = 0,$$

$$\chi(i) = 2X_{B_{2u}}(i) = -2, \quad \chi(\sigma^b) = 0.$$

In addition, using (4.11), we can obtain the expansion (4.10) in the form

$$\chi = \chi_{A_u} + \chi_{B_u}. \quad (4.12)$$

It follows from (4.12) that a molecular term belonging to the irreducible representation B_{2u} corresponds in the crystal to two types of excitons belonging to the irreducible representations A_u and B_u , respectively.

Since the ground state of the crystal belongs to the totally-symmetric representation A_g , the electric di-

pole moments of transitions to the exciton states will transform in the same way as the wave functions of the excitons. Hence, the irreducible representations corresponding to the exciton wave functions will characterize the directions of the dipole moments of the transitions to the exciton states. In particular, for anthracene the exciton state belonging to the irreducible representation A_u involves a dipole moment lying along the monoclinic axis, while the exciton state of type B_u is characterized by a transition moment lying in the xy plane, i.e., in the plane normal to the monoclinic axis.

5. CALCULATION OF THE RESONANCE-INTERACTION MATRIX

It was shown in Sec. 2 that in exciton states having a wave vector \mathbf{k} , the effect of the interaction between the molecules of the crystal is manifested through the quantity D_f and the matrix elements of the resonance-interaction matrix $L_{\alpha\beta}(\mathbf{k})$, which are defined by the summation (2.7).

In calculating them, one expands the operator for the interaction energy $V_{\mathbf{n}\alpha, \mathbf{m}\beta}$ of two molecules (the Coulomb interaction of the electrons and nuclei of the two molecules) in a series of inverse powers of the distance between the centers of the molecules. The individual terms of such a series characterize the multipole-multipole interactions of various orders. If the molecules are neutral, the first term of the series gives the dipole-dipole interaction. In centrosymmetric neutral molecules, the mean value of the dipole moment in any stationary state is zero. Hence, only the terms beginning with the quadrupole-quadrupole interaction will contribute to D_f . In this case, the energy of interaction between the two molecules, and hence also its variation upon excitation of one molecule, will decline as R^{-5} with increasing intermolecular distance R . Hence in calculating D_f , we can take into account the interaction of a given molecule with only its nearest neighbors.

In this expansion of $V_{\mathbf{n}\alpha, \mathbf{m}\beta}$, the matrix elements (2.8) entering into the resonance-interaction matrix

$$L_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{n}} M_{0\beta, \mathbf{n}\alpha} e^{i\mathbf{k}\mathbf{n}}, \quad (5.1)$$

are also represented in series form. If the electric dipole moment in the molecule

$$\mathbf{d}_\alpha = \int \varphi_{\mathbf{n}\alpha}^* \mathbf{e}r(\mathbf{n}\alpha) \varphi_{\mathbf{n}\alpha} d\tau \quad (5.2)$$

differs from zero, we can keep only the first non-vanishing term in the series, which will correspond to the dipole-dipole interaction of the transition moments (5.2). In this approximation,

$$M_{0\beta, \mathbf{n}\alpha} = R^{-5} \{(\mathbf{d}_\alpha^* \mathbf{d}_\beta) \mathbf{R}_{\mathbf{n}\alpha\beta}^2 - 3(\mathbf{d}_\alpha^* \mathbf{R}_{\mathbf{n}\alpha\beta})(\mathbf{d}_\beta \mathbf{R}_{\mathbf{n}\alpha\beta})\}, \quad (5.3)$$

where $\mathbf{R}_{\mathbf{n}\alpha\beta}$ is the vector joining the centers of the molecules 0β and $\mathbf{n}\alpha$.

Table III

Molecule	Transition, frequency, cm^{-1}	Oscillator strength	$10^8 R$, cm	$10^8 l$, cm	$\eta = l/R$
Anthracene . . .	$\sim 40\,000$	2.3	~ 9	1.3	0.14
Anthracene . . .	$\sim 26\,000$	0.3	~ 9	1.0	0.11
Naphthalene . . .	$\sim 32\,000$	0.001	~ 7	0.03	0.004

We shall introduce a rectangular system of coordinates x, y, z , with z lying along the vector $\mathbf{R}_{n\alpha\beta}$, and we shall denote by $\cos \theta_{0\beta}^x, \dots, \cos \theta_{n\alpha}^z$, the cosines of the angles between the x, y, z axes and the transition electric moments of the corresponding molecules; then

$$M_{0\beta, n\alpha} = \mathbf{R}_{n\alpha\beta}^{-3} |d_\alpha|^2 \{ \cos \theta_{0\beta}^x \cos \theta_{n\alpha}^x + \cos \theta_{0\beta}^y \cos \theta_{n\alpha}^y - 2 \cos \theta_{0\beta}^z \cos \theta_{n\alpha}^z \}. \quad (5.4)$$

If all the molecules in the unit cell are identical, then the quantity $|d_\alpha|^2$ will not depend on the subscript α , and can be expressed in terms of the oscillator strength F of the corresponding transition in a single molecule, the circular frequency ω of the transition, and the mass m of an electron:

$$|d_\alpha|^2 = \frac{e^2 \hbar F}{2m\omega}. \quad (5.5)$$

It follows in particular from (5.4) and (5.5) that in crystals having one molecule in a unit cell formed by three mutually-perpendicular basis vectors \mathbf{a}_i , the matrix element for transfer of excitation to a neighboring molecule in the direction of a basis vector \mathbf{a}_i is roughly equal to

$$M_i = \frac{e^2 \hbar F}{2m\omega a_i^3}, \quad (5.5a)$$

where F is the oscillator strength of the transition of frequency ω , having a dipole moment normal to \mathbf{a}_i .

In a molecular crystal the molecules are in direct contact with one another. Consequently, a doubt might arise as to the validity of expanding the Coulombic-interaction operator $V_{0\beta, n\alpha}$ in a series of inverse powers of the distance between the centers of the molecules. However, we must bear in mind the fact that actually the parameter of smallness in this case is not the ratio of the dimensions of the molecules to their mutual distance (this ratio is near unity for adjacent molecules), but the ratio η of the length $l = (1/e)d_\alpha$ of the transition dipole moment (5.2) to the intermolecular distance R . Table III gives the corresponding values for several typical electronic transitions.

We see from Table III that for the very strong transitions occurring in the far ultraviolet for anthracene, the parameter η is small even for adjacent molecules.

It follows directly from Eq. (5.4) that the matrix elements are real and symmetric, and in the dipole approximation they are proportional to the oscillator strength of the transition and to a geometric factor depending on the distance between the molecules and their

mutual orientation. The matrix elements (5.1) of the resonance-interaction matrix are also proportional to the oscillator strength of the molecular transition; they are symmetrical with respect to the subscripts α and β , and are real for centrosymmetric crystals.

We can calculate the series in (5.1) by termwise summation of the resonance interactions of the given molecule 0β with all the molecules $n\alpha$ lying on spheres of continually-increasing radii R . As R increases, the number of terms increases in proportion to R^2 , while the absolute value of each term declines as R^{-3} . Consequently, the series (5.1) converges rather slowly. Craig and Walsh^[18] consider that in calculating (5.1) it is enough to take into account only the molecules lying within a sphere of radius $\sim 20 \text{ \AA}$; on the contrary, Fox and Yatsiv^[2] state that one must take into account the contribution of molecules even outside this sphere.* Numerical calculations of the series (5.1) with $\mathbf{k} \approx 0$ have been performed in a number of studies.^[18-25]

One can also calculate the series (5.1) by a method analogous to that first applied by Ewald^[26] in studying ionic crystals. To do this, we shall represent (5.1) in the form

$$L_{\alpha\beta}(\mathbf{k}) = -d_\beta \mathcal{E}_\alpha(\beta), \quad (5.6)$$

where

$$\mathcal{E}_\alpha(\beta) = \sum_n R_{n\alpha\beta}^{-5} [3\mathbf{R}_{n\alpha\beta} (\mathbf{d}_\alpha^* \mathbf{R}_{n\alpha\beta}) - \mathbf{d}_\alpha^* R_{n\alpha\beta}^2] e^{i\mathbf{k}\mathbf{n}} \quad (5.7)$$

is the electric-field intensity created by all the molecules α at the site of the molecule 0β .

One can show that the field (5.7) can be written in the form of two terms for small values of the wave vector \mathbf{k} :

$$\mathcal{E}_\alpha(\beta) = -\frac{4\pi}{v} \mathbf{s} (\mathbf{s} \mathbf{d}_\alpha^*) + \mathcal{E}_{\text{int}}^\alpha(\beta), \quad (5.8)$$

where \mathbf{s} is a unit vector in the direction of \mathbf{k} ; $\mathcal{E}_{\text{int}}^\alpha$ is

*In cases in which, for small \mathbf{k} values, even molecules located at distances of the order of the wavelength of the light can contribute appreciably to the series in (5.1), we must take into account the retardation of the interaction between molecules. That is, we must replace the Coulomb interaction operator by a retarded-interaction operator. A study of how this effect influences the van der Waals interaction shows that it leads to a more rapid decline in the interaction energy at large distances. The role of this effect in the theory of excitons has been poorly studied thus far.

the part of the field intensity not depending on the direction of \mathbf{k} ; and v is the volume of the unit cell.

Substituting (5.8) into (5.7), we have

$$L_{\alpha\beta}(\mathbf{k}) = L_{\beta\alpha}(\mathbf{k}) = \frac{4\pi}{v} (\mathbf{s}d_{\beta}) (\mathbf{s}d_{\alpha}^*) - d_{\beta} \mathcal{E}_{\text{int}}^{\alpha}(\beta).$$

Let us consider the diagonal matrix elements

$$L_{\alpha\alpha}(\mathbf{k}) = \frac{4\pi}{v} |\mathbf{s}d_{\alpha}|^2 - d_{\alpha} \mathcal{E}_{\text{int}}^{\alpha}(\alpha). \quad (5.9)$$

If all the molecules in the crystal are identical, the configuration of the crystal about each molecule is independent of the index α . In this case

$$d_{\alpha} \mathcal{E}_{\text{int}}^{\alpha}(\alpha) = d_{\beta} \mathcal{E}_{\text{int}}^{\beta}(\beta) \quad \alpha, \beta = 1, 2, \dots, \sigma.$$

However, the first term in (5.9) depends on the direction of \mathbf{s} with respect to the dipole moment of the quantum transition in the molecule. The directions of the transition dipole moments in anisotropic molecules are determined by their orientation. The molecules contained within one unit cell generally have differing orientations. Hence, the scalar product $\mathbf{s} \cdot d_{\alpha}$ will not equal the scalar product $\mathbf{s} \cdot d_{\beta}$ for an arbitrary direction of the vector \mathbf{s} . However, for directions of the \mathbf{k} vectors normal to the symmetry plane of the crystal, the conditions are obeyed:

$$\mathbf{s}d_{\alpha} = \mathbf{s}d_{\beta} \quad \text{for all } \alpha, \beta = 1, 2, \dots, \sigma.$$

In this case, according to (5.9), equations are obeyed at small \mathbf{k} values coinciding with Eqs. (4.9), which have been proved for all absolute values of \mathbf{k} .

It is highly important that in the general case the value of (5.1) depends on the wave vector \mathbf{k} . This indicates that in the region $\mathbf{k} \approx 0$ this expression is not an analytical function, and it cannot be expanded in a power series in k_x , k_y , and k_z about the point $\mathbf{k} = 0$. However, for every given direction of \mathbf{k} , the function $L_{\alpha\beta}(\mathbf{k})$ is an analytic function of the absolute magnitude of \mathbf{k} and can be expanded in a power series in $|\mathbf{k}|$.

In certain molecules the electronic 0-0 transitions in the near ultraviolet are forbidden (benzene) or have very low probabilities (see Table III, naphthalene). In studying the corresponding excited states in crystals, we must calculate the matrix elements (5.1) with account taken of interactions of quadrupole-quadrupole or even octopole-octopole type. The contributions made by such types of interactions to the matrix elements (5.3) will decline rapidly with increasing distance between the molecules (as R^{-5} and R^{-7} for quadrupole-quadrupole and octopole-octopole interactions, respectively). These terms make a relatively small contribution to the matrix elements (5.1) of the resonance interaction, practically independent of \mathbf{k} when its absolute value is not very large.* However,

*If the excitation energy $E_{\mu}(\mathbf{k})$ in the band μ has maximum and minimum values for \mathbf{k}_1 and \mathbf{k}_2 , respectively, the width of this band is $E_{\mu}(\mathbf{k}_1) - E_{\mu}(\mathbf{k}_2)$. When $E_{\mu}(\mathbf{k})$ depends only slightly on \mathbf{k} , the

we must bear in mind the fact that the molecules in the crystal are somewhat deformed by the local field of the crystal (close packing). In line with this, a forbidden transition in the free molecule can become allowed in the crystal (see Sec. 7, benzene), while a weak transition can be strengthened (see Sec. 7, naphthalene). In these cases the role of the dipole-dipole interaction in the matrix elements (2.8) calculated for the altered wave functions is enhanced, and the dependence on the wave vector \mathbf{k} in the resonance-interaction matrix (5.1) becomes appreciable. That is, the molecular excitation in the crystal is transformed into a band of excited states, or an excitation involving excitons.

6. EXCITON AND LOCALIZED EXCITATIONS IN A CRYSTAL

We have considered in the previous sections in studying the excited states of a crystal that the molecules are rigidly fixed at sites in an ideal crystal lattice. In this approximation, each intramolecular excitation of the free molecular corresponds, in a crystal containing σ molecules per unit cell, to σ bands of quasicontinuous excited states (excitons) $E_{\mu}(\mathbf{k})$. The energy sublevels in each band differ in their values of the wave vector \mathbf{k} , the number of which equals the number of unit cells in the crystal [see (1.7)].

Under the influence of an electromagnetic wave having an electric field intensity

$$\mathcal{E} = \mathcal{E}_0 \exp \{i(\mathbf{Q}\mathbf{r} - \omega t)\}$$

in an ideal crystal of large dimensions (in comparison with the wavelength of the light), exciton states arise for which

$$\text{a) } \mathbf{k} = \mathbf{Q}, \quad (6.1)$$

$$\text{b) } E_{\mu}(\mathbf{k}) = \hbar\omega \quad (6.2)$$

and c) the electric field intensity is parallel to the specific dipole moment of the transition, as discussed in Sec. 3. Condition (6.1) corresponds to the law of conservation of momentum: the momentum of the photon equals the momentum of the exciton. Condition (6.2) defines the law of conservation of energy, and finally, the third condition (polarization) is determined by the vector nature of the electromagnetic field. The requirement that all three of these conditions be satisfied at the same time implies that, with a given direction of propagation and a certain polarization of the

width of the band is small. However, the resonance splitting can be considerable, since it is determined by the difference in excitation energies corresponding to fixed \mathbf{k} (we are usually interested in $\mathbf{k} \approx 0$) in bands differing in the index μ [(see, e.g., (1,19)]. The octopole-octopole and higher multipole interactions play a small role in broadening the bands, but they can have an appreciable value in the resonance splitting of molecular levels when the corresponding dipole-dipole interactions are small. [25, 27-29]

light, only one of the exciton states is excited in the crystal.

We shall now consider what qualitative changes in the energy states and absorption spectra of a crystal can result from taking into account the interaction of the exciton states with phonons, i.e., with the vibrations of the molecules in the crystal. Owing to the interactions of excitons with phonons in the crystal, excited states will be manifested, corresponding to the simultaneous formation of an exciton and a phonon (or several phonons), along with the transitions in which phonons do not participate (direct transitions). A transition from the ground state to such excited states is possible when the following conditions are satisfied simultaneously: a) the law of conservation of energy

$$E_{\mu}(\mathbf{k}) + \hbar\Omega_{\nu}(\mathbf{q}) = \hbar\omega, \quad (6.3)$$

where $\hbar\Omega(\mathbf{q})$ is the energy of a phonon of the branch ν , and \mathbf{q} is its wave vector; b) the law of conservation of momentum

$$\mathbf{k} + \mathbf{q} = \mathbf{Q} \quad (6.4)$$

and c) certain polarization relations.

According to (6.3) and (6.4), transitions involving phonons can go not to just one, but to various sublevels of the exciton bands. This results in a widening of the absorption bands. The intensity distribution in such a band depends on the value of the exciton-phonon coupling with the various branches of the phonon vibrations. The theory of this phenomenon has been developed on the basis of certain models by Davydov, Rashba, and Lubchenko^[30-32] for molecular crystals, and by Toyozawa^[33] for ionic crystals.

In addition to broadening the absorption bands, the fact that the molecules in the crystal can be displaced has a considerable effect in some cases on the nature of the excited states of the crystal. In fact, when a molecule goes over to an excited state, the energy of its van der Waals interaction with the surrounding molecules changes. The change in the interaction gives rise to a tendency toward deformation of the crystal structure in the vicinity of the excited molecule. On the other hand, the resonance interaction between identical molecules leads to a "spreading" of the molecular excitation throughout a certain region of the crystal. When the resonance interaction proves to be more essential (small D_f values and heavy molecules), an exciton state is formed in the crystal. In this case, roughly speaking, the excitation is transferred from one molecule to another so rapidly that local deformation of the structure cannot take place. Conversely, when the resonance interactions are weak, the values of D_f are large, or the crystal structure is easily deformed, local deformation of the crystal occurs simultaneously with excitation; such an excited state can be conveniently called a local excitation, since its displacement through the crystal takes place very slowly.

In their properties, local excitations resemble the excitations of impurity molecules in a crystal, where the impurity molecule shows no resonance interaction with the solvent molecules (the impurity concentration being low and its excitation energy differing considerably from the energy of the intrinsic absorption).

Unfortunately, numerical estimation of the quantities determining which type of excited state can be realized is very complex in real crystals. The resonance interaction is characterized by the matrix $L(\mathbf{k})$ with the matrix elements (5.1). This matrix determines the width of the exciton bands. Generally, it is proportional to the oscillator strength of the corresponding transition in the molecule. For very crude estimates, we can use Eq. (5.5a). The quantity D_f can be calculated by Eq. (2.7). The deformability of the crystal structure can be estimated from the frequencies of the phonon excitations in the crystal.

Thus, in real crystals, depending on the relative values of $L(\mathbf{k})$, D_f , and the deformability of the structure, different types of excited states are possible. In the two limiting cases, these amount either to exciton states, as discussed in Secs. 1-4, or localized excited states. For certain excited states of molecules, intermediate cases can also be realized. The two limiting types of excited states differ essentially in their properties. Thus they are easily identified in experimental studies. In fact, absorption due to creation of excitons essentially reflects the collective properties of the excitation. Above all, this is manifested in the resonance splitting (Davydov splitting) and in the characteristic polarization of the absorption bands. Absorption involving the formation of localized excitation differs little from the absorption described by the oriented-gas model. The corresponding absorption bands are called molecular absorption bands.

The discussion given above has not taken into account the probability of transformation of the excitation energy or part of it into thermal energy of molecular vibrations in the crystal. Such an approximation is justified only for the lowest purely-electronic excitations and their combinations with certain totally-symmetric intramolecular vibrations. The time for radiationless transformation of the energy of such excited states into thermal energy at low temperatures in molecular crystals of aromatic compounds is usually longer than the lifetime of the corresponding excited states for light emission (10^{-7} - 10^{-9} sec).

For molecular excitations that are combinations of electronic excitation with non-totally-symmetric intramolecular vibrations, the energy of the vibrational component of the excitation is transformed relatively rapidly (10^{-12} - 10^{-13} sec) into vibrational energy of the crystal, and the intramolecular excited state cannot be considered as a whole. Roughly speaking, here the energy of the vibrational component is transformed into thermal energy before the entire electronic-vibrational excitation can be transferred from one molecule

to another. In line with this, as a rule, the molecular terms consisting of combinations of electronic excitations with non-totally-symmetric vibrations of the atoms in the molecule form only localized excitations in the crystal.


The high probability of transformation (at low temperature) of the vibrational component of the excitation into thermal energy is evidenced by the emission spectrum. The luminescence of very pure crystals at low temperatures always arises from the states corresponding to the purely electronic transition, even though the electronic-vibrational states are also excited. The probability is especially great of transformation of the energy of the non-totally-symmetric intramolecular vibrations into vibrational energy of the crystal, since such molecular vibrations are strongly coupled with the rotational rocking motion of the molecules in the crystal. Unfortunately, it has not yet been possible to make qualitative theoretical estimates of the role of radiationless transitions in the spectroscopic properties of crystals.

7. EXPERIMENTAL CONFIRMATION OF THE EXISTENCE OF EXCITON STATES IN CRYSTALS

The first experimental proofs of the existence of exciton states in molecular crystals were found by Obreimov, Prikhot'ko, and their associates^[34-35] in studying the polarized-light absorption spectra of single crystals at low temperatures. Subsequently, the splitting of the non-degenerate molecular terms in the polarized-light absorption spectra of crystals has been observed in a large number of other studies (see, e.g.^[25,36-40]). Certain results of the experimental studies have been presented in reviews.^[11,12,40,41] In this section, to illustrate the theory, we shall speak only of the main peculiarities of the absorption spectra of certain aromatic molecular crystals.

The molecules of aromatic hydrocarbons usually consist of six-membered rings of carbon atoms having hydrogen atoms arranged around the periphery. In all these molecules, the electric moment of the transition to the lowest electronic excited state lies in the plane of the molecule.

A. The Anthracene Crystal

The anthracene molecule  ($C_{14}H_{10}$) is

planar and has the symmetry D_{2h} . The anthracene crystal belongs to the monoclinic system C_{2h} . The unit cell of dimensions $a = 8.56 \text{ \AA}$, $b = 6.04 \text{ \AA}$, and $c = 11.6 \text{ \AA}$ ($a \perp b$, monoclinic angle 125°) contains two molecules^[42] arranged at the center and the corner of the ab face. One molecule is transformed into the position of the other by reflection in the ac plane with subsequent translation by the components $a/2$, $b/2$. The molecules are oriented with their long axes almost

parallel to the c axis of the crystal, and their intermediate axis forms an angle of 28.6° with the monoclinic b axis. Single crystals of anthracene are obtained by sublimation in the form of thin plates in the plane of the basis vectors a and b . The first electronic transition ($27,570 \text{ cm}^{-1}$) belongs to an intense dipole transition. Hence, resonance interactions must play a large role in the absorption spectrum of the anthracene crystal.

Many studies^[37-39,43-45] have been devoted to studying the absorption spectrum of single crystals of anthracene. The structure of the absorption spectrum in polarized light incident normal to the ab plane of the crystal has been studied. At present, the region of the spectrum beginning in the crystal at frequencies of about 25000 cm^{-1} has been relatively well studied. The most precise data were obtained by Brodin and Marisova,^[46] who eliminated certain methodological errors entering into the earlier studies. Figure 2 shows the curves that they obtained for the absorption of light by an anthracene crystal of thickness 0.1μ at a temperature of 20°K . The solid curve corresponds to absorption with the electric field of the radiation parallel to the b axis (the b component). The dotted curve corresponds to the a component. The three main maxima of the one curve are shifted with respect to the corresponding maxima of the other curve, forming components of resonance-splitting doublets. Table IV, which has been compiled from the data of^[46,47],

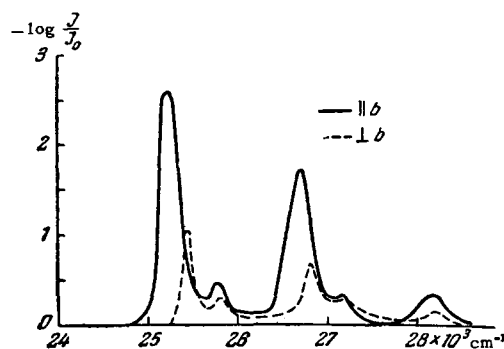


FIG. 2. Frequency-dependence of the absorption coefficient of an anthracene crystal. Crystal thickness 0.1μ . Temperature 20°K .

gives the values of the molecular excitation frequencies and their corresponding frequencies in the crystal, the value of the resonance splitting ΔE , and the polarization ratio $P(b/a)$, i.e., the ratio of the integral intensities of the two components of the doublet.*

*Anthracene absorbs very strongly. Hence one has to use single crystals of thickness $0.07-0.3 \mu$. As Brodin^[47,48] has shown, when radiation of certain wavelengths is absorbed in crystals of such small thicknesses, the linear relation of $\log(I/I_0)$ to the thickness fails. The data given in Table IV refer to a thickness of 0.1μ . They differ somewhat for other crystal thicknesses. This effect and a possible explanation will be discussed in more detail in Sec. 9.

Table IV. Fundamental absorption bands in anthracene

Excitations of the molecule			Excitations of the crystal			
N _i	Transition type	Frequency, cm ⁻¹	b-component, cm ⁻¹	a-component, cm ⁻¹	ΔE	P (b/a)
1	00	27 570	25 213	25 432	220	5
2	00+1430	29 000	26 680	26 830	150	3
3	00+2×1430	30 430	28 200	28 280	80	3.2

We must bear in mind the fact that the resonance splittings indicated in Table IV are the frequency differences of the maxima of the two absorption bands. These bands are relatively broad, and it is not yet known where the frequencies of the electronic transitions without phonon participation are located within them. Hence, the values of ΔE only provisionally reflect the value of the resonance splitting $E_2(Q) - E_1(Q)$.

The second and third molecular transitions indicated in Table IV belong to single and double combinations of the 1430 cm⁻¹ totally-symmetric vibration with the electronic transition. All three molecular transitions indicated in Table IV have a transition dipole moment lying in the plane of the molecule along the short axis (irreducible representation B_{2u}, Table II). The resonance splitting in all the fundamental absorption bands in the frequency range $(25-30) \times 10^3$ cm⁻¹ shows that this absorption is due to exciton states of the crystal.

We should note that in many earlier experimental studies (see, e.g. [37-39]), the value of the resonance splitting of the electronic transition was taken to be 20 cm⁻¹, rather than 220 cm⁻¹, as is given in Table IV. As Brodin has shown, [46,47] the erroneous value of the splitting was obtained through using radiation that was not strictly enough polarized in measuring the b component. An infinitesimal admixture of radiation polarized along the a component results in a considerable distortion of the spectrum of the b component. Qualitatively, this phenomenon is illustrated by Fig. 3. In this diagram, solid curve 1 and the dotted curve correspond to the absorption curves for the b and a com-

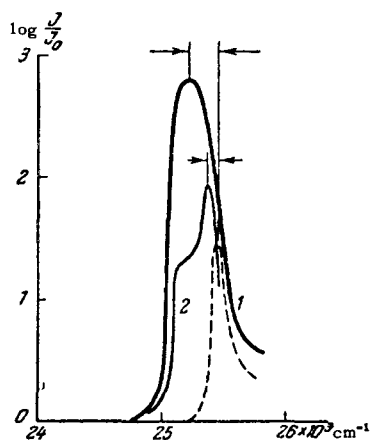
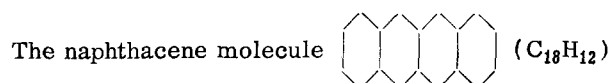


FIG. 3. Diagram illustrating the deformation of the absorption curve when light that is not strictly polarized is used.

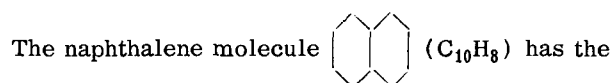
ponents of the spectrum. Solid curve 2 defines the contour of the absorption band of the b component of the spectrum when a small admixture of the a component is present in the incident light. We see that the a-polarized light "penetrating" at the left of the a absorption band is practically not absorbed by the crystal, and essentially deforms the absorption band and considerably decreases the distance between the maxima of the observed curves. Some studies [28,49] performed after [46] with special precautions on the purity of polarization have confirmed the large size of the resonance splitting of the electronic transition in anthracene.

B. The Naphthacene Crystal



and crystal belong to the same symmetry groups as anthracene. The unit cell of the crystal contains two molecules, and the crystal structure differs little from that of anthracene. The first transition in the molecule ($\sim 22,200$ cm⁻¹) also belongs to the irreducible representation B_{2u}, with a transition dipole moment oriented along the short axis of the planar molecule. The oscillator strength of this transition apparently exceeds that of the first electronic transition in the anthracene molecule. The large oscillator strength of the transition leads to a large resonance interaction in the crystal. If we further take into account the large dimensions of the molecule and the low frequencies of rotational oscillation, we can conclude that in the naphthacene crystal the conditions are very favorable for exciton formation upon absorption of light. This conclusion is confirmed by the nature of the absorption spectrum of the naphthacene crystal, as studied by Éichis [50]. Table V gives the values that Éichis found for the frequencies at the maxima of the absorption curves for single crystals at a temperature of 77°K, and the frequencies of the excited states of the molecule obtained in a study of naphthacene vapor (in a layer 15 cm thick at 20°C).

C. The Naphthalene Crystal



symmetry D_{2h}. The crystal belongs to the monoclinic space group C_{2h}⁵ with two molecules per unit cell.

Table V. Fundamental absorption bands of naphthacene

Excitations of the molecule			Excitations of the crystal		
N ₂	Transition type	Frequency, cm ⁻¹	a-component, cm ⁻¹	b-component, cm ⁻¹	ΔE, cm ⁻¹
1	0 0	22 200	19 840	19 235	575
2	00+1425	23 625	21 145	20 715	430
3	00+2800	25 000	22 455	22 320	225

Naphthalene crystallizes in the form of thin plates developed in the *ab* plane. X-ray diffraction studies have established^[51] that the molecules in the crystal are oriented with their long axes almost parallel to the *c* axis of the crystal, while their intermediate axes form an angle of 29.5° with the monoclinic axis. The molecules in the crystal are somewhat deformed (the length of the C—C bonds varies by an amount ~ 0.006 Å).

In contrast with the anthracene and naphthacene molecules, the first electronic transition in the naphthalene molecule (frequency 32020 cm⁻¹) is apparently oriented along the long axis of the molecule,^[52] and is very weak (with oscillator strength 10⁻³). The perturbations of the molecule produced by the non-totally-symmetric vibrations alter the electronic state of the molecule as well. Thus, the excitation involving combination of the electronic transition with the non-totally-symmetric vibration at 438 cm⁻¹ belongs to the irreducible representation B_{2u} and has a relatively large transition dipole moment oriented along the intermediate axis of the molecule. Roughly speaking, the non-totally-symmetric vibration results in a new state of the molecule whose wave function has a small admixture of the wave function of the second electronic transition. The deformation of the naphthalene molecule in the crystal also leads to enhancement and change of orientation of the transition electric dipole moment.

The spectrum of the naphthalene crystal has been studied in [25,35,53,54]. Table VI gives the characteristics of the fundamental transitions in the naphthalene molecule and in the crystal at a temperature of 20°K.

Table VI indicates that the molecular transitions 1 and 3 correspond to exciton states in the crystal, while transitions 2 and 4 correspond to localized states. The total band intensity of the second transition in the crystal is almost equal to the total intensity of the bands corresponding to the purely-electronic transition 1. For the free molecule, the intensity of the second

transition is almost ten times as great as that of the first transition. Apparently this redistribution of intensity is due to the deformation of the molecule in the crystal.

The large value of the polarization ratio of the two components of the doublet corresponding to the first electronic transition is of especial interest. As Prikhot'ko and Soskin^[54] have shown, the 31623-cm⁻¹ band in the *b* component is 160 times as intense as the 31476-cm⁻¹ band in the *a* component. Such a great difference in intensities has aroused doubt as to whether they belong to a single electronic excitation of the free molecule. These doubts have been completely answered by some studies performed by Sheka,^[55] showing a clear picture of a process of exciton doublet formation in the crystal.

Sheka studied the absorption spectra of solid solutions of naphthalene and deuterionaphthalene (C₁₀D₈) over a broad concentration range. The spectrum of the deuterionaphthalene molecule is shifted by 115 cm⁻¹ to shorter wavelengths than in the spectrum of ordinary naphthalene. When the concentration of naphthalene is low, there is no resonance interaction between its molecules, and the electronic transition corresponds in the crystal to a single absorption band of frequency 31541 cm⁻¹. As the naphthalene concentration is increased, resonance interactions begin to play a role, and this band splits into two bands whose separation continuously increases. On going to the pure naphthalene crystal, it forms an exciton doublet, as indicated in Table VI. This process is demonstrated by the diagram in Fig. 4, which is taken from the paper of Sheka.^[55] The diagram also shows how the doublet splitting of exciton bands of the deuterionaphthalene crystal declines as the concentration of naphthalene in the solution is increased. The right-hand side of Fig. 4 corresponds to a solution in which the impurity is the deuterionaphthalene molecules.

Table VI. Fundamental excited states in naphthalene

Excitations of the molecule			Excitations of the crystal			
N ₂	Transition type	Frequency, cm ⁻¹	a-component, cm ⁻¹	b-component, cm ⁻¹	ΔE, cm ⁻¹	P (b/a)
1	00	32 020	31 476	31 623	147	160
2	00+438	32 458	31 960	31 960	0	6.6
3	00+702	32 722	32 231	32 261	30	15
4	00+941	32 931	32 413	32 413	0	1

Table VII. Fundamental excited states in benzene

Excitations of the molecule			Excitations of the crystal, cm^{-1}			
N \ddot{u}	Transition type	Frequency, cm^{-1}	a-component	c-component	b-component	ΔE
1	00	38 089	37 803	37 843*	—	40
2	00+523	38 612	from 38 351 to 38 485	from 38 351 to 38 485	from 38 351 to 38 585	0
3	00+925	39 014	38 724	38 768	—	44
4	00+523+925	39 537	from 39 275 to 39 372	from 39 275 to 39 372	from 39 275 to 39 372	0
5	00+2 \times 925	39 939	39 667*	39 690*	—	23
6	00+3 \times 925	40 864	40 600	40 615	—	15

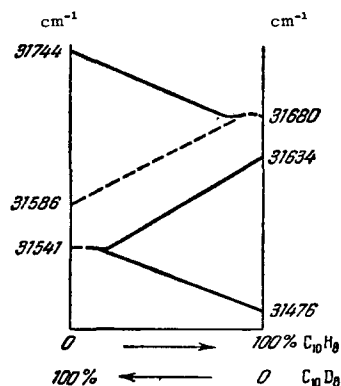


FIG. 4. The variation in the splitting with varying concentrations of naphthalene and deuteronaphthalene in solid solution.

D. The Benzene Crystal

In the benzene molecule C_6H_6 all the atoms are arranged in a plane, and its symmetry properties are characterized by the group D_{6h} . The absorption of light in the near ultraviolet involves the transition of the free molecule from the ground state to an electronic excited state of the irreducible representation B_{2u} .* The purely-electronic transition of this type is forbidden in the dipole approximation. It corresponds to a frequency of 38089 cm^{-1} . However, the transition to the state formed by combination of the electronic excitation with the non-totally-symmetric vibration E_{2g} (of frequency 520 cm^{-1}) is allowed.

The absorption spectrum of single crystals of benzene in polarized light has been studied by Broude, Medvedev, and Prikhot'ko.^[36,57,58] According to X-ray diffraction studies,^[59-61] the benzene crystal belongs to the orthorhombic space group V_h^{15} with four molecules in the unit cell. The latter is formed by three mutually perpendicular vectors a , b , and c ,

*We shall use the notation for the irreducible representations and the character table of the group D_{6h} from^[56]. The lines of intersection of the nodal planes of a wave function of the irreducible representation B_{2u} with the benzene ring pass through the carbon atoms.^[11]

whose absolute lengths are, respectively, 7.28, 9.45, and 6.73 \AA . In the crystal, the benzene molecule is somewhat distorted (the changes in the C—C bonds are of the order of 0.005 \AA), and the electronic transition (38089 cm^{-1}) becomes allowed. Table VII gives some results of investigations^[36,57,58] at a temperature of 20°K of the absorption spectra of single crystals of benzene of different orientations. The states marked by asterisks are actually doublets (with spacings $\sim 1-7 \text{ cm}^{-1}$). The second and fourth molecular levels in the crystal correspond to localized excitations of complex structure. In all three components of the spectrum, the structure of the second and fourth bands remains the same. A difference is observed only in their relative intensities. This is clearly visible in Fig. 5, which shows portions of the absorption spectrum (for all three components), as obtained by Broude in studying two single crystals having different planes of development.

The absorption bands of the crystal corresponding to intramolecular transitions 1, 3, 5, and 6 belong to exciton excitations, and thus they appear with differing frequencies in the different components of the spectrum.

In studying the spectra of solid solutions of benzene in deuterobenzene, Broude and Onoprienko^[62] found a gradual development of resonance splitting as the concentration of the molecules of a given type was increased. At very low concentrations of benzene in deuterobenzene, the absorption band corresponding to the electronic transition is single. However, even at a concentration of 10–15%, an appreciable splitting of this band into two components is observed. The amount of splitting is $3-4 \text{ cm}^{-1}$. At a concentration of 50%, the resonance splitting is as much as 20 cm^{-1} . The splitting increases almost linearly with the concentration, becoming 40 cm^{-1} at 100% concentration.

Thus we see from the example of the absorption spectra of crystals of anthracene, naphthalene, naphthalene, and benzene that the absorption bands of crystals in polarized light at low temperatures can be roughly divided into two types: a) bands involving excitation of excitons, manifested in the different components of the spectrum with different intensities and different frequencies; b) bands involving formation of

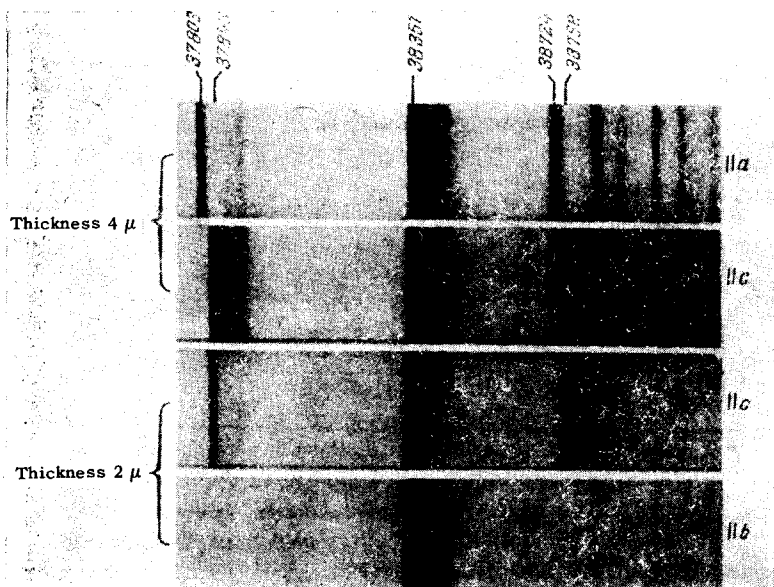


FIG. 5. Absorption spectra for light having different polarizations in two single-crystal specimens of benzene of differing thicknesses and different crystallographic planes of development.

localized excitations. In the near ultraviolet, the spectra of anthracene and naphthacene show only exciton excitations. The spectra of naphthalene and benzene contain both exciton and localized excitations. The localized excitations involve combinations of electronic excitation with the non-totally-symmetric vibrations of the atoms in the molecule.

The form and nature of the exciton absorption bands in the spectra of molecular crystals is highly varied. In the spectra of anthracene and naphthacene, they are broad intense bands, in agreement with the large oscillator strengths of the molecular transitions. In the spectrum of benzene, the exciton absorption bands are relatively narrow. In the spectrum of naphthalene, the bands of the first exciton doublet differ greatly in intensity. In the other cases, the intensities of the components of doublets are of the same order of magnitude. There is as yet no theory to explain all these varied cases.

It has been recently established that under certain conditions the exciton states even exert a considerable influence on the absorption spectrum of impurity molecules, at low concentrations of the impurity molecules, when the distance between them is greater than about one-fourth of the wavelength of the light, they participate in the absorption as independent centers. Here the interaction of the impurity molecules with those of the main substance shifts the absorption bands to longer wavelengths by an amount equal to the change in the van der Waals interaction energy of an impurity molecule with the surrounding molecules of the main crystal upon transition to the excited state. Let $\varphi_{n\alpha}$ and χ_i be the wave functions of the molecules of the main substance and the impurity. Then the change in energy is

$$\Delta E_i = \sum_{n\alpha} \left\{ \int |\chi_i'|^2 V_{i, n\alpha} |\varphi_{n\alpha}^0|^2 d\tau - \int |\chi_i^0|^2 V_{i, n\alpha} |\varphi_{n\alpha}^0|^2 d\tau \right\}.$$

Here the intensity and polarization of the absorption are determined by the magnitude and direction of the dipole moment of the transition in the impurity molecule. Such a simple pattern is possible only in case that the difference $\Delta\epsilon$ between the excitation energy of the impurity molecule and the nearest edge of the exciton band is considerably greater than the width ΔL of the exciton band.

As Rashba^[63,64] has shown, if the condition $|\Delta\epsilon| \gg \Delta L$ is violated, the quantum state of the absorption center becomes considerably more complex. In this case, the interaction of the impurity molecule with the molecules of the crystal is greatly increased, and the excitation is distributed over a region of the crystal surrounding the impurity molecule. The size of this region increases as the excited level of the impurity molecule approaches the edge of the exciton band, and when $|\Delta\epsilon| \ll \Delta L$, it is considerably larger than the lattice parameter. The dipole moment of the transition to such an excited state is determined by the entire region of excitation, rather than by the impurity molecule alone. Principally the molecules of the main crystal take part in the excited state, while the role of the impurity molecule is reduced mainly to confining the excitation within a limited region of the crystal. The magnitude and direction of the dipole moment of a transition to such an excited state can differ essentially from those of the dipole moment of a transition in an isolated impurity molecule.

In the simplest case, in which the impurity molecule differs from the solvent molecules only by a shift in the energy levels (molecules of differing isotopic composition), the intensity of the impurity absorption will decline as $(\Delta\epsilon)^{1/2}$ or increase as $(\Delta\epsilon)^{-3/2}$ as $\Delta\epsilon$ decreases, depending on whether the optical transition to the nearest edge of the exciton band is forbidden or allowed, i.e., depending on whether the value of the

sublevel $k = Q$ is far from or near the nearest edge of the exciton band. The polarization ratio also varies along with the intensity of the impurity absorption. According to theory,^[63,64] the polarization ratio for an impurity band is given by the formula

$$P\left(\frac{b}{a}\right)_{\text{impurity}} = P\left(\frac{b}{a}\right) \left(\frac{\omega - \omega_A}{\omega - \omega_B}\right)^2,$$

where ω , ω_A , and ω_B are the frequencies of the absorption bands of the impurity and the A and B components of the exciton doublet, and $P(b/a)$ is the polarization ratio of the exciton doublet of the main substance of the crystal. When $|\omega - \omega_A| \ll \omega - \omega_B$, we obtain the simple relation

$$P\left(\frac{b}{a}\right)_{\text{impurity}} = (\Delta\epsilon)^2 P\left(\frac{b}{a}\right).$$

The theory of Rashba^[63,64] has been corroborated well experimentally by Broude and Sheka^[65-67] in a study of the spectra of solid solutions of naphthalene in deuterionaphthalene. In these solutions the solvent and impurity are molecules differing only in isotopic composition. The crystal structure around an impurity molecule is practically undistorted. The energy levels in the naphthalene molecule are shifted upon deuteration by about 15 cm^{-1} per hydrogen atom replaced by deuterium. Hence, having deuterionaphthalene with different degrees of deuteration (C_{10}D_8 , $\text{C}_{10}\text{H}_4\text{D}_4$, etc.), they could study the peculiarities of the impurity absorption for different values of $\Delta\epsilon$.

In^[65], they studied two absorption regions at $T = 20^\circ\text{K}$: a) the region near the absorption band A (the a component) of the A-B exciton doublet corresponding to the electronic transition in the solvent molecules; b) the region near the absorption band C corresponding to local excitation (a combination of electronic excitation with a non-totally-symmetric vibration). The obtained results are illustrated by the diagram in Fig. 6. The absorption bands A and B belong to the exciton doublet of the solvent, and the band C to local absorption. The absorption bands Π^1 , Π^2 , and Π^3 are due to impurity molecules of differing isotopic composition. We see from Fig. 6 that, as the impurity-molecule level approaches the exciton band, the polarization ratio varies by a factor of 60: in band Π^1 the polarization ratio $P(b/a) = 6$, while in band Π^3 this ratio is $1/10$. On the other hand, in the vicinity of

band C, which corresponds to local excitation of the crystal, the intensities and polarization ratios of the impurity absorption bands do not depend on $\Delta\epsilon$.

Thus by studying the laws obeyed by impurity absorption spectra as a function of the distance of the impurity band from an absorption band in the spectrum of the crystal, we can determine whether the latter band involves local or exciton excitation of the crystal. Here, quantitative measurements of the relation of the change in intensity of the impurity absorption to changes in $\Delta\epsilon$ permit us to determine certain structural peculiarities of the exciton band (its width and the position of the sublevel having $k = Q$).

8. EXCITON LUMINESCENCE

The exciton and local excited states that arise in a crystal under the action of light are non-equilibrium states. The energy of these excited states can be completely or partially transformed into thermal energy of emission (luminescence), or produce a photoeffect, photochemical reactions, etc. The most characteristic property of exciton states is the fact that they encompass large regions of the crystal (in comparison with the lattice constants) and generally move from one region to another. Such a migration of excitation energy is highly essential. It is the basis for a number of phenomena, e.g., such as sensitized luminescence or quenching, in which the excitation energy of the main substance of the crystal is transferred to impurities, which emit it or transform it into thermal, chemical, or other forms of energy.

The nature of the course of the abovementioned processes is determined by the structure of the energy bands of the excitons and their interaction with the lattice vibrations of the crystal, lattice defects, and extra impurities. The kinetics of these processes essentially depends on the temperature. The topic of this section will be the qualitative description of the phenomena involved with luminescence.

The process of luminescence is one of the possibilities among the competing processes of transformation of part or all of the electronic-vibrational excitation energy of the molecules of the crystal into other forms of energy. Among these competing processes, those of radiationless transformation of part or all of the excitation energy into thermal energy of lattice vibrations, i.e., phonon energy, are especially important. A quantitative theory of radiationless transformations of excitation energy into phonon energy has not yet been developed. To describe these processes, we must principally use experimental data.

Radiationless processes in solids are responsible for the establishment of thermal equilibrium, i.e., the statistical distribution of the energy over all the degrees of freedom of the crystal. The probability of radiationless transitions, and hence, the rate of establishment of thermal equilibrium, depends on the

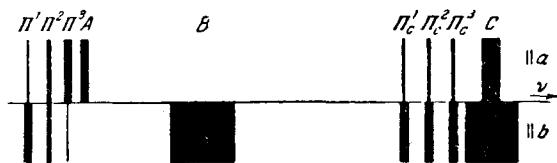


FIG. 6. The variation in the polarization ratio for impurity absorption bands as a function of the distance to the nearest fundamental absorption bands in the crystal.

strength of coupling of the corresponding excitations with the phonon vibrations of the crystal. Apparently, the coupling between the intramolecular vibrations and the lattice vibrations is considerably greater than the coupling between the electronic excitation of the molecules and the lattice vibrations. Consequently, at low temperatures the electronic-vibrational excitation relatively quickly (within $\sim 10^{-12}$ – 10^{-13} sec) loses the excitation energy involved in the intramolecular vibrations. Hence, luminescence takes place from the lowest electronic excited state to the ground state, or to vibrationally-excited levels of the ground electronic state. In the absorption of light, the transitions take place from the ground state to electronic or electronic-vibrational excited states. This type of transitions in impurity molecules in solid solutions is illustrated by Fig. 7 for the low-temperature case. The absorption spectrum begins with the band of the purely electronic transition (frequency ω'_0), and extends to shorter wavelengths (frequencies ω'_1 , ω'_2 , etc.). The frequency differences are equal to the intramolecular vibrational frequencies in the excited state of the molecule. The luminescence spectrum begins with the frequency ω_0 of the electronic transition, and extends to longer wavelengths (frequencies ω_1 , ω_2 , etc.). The frequency differences $\omega_i - \omega_0 = \Omega_i$ correspond to the intramolecular vibrations in the ground state of the molecule. If the coupling of the electronic excitation with the lattice phonons is small, then $\omega_0 \approx \omega'_0$, and the absorption and luminescence spectra will meet at the frequency ω_0 . As the temperature is increased, the intramolecular vibrational degrees of freedom will be "populated" in proportion to the Boltzmann factor $\exp(-\hbar\Omega_i/kT)$ in both the ground and excited electronic states, and hence the absorption and luminescence spectra will overlap.

In addition to the establishment of an equilibrium energy distribution between the lattice phonons and the intramolecular vibrational degrees of freedom of the molecules, experiment shows that a quasiequilibrium distribution among the electronic excitations of differ-

ent types is established in the crystal during the lifetime of the electronic excitation (10^{-8} – 10^{-9} sec), provided that their energy difference does not greatly exceed the mean energy of the phonons. For example, when there are two types of excited states having energies E_1 and E_2 , the ratio of the numbers of excited states of these types is given by the equation

$$\frac{N(2)}{N(1)} = \frac{p_2}{p_1} \exp\left(-\frac{E_2 - E_1}{kT}\right), \quad (8.1)$$

where p_i is the multiplicity of the corresponding state, and T is the temperature. After an equilibrium distribution has been established, when $E_2 - E_1 \gg kT$, only excited states of type E_1 are present in the crystal. The sublevels of any exciton band in the crystal also obey Eq. (8.1).

A light wave having a frequency ω and a wave vector \mathbf{Q} excites in the crystal a state having energy $E(\mathbf{k}) = \hbar\omega$ with $\mathbf{k} = \mathbf{Q}$. Owing to establishment of a quasiequilibrium distribution at $T = 0$, the exciton state will "fall" to the sublevel having the value of \mathbf{k} for which $E(\mathbf{k})$ has its minimum value E_0 . When $T \neq 0$, the sublevels of the exciton band are "populated" in accordance with the Boltzmann factor

$$\exp\left\{-\frac{E(\mathbf{k}) - E_0}{kT}\right\}. \quad (8.2)$$

Owing to the establishment of a quasiequilibrium distribution within the lifetime of the electronic excitation, the luminescence of the crystals begins with the band belonging to the electronic excitation of lowest energy.*

We proceed now to study the peculiarities of the luminescence of molecular crystals in which exciton states play a large role.

A. Luminescence of Pure Crystals

First we shall discuss the luminescence of ideal crystals not containing impurities nor defects, and having sufficiently large dimensions. Let the crystal belong to the anthracene type, in which light excites only exciton states. As we shall see below, the nature of the luminescence of such crystals depends essentially on the temperature and the structure of the exciton band.

We shall assume that the light excites only an exciton of the lowest band $E(\mathbf{k})$. The range of variation of the absolute values of the wave vector \mathbf{k} is roughly defined by the interval 0 to π/a , where a is the mean value of the lattice constant. Owing to the law of con-

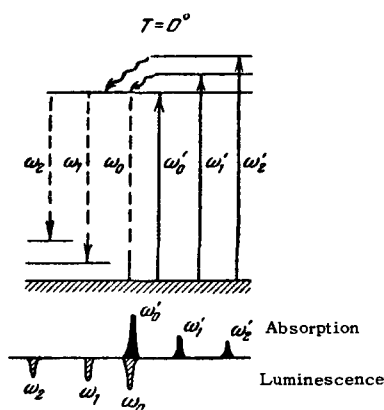


FIG. 7. Diagram of the absorption and luminescence spectra of impurity molecules at low temperature.

*Here we are discussing only singlet excited states. Aromatic molecules also have triplet states of lower energy. Under ordinary conditions, the transition from singlet excited states to triplet states is strongly forbidden, and as a rule takes more time than the lifetime of the singlet excited state. There are also indications^[66] that in a solid solution of azulene in naphthalene, the luminescence takes place from the second excited state of the azulene molecule, rather than the first.

ervation of quasimomentum, only the sublevel of the exciton band having the value $\mathbf{k} = \mathbf{Q}$ is excited, where $|\mathbf{Q}| = 2\pi/\lambda$. Since $\lambda \gg a$, a sublevel of the exciton band corresponding to the center ($\mathbf{k} \approx 0$) of the Brillouin zone is excited.

We now discuss the two possible limiting cases:

a) The value of $E(\mathbf{Q})$ is near the bottom of the exciton band (energy E_0) (the case of positive effective mass of the exciton), so that the following inequality is satisfied:*

$$E(\mathbf{Q}) - E_0 \ll kT. \quad (8.3)$$

b) The value of $E(\mathbf{Q})$ is so far from the bottom of the band E_0 that the following inequality is satisfied:

$$E(\mathbf{Q}) - E_0 \gg kT. \quad (8.4)$$

Let us consider the case in which inequality (8.3) is satisfied. In this case a band is observed in the absorption spectrum with the frequency

$$\omega_1 = \frac{1}{h} E(\mathbf{Q})$$

and with fully defined polarization. Upon absorption of light, a quasiequilibrium state is established, and the excitons fill a certain region of the exciton band near the value $\mathbf{k} = \mathbf{Q}$, which broadens with rising temperature. However, in view of the law of conservation of quasimomentum, luminescence with direct transition to the ground state is possible only from the sublevel $\mathbf{k} = \mathbf{Q}$. Hence, we should observe in the luminescence spectrum a polarized band in resonance coincidence with the absorption band.

Luminescence from states in the exciton band having wave vectors $\mathbf{k} \neq \mathbf{Q}$ in an ideal crystal structure can also take place with the participation of phonons of momentum \mathbf{q} satisfying the equation $\mathbf{k} + \mathbf{q} = \mathbf{Q}$. Transitions involving phonons have low probability. They give rise to a weak background about the fundamental frequency ω_1 . With increasing temperature, the intensity of the background rises (the probability

of the transitions increases), and it broadens toward shorter wavelengths, since the region of occupied states having $\mathbf{k} \neq \mathbf{Q}$ expands. Luminescence from states having $\mathbf{k} \neq \mathbf{Q}$ is also possible at sites of disturbance of the translational symmetry of the crystal (lattice defects, the surface of the crystal). Transitions of this type also have low probability. They give rise to a background about the ω_1 band with intensity independent of the temperature, provided that the lattice defects are not due to thermal motion. The background due to disturbance of translational symmetry cannot show a strict polarization.

Rather than going directly to the ground state, transitions can also occur from exciton states to vibrational sublevels of the ground state corresponding to the "vibrational bands," i.e., the bands arising from the intramolecular vibrations when the molecules are combined to form the crystal. Each intramolecular vibration corresponds, in a crystal containing σ molecules per unit cell, to σ vibrational bands having energies $\hbar\Omega_i(\mathbf{q})$, $i = 1, 2, \dots, \sigma$, where \mathbf{q} is the wave vector. The allowed electronic transitions combine with the vibrational band states corresponding to the totally-symmetric molecular vibrations. The widths of these vibrational bands and their mutual separations are practically zero, i.e., $\Omega_i(\mathbf{q}) = \Omega$, since these totally-symmetric intramolecular vibrations show no resonance interaction.* Quantum transitions from the exciton states to the vibrational-band states with emission of photons (ω, \mathbf{Q}) are possible when the selection rules are satisfied:

$$\hbar\omega = E_\mu(\mathbf{k}) - \hbar\Omega(\mathbf{q}), \quad \mathbf{k} + \mathbf{q} = \mathbf{Q}. \quad (8.5)$$

These selection rules can be satisfied with any value of \mathbf{k} . Hence, transitions from all the occupied sublevels of the exciton band are possible with some probability.

A second peculiarity of the transitions to the vibrational-band states (in crystals containing at least two molecules per unit cell) is that they give rise to emission of unpolarized radiation. We shall show this with the example of crystals containing two molecules per unit cell, with a symmetry corresponding to the group C_{2h} (see Table I). The two vibrational bands of such a crystal belonging to a single totally-symmetric molecular vibration of the irreducible representation A_{1g} of the symmetry group D_{2h} (see Table II) are characterized by the irreducible representations A_g and B_g . We can convince ourselves of this by using formulas (4.9) and (4.10). The dipole moment of the transition

*If the effective mass is positive, i.e., the energy of the exciton increases with increasing quasimomentum, then in an isotropic crystal

$$E(\mathbf{Q}) - E_0 = \frac{\hbar^2 \mathbf{Q}^2}{2m^*}.$$

Further, if we substitute in the value (1, 20) for the effective mass, we find

$$E(\mathbf{Q}) - E_0 = \left(\frac{Qa}{2}\right)^2 \Delta L,$$

where ΔL is the width of the exciton band, and a is the lattice constant. For a quantum transition having an energy $\sim 3 \times 10^4$ cm^{-1} , with $a \approx 10^{-7}$ cm , we have

$$E(\mathbf{Q}) - E_0 \approx 10^{-4} \Delta L.$$

If the effective mass of the exciton is negative, then $E(\mathbf{Q}) - E_0 \approx \Delta L$. In anisotropic crystals, $E(\mathbf{k})$ is not in general an analytic function of \mathbf{k} . Hence the difference $E(\mathbf{Q}) - E_0$ can have a value considerably greater than (8, 3a).

*The vibrational bands corresponding to the intramolecular vibrations manifested in the infrared spectrum have a finite width due to the resonance interaction between the dipole moments of the transitions in the molecules. Excitations of this type show the properties of the exciton states for electronic excitation. In particular, in crystals having several molecules per unit cell, one can observe resonance splitting of the infrared absorption bands.

from the exciton state A_u to the vibrational band A_g (just like the transition to the ground state of the crystal) belongs to the irreducible representation $A_u \times A_g = A_u$. That is, it lies along the monoclinic axis of the crystal. However, the dipole moment of the transition from the same state to the vibrational band B_g belongs to the irreducible representation $A_u \times B_g = B_u$. That is, it is normal to the monoclinic axis.

Thus, along with the polarized band of frequency ω_1 belonging to the transition to the ground state, the luminescence of the crystal can show unpolarized bands in the frequency range $\omega_1 = \omega_1 - \Omega_i$, where the Ω_i are the frequencies of the intramolecular vibrations in the ground electronic state of the molecule. With increasing temperature, the electronic-vibrational luminescence bands broaden (a larger number of sublevels of the exciton band is being filled) and their intensities increase.

Figure 8 shows an energy-level diagram of the crystal under the condition that inequality (8.3) is satisfied. Only one intramolecular vibration is taken into account. The solid arrow indicates the transition that takes place in absorption. The dotted arrows indicate the transitions occurring in luminescence. Band A belongs to the transition to the ground state. It is in resonance coincidence with the absorption band. Band B characterizes the transitions to the vibrational sublevels of the ground state.

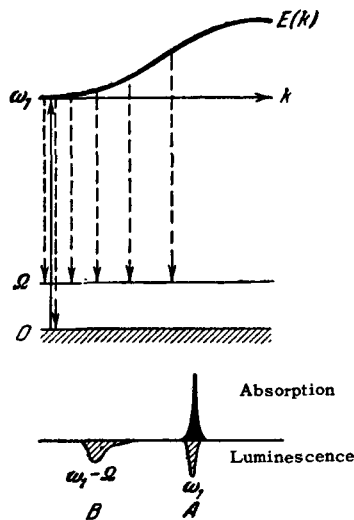


FIG. 8. Diagram of the absorption and luminescence spectra of a pure crystal produced by an excitation band having a positive effective exciton mass.

We shall now discuss the case in which inequality (8.4) is satisfied. Figure 9 shows a diagram of the energy bands in which the value of $E(Q)$ is near the upper edge of the band (negative effective mass). Upon absorption of light one observes a band in the region of the frequency $\omega_1 = E(Q)/\hbar$. After the light has been absorbed and a quasiequilibrium distribution has set in, the crystal will contain excitons having k values

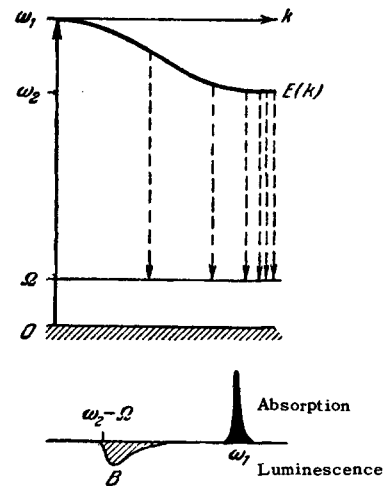


FIG. 9. Diagram of the absorption and luminescence spectra of a pure crystal produced by an excitation band having a negative effective exciton mass.

near the bottom of the exciton band. In Fig. 9 these values correspond to $|k| = \pi/a$. Direct transition from these states to the ground state of the crystal is forbidden by the selection rule $k = Q$, while transitions involving phonons have low probability. These transitions are subject to competition from radiationless transformation of the excitation energy into heat and transitions to the vibrational bands corresponding to the intramolecular vibrations. In Fig. 9 the latter transitions are indicated by the dotted arrows.

Thus, when inequality (8.4) is satisfied, luminescence from the exciton states is hindered, since the most probable luminescence band, which is in resonance coincidence with the absorption band, is either absent or very weak (owing to a slight occupancy of the corresponding sublevel of the exciton band). The luminescence spectrum will contain only the bands B belonging to transitions involving excitation of intramolecular vibrations. These bands occur on the long-wavelength side of the absorption band at distances of $\Omega_i + [E(Q) - E(\pi/a)]/\hbar$. With increasing temperature, the widths and intensities of the bands will increase in accordance with the more complete filling of the sublevels of the exciton band, attaining a value ΔL at $\Delta L \approx kT$. Hence, at high enough temperatures, the width of the electronic-vibrational luminescence bands will roughly characterize the width of the exciton band, provided that the latter does not overlap other bands.

If the crystal has several exciton bands and localized excited states, the absorption spectrum must show, in accordance with the selection rules, several absorption bands of definite polarizations. At low temperatures, after a quasiequilibrium distribution has set in, only excitons having energies near the energy E_0 of the bottom of the first exciton band will remain in the crystal. In accordance with what has been said, the nature of the luminescence in this case will depend on

the ratio of the quantities kT and $E(Q) - E_0$. At high enough temperatures under conditions of quasiequilibrium distribution, the crystal will contain excited states even in the region of the second exciton band. If here $E_2(Q) - E_0 \ll kT$, the luminescence spectrum must show two polarized bands in resonance coincidence with the absorption bands. If $E_2(Q) - E_0 \gg kT$, and $\min(E_2(k) - E_0) \ll kT$, luminescence from states of the second band is possible only for transitions to the vibrational sublevels of the ground state.

B. Luminescence of Crystals Containing Impurities

As a rule, even well-purified crystals contain impurities. Sometimes such impurities are artificially introduced. Various types of lattice defects and thermal density fluctuations are also, so to speak, impurities. Below we shall take impurity molecules to mean local inclusions of any arbitrary type.

If the energy of the excited states of the impurity molecules is somewhat lower than that of the first exciton zone, then when a quasiequilibrium distribution is established, the excitation energy of the crystal will be transformed at low temperatures into excitation energy of the impurity molecules. If here the probability of radiationless transformation of the excitation energy into heat is less than the probability of emission, the impurity molecules will be sources of luminescence. Although under these conditions the luminescence centers are the impurity molecules, excitons play a large role in the luminescence. They transfer the energy absorbed by the molecules of the main substance to the impurity molecules.

The exciton excitation energy moves through the crystal, and on reaching the impurity molecules, raises them to the excited state. In their motion through the crystal, the excitons are scattered by phonons. If the lifetime of the excitons is appreciably greater than the mean time between two collisions of them with phonons, the distribution of the excitons in the crystal can be described by means of a diffusion equation.* The concept of the diffusional nature of the motion of excitons has been used in the studies of Agronovich and Faïdysh [71] and a number of other studies. [72-78]

The migration of excitation energy in a crystal has been proved in many experimental studies. Within 10^{-8} sec, an exciton can travel a distance amounting to tens or hundreds of thousands of lattice parameters. The migration and transfer of excitation energy from the main substance of the crystal to small quantities of

*Along with the exciton mechanism of energy migration a re-absorption mechanism is also possible. Here the main substance emits radiation which is absorbed by the impurity. Wolf[69] has shown that the efficiency of the latter mechanism in naphthalene crystals containing an anthracene impurity is several orders of magnitude lower than the efficiency of the former mechanism. The relative roles of the two energy-migration mechanisms have been studied theoretically by Agronovich.[70]

impurities, which become emission centers, serve to explain why at low temperatures the major part of the luminescence comes from the impurity-molecule levels, even when the concentration of the impurity does not exceed a hundredth or a thousandth of one weight percent. For example, Lipsett and Dekker [79] have shown that at a concentration of naphthalene in crystalline anthracene of 10^{-6} mole fraction, the luminescence intensity of the naphthalene is comparable to that of the anthracene molecules. Here the naphthalene molecules receive directly only a 10^{-6} fraction of the energy absorbed by the crystal. At the same concentrations of naphthalene molecules in a liquid or glassy solid solution, there is no luminescence from naphthalene. Borisov and Vishnevskii [80] have shown that an appreciable luminescence of anthracene in a naphthalene crystal appears even when the distance between the anthracene molecules amounts to $\sim 0.1 \mu$.

Very small amounts of impurities practically cannot be detected by chemical methods of analysis. In connection with this, in a number of studies an impurity luminescence has been taken to be the luminescence of the pure crystal. Thus, for example, it was considered for a long time that the principal luminescence spectrum of the naphthalene crystal, beginning with the band of frequency 31062 cm^{-1} , is due to naphthalene molecules. Only in 1959 did Prikhot'ko and Shpak [81] convincingly demonstrate that this luminescence is due to the presence in the naphthalene of small amounts of β -methylnaphthalene, α -naphthol, and other impurities.

Shpak and Sheka [82-84] have conducted the fullest study of the impurity and intrinsic luminescence of naphthalene. They showed that in naphthalene crystals containing a slight admixture of β -methylnaphthalene, the absorbed light energy (at 20.4°K) is transferred by excitons migrating through the crystal to the impurity molecules, which become the emission centers. As the crystal is purified of its impurities, a luminescence band of frequency 31480 cm^{-1} begins to appear in the a component. This is very near to the band having a maximum at 31476 cm^{-1} in the absorption spectrum (see Table VI). The polarization of the luminescence and its resonance coincidence with the band in the absorption spectrum indicate that this luminescence band belongs to direct transitions from the exciton state to the ground state. As was shown above, such a luminescence is possible when the sublevel $E_a(Q)$ is near the bottom of the band. Thus, the nature of the luminescence shows that the excitons in the a band of the naphthalene crystal in the region $k \approx 0$ have a positive effective mass.

At a temperature of 20°K , the value of kT ($\sim 14 \text{ cm}^{-1}$) is about one-tenth of the energy difference between the bottom E_0 of the first band in the a component and the value $E_b(Q)$ (31623 cm^{-1}) in the corresponding band of the b component. Hence the sublevels $E_b(Q)$ are not filled in the quasiequilibrium

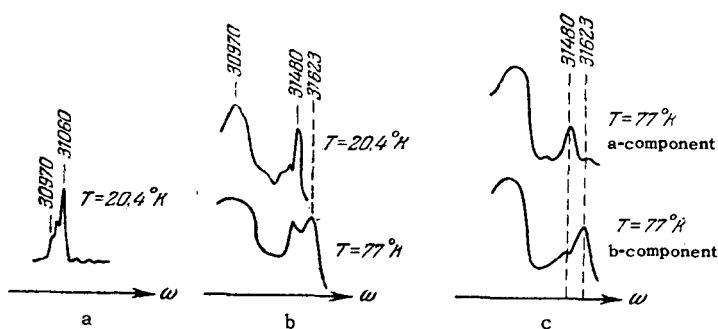


FIG. 10. Traces of luminescence spectra of naphthalene single crystals. a) A crystal containing a small admixture of β -methylnaphthalene; b) the luminescence of a pure crystal without polarization taken into account; c) polarized luminescence of a pure crystal.

state, and do not participate in the luminescence. However, when the temperature of the crystal is raised to 77°K, the luminescence spectrum of naphthalene shows another band of frequency of 31623 cm^{-1} polarized in the b direction. The position of this band coincides with the band observed in the b component of the absorption spectrum. We can easily understand such a change in the luminescence spectrum by taking into account the fact that at 77°K the value of kT (54 cm^{-1}) is only 2.7 times smaller than $E_b(Q) - E_0$, while the probability of transitions to the ground state from the level $E_b(Q)$ is 160 times as great as that for transitions from the $E_a(Q)$ level.

Figure 10 shows traces of the luminescence spectra obtained by Shpak and Sheka.^[84] Figure 10a illustrates the luminescence of a naphthalene crystal containing a small admixture of β -methylnaphthalene at 20.4°K. A luminescence band with a maximum at 31060 cm^{-1} corresponding to emission from the impurity is quite visible. Figure 10b shows traces of the luminescence of a very pure naphthalene crystal at temperatures of 20.4° and 77°K. The measurements were made without taking the polarization into account. The impurity luminescence band is hardly noticeable. At 20.4°K there is an exciton luminescence band at 31480 cm^{-1} , while at 77°K there are two exciton luminescence bands corresponding to the resonance doublet of bands in the absorption spectrum. The exciton nature of

these bands is confirmed by a study of their polarization (Fig. 10c). Figures 10b and c also show a broad unpolarized luminescence band having a maximum near 30970 cm^{-1} . This band corresponds to transitions from sublevels of the exciton band to the vibrational sublevels of the ground state corresponding to the totally-symmetric intramolecular vibration at 512 cm^{-1} , which is well-known in the Raman spectrum. As we should expect, this electronic-vibrational band is unpolarized. Its width is about 200 cm^{-1} . In Fig. 11, taken from the paper of Broude, Shpak, and Sheka,^[85] the solid curves show the contours of this electronic-vibrational luminescence band and of the absorption band corresponding to the reverse transitions from the vibrational sublevels of the ground state to the electronic band.*

The coupling of the electronic transitions with phonons in the naphthalene crystal is weak. Hence, in a first approximation we can neglect the broadening of the bands due to interaction with phonons. In this approximation, the shape of the absorption band must be defined by the curve

$$F_{\text{abs}}(E) = \rho(E - E_0) W(E, \Omega) \exp\left(-\frac{\hbar\Omega}{kT}\right), \quad (8.6)$$

where $\rho(E - E_0)$ is the density of distribution of sublevels of energy E in the exciton band, and $W(E, \Omega)$ is the probability of a dipole transition between the sublevels of the exciton band and the vibrational state Ω . If we assume that the probability of radiationless transformation of the excitation energy into heat is the same for all the sublevels of the exciton band, the shape of the luminescence band must be expressed by the curve

$$F_{\text{lum}}(E) = AF_{\text{abs}}(E) \exp\left(-\frac{E - E_0}{kT}\right). \quad (8.7)$$

In Fig. 11, the dotted curve represents the function $F_{\text{lum}}(E)$ obtained from the absorption curve $F_{\text{abs}}(E)$ by using (8.7).

Thus, by studying the polarization and temperature-dependence of the intensity of the luminescence bands

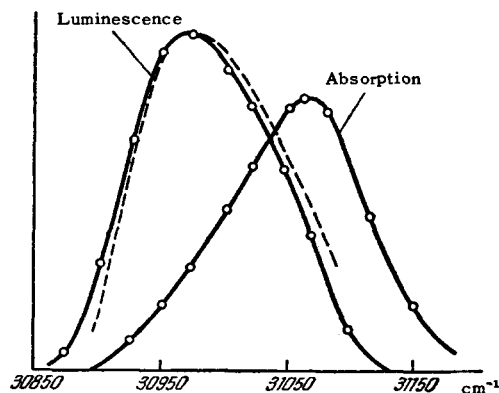


FIG. 11. Absorption and luminescence spectra of a naphthalene single crystal at 100°K corresponding to transitions between an electronic excited state and the 512- cm^{-1} vibrational level of the ground state of the molecule.

*In the naphthalene crystal, the exciton bands of the two resonance-splitting components partially overlap.^[85] Hence, the transitions actually take place between the sublevels of this complex band and the vibrational sublevels of the ground state.

of pure enough single crystals, and comparing them with the absorption spectrum, in a number of cases one can establish their nature unequivocally. Sharply polarized luminescence bands, whose polarization coincide with those of the components of the resonance doublets in the absorption spectrum, belong to transitions from the exciton bands directly to the ground state. At low temperatures one observes only the long-wavelength component of the doublet in the luminescence spectrum. Transitions from the exciton bands to the vibrational sublevels of the ground state correspond in the luminescence spectrum to relatively broad, diffuse, and unpolarized bands. Their width increases considerably with the temperature. They are easily distinguished from the luminescence bands of impurities and local excitations, which are relatively narrow and whose width varies little with the temperature.

The abovementioned peculiarities of the various bands in the luminescence spectrum are also well confirmed in the study of the luminescence spectrum of the anthracene crystal. The luminescence of anthracene usually observed at low temperatures involves emission by impurities, as Prihot'ko and Fugol'^[86] have shown. The luminescence of very pure anthracene at 4.2°K has been studied by Alexander et al.^[87] Shpak and Sheremet^[88] have conducted the most complete studies of the polarized luminescence of anthracene at temperatures of 20.4°, 77°, and 290°K. The fundamental results obtained in these studies amount to the following. They showed that at 20.4°K the luminescence spectrum of very pure anthracene crystals in the b component begins with a broad intense band (of width $\sim 60 \text{ cm}^{-1}$) having a maximum in the frequency region of 25055 cm^{-1} . The polarization and position of the short-wavelength tail of this band coincide with those of the band in the b component of the absorption spectrum. Some broad luminescence bands are arranged on the long-wavelength side of the first luminescence band. They apparently correspond to transitions from levels of the exciton band to the vibrational sublevels of the ground state belonging to the totally-symmetric intramolecular vibrations at 394, 1167, 1262, 1402, 1558, and 1644 cm^{-1} in the Raman spectrum. These same bands are observed in the a component of the luminescence spectrum.

Besides the bands cited above, at 77°K a luminescence band appears in the a component of the spectrum in the frequency region 25200 cm^{-1} . The short-wavelength edge of this band extends to the frequency 25300 cm^{-1} , and partially overlaps with the absorption band corresponding to the component of the resonance doublet (having a maximum at 25432 cm^{-1}). This luminescence band is absent in the b component of the spectrum.

The width of the luminescence bands belonging to the transitions from the sublevels of the exciton bands to the ground state arises from the interaction of the electronic transitions with the lattice vibrations. Owing

to these interactions, transitions become allowed from various sublevels of the exciton band, under the condition $\mathbf{k} + \mathbf{q} = \mathbf{Q}$. In anthracene the exciton bands are wider than in naphthalene and benzene. This involves the considerable interaction of the electronic excitation (high oscillator strength, see Table III) with the lattice vibrations of the crystal. The relatively large interaction of the electronic excitation with the lattice vibrations is evidenced by both the considerable broadening of the luminescence bands with increasing temperature (up to 500 cm^{-1} at 290°K) and the only partial overlap of the exciton luminescence and absorption bands.

9. EXCITONS IN CRYSTALS OF SMALL THICKNESS

In studying the absorption of light by strongly-absorbing crystals (anthracene, etc.), one must use single crystals of thicknesses of several tenths of a micron. The theory presented above has pertained to crystals of sufficiently large dimensions. Using a simple model, we shall try in this section to elucidate the peculiarities of the interaction of crystals of small thickness with light (see^[90]).

We shall consider a cubic crystal having a lattice constant a containing one isotropic molecule per unit cell, extending to infinity in the directions of the x and y axes, and consisting of N_3 molecular layers in the z direction. We shall study the possible energy values of the exciton states of such a crystal, assuming that the molecules are rigidly fixed at the lattice sites $\mathbf{m} = \sum m_i \mathbf{a}_i$, where the m_i are integers.

In plates of large area, the choice of boundary conditions in the xy plane plays no essential role. Hence we can assume the condition of periodicity 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 amount to the requirement that there are no molecules for values $m_3 \leq 0$ and $m_3 \geq N_3 + 1$. We shall assume that at these values of m_3 , the wave functions of the exciton states of the crystal are also zero. The total number of molecules in the crystal $N = N_1 N_2 N_3$.

Let $\Delta\epsilon$, φ_0 , and φ_f be respectively the excitation energy, and the wave functions of the ground and excited states of the isolated molecule. Then, in the Heitler-London approximation, the energy operator of the crystal in the second-quantization representation (see, e.g.,^[91]) has the form

$$\Delta H = (\Delta\epsilon + D) \sum_{\mathbf{m}} B_{\mathbf{m}}^{\dagger} B_{\mathbf{m}} + \sum_{\mathbf{m}, \mathbf{m}'} B_{\mathbf{m}}^{\dagger} B_{\mathbf{m}'} M_{\mathbf{m}\mathbf{m}'}, \quad (9.1)$$

where D and $M_{\mathbf{m}\mathbf{m}'}$ are defined by (1.9) and (1.11), respectively. $B_{\mathbf{m}}^{\dagger}$ and $B_{\mathbf{m}}$ are the operators for creation and annihilation, respectively, of an excited state of type f in the molecule \mathbf{m} . These operators satisfy the commutation relations

$$B_{\mathbf{m}} B_{\mathbf{m}}^{\dagger} - B_{\mathbf{m}}^{\dagger} B_{\mathbf{m}} = \delta_{\mathbf{m}\mathbf{m}'}. \quad (9.2)$$

The energy operator (9.1) can be diagonalized by trans-

forming from the operators B_m to new operators $A(\mathbf{k})$ using the unitary transformation

$$B_m = \sum_{\mathbf{k}} A(\mathbf{k}) u_m(\mathbf{k}), \quad (9.3)$$

where

$$u_m(\mathbf{k}) = \sqrt{\frac{2}{N}} \sin(k_3 m_3 a) \exp\{i(k_1 m_1 + k_2 m_2) a\}$$

is a complete orthonormalized,

$$\sum_m u_m^*(\mathbf{k}') u_m(\mathbf{k}) = \delta_{\mathbf{k}\mathbf{k}'},$$

system of functions satisfying the abovementioned boundary conditions for the values

$$k_i = \frac{2\pi}{N_i a} \nu_i, \quad -\frac{N_i}{2} < \nu_i \leq \frac{N_i}{2}, \quad N_i \gg 1, \quad i = 1, 2; \\ k_3 = \frac{\pi \nu_3}{a(N_3 + 1)}, \quad \nu_3 = 1, 2, \dots, N_3. \quad (9.4)$$

The new operators satisfy the commutation relations

$$A(\mathbf{k}') A^\dagger(\mathbf{k}) - A^\dagger(\mathbf{k}) A(\mathbf{k}') = \delta_{\mathbf{k}\mathbf{k}'},$$

The operators $A^\dagger(\mathbf{k})$ are the operators for creation of exciton states, while the operators $A(\mathbf{k})$ annihilate the corresponding exciton states.

Substituting (9.3) into (9.1), we obtain the operator for the excitation energy of the crystal

$$\Delta H = \sum_{\mathbf{k}} E(\mathbf{k}) A^\dagger(\mathbf{k}) A(\mathbf{k}), \quad (9.5)$$

$$E(\mathbf{k}) = \Delta \varepsilon + D + L(\mathbf{k}), \quad (9.6)$$

where

$$L(\mathbf{k}) = \sum'_m u_n(\mathbf{k}) M_{nm} u_m(\mathbf{k}).$$

The excitation-energy operator (9.5) is diagonal with respect to the operators $\hat{N}(\mathbf{k}) \equiv A^\dagger(\mathbf{k}) A(\mathbf{k})$ of the numbers of occupied exciton states. The eigenfunctions (9.5) can be written in the form $|\dots N(\mathbf{k}) \dots\rangle$, where the quantum numbers $N(\mathbf{k}) = 0, 1, 2, \dots$ indicate the number of exciton states of each type. The state of a crystal having one electronic excitation corresponding to a definite value of \mathbf{k} is characterized by the excitation energy (9.6). The set of excited states (9.6) corresponding to all values of \mathbf{k} satisfying the conditions (9.4) forms a band of exciton states. With fixed values of k_1 and k_2 , the excitation energy (9.6) takes on N_3 discrete values.

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

$$H_{\text{int}} = - \sum_m \mathcal{E}(\mathbf{m}) \mathbf{d}(\mathbf{m}) = \omega e^{-i\omega t} + \omega^* e^{i\omega t}, \quad (9.7)$$

where $\mathcal{E}(\mathbf{m})$ is the value of the electric field intensity at the m -th lattice site, and $\mathbf{d}(\mathbf{m})$ is the dipole-moment operator of the molecule. Let $\mathcal{E}(\mathbf{m})$ correspond to the external field of a plane electromagnetic wave incident normal to the surface of the crystal plate, and

the thickness of the plate be such ($N_3 > 100$) that we can still speak of the macroscopic concepts of the refractive index and the absorption coefficient. Then, inside the plate, if the absorption is small,

$$\mathcal{E}(\mathbf{m}) = 2\mathcal{E}_0 \sin(Qm_3 a - \omega t), \quad (9.8)$$

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

In the occupancy-number representation, the dipole-moment operator of the molecule is

$$\mathbf{d}(\mathbf{m}) = \langle \varphi_f | \mathbf{e} \mathbf{r} | \varphi_0 \rangle (B_m^\dagger + B_m). \quad (9.9)$$

Substituting this expression and (9.8) into (9.7), and using the canonical transformation (9.3), we obtain the value of w in the operator (9.7) in the representation of occupancy numbers of exciton states.

$$w = \mathcal{E}_0 \langle \varphi_f | \mathbf{e} \mathbf{r} | \varphi_0 \rangle \sqrt{\frac{N}{2}} \sum_{\mathbf{k}} (A_f^\dagger(\mathbf{k}) + A_f(\mathbf{k})) \delta_{k_1 0} \delta_{k_2 0} \Delta(k_3 - Q), \quad (9.10)$$

where

$$\Delta(x - y) \approx \frac{\cos\left\{\frac{1}{2}(N_3 + 1)(x - y)a\right\} \sin\left\{\frac{1}{2}N_3(x - y)a\right\}}{N_3 \sin\left\{\frac{1}{2}(x - y)a\right\}}. \quad (9.11)$$

The function $\Delta(x - y)$ equals unity when $x = y$, and vanishes when $|x - y| = \pi/(N_3 + 1)a$, or $2\pi/N_3 a$. When $N_3 \rightarrow \infty$, this function is reduced to the Kronecker delta δ_{xy} .

It follows from (9.10) that when the frequency and the direction of the wave vector are fixed, the light wave interacts only with excitons characterized by the values $k_1 = k_2 = 0$, and

$$k_3 \equiv \left| \frac{\pi \nu_3}{a(N_3 + 1)} \right| \approx Q = \frac{\omega}{c} n. \quad (9.12)$$

Since k_3 is discrete, Eq. (9.12) is not satisfied in the general case for fixed values of N_3 and Q . For example, for radiation of frequency 25100 cm^{-1} with $n = 4.5$, this equation is satisfied for $\nu_3 = 1$ only with a crystal thickness* $L_0 \equiv (N_3 + 1)a = 0.044 \mu$. The value of w sharply diminishes for small deviations of the crystal thickness from this value. When the crystal thickness takes on values that are multiples of L_0 , w again shows a maximum. In fact, when $a(N_3 + 1) = \nu_3 L_0$ ($\nu_3 = 2, 3, \dots$), Eq. (9.12) is again satisfied. For large crystal thicknesses, the discrete step between consecutive permissible values of k_3 decreases, and Eq. (9.12) is satisfied practically for any crystal thickness.

In studying the bulk properties of a crystal, it is sufficient to know its complex polarizability. In order to determine the polarizability, we must calculate the mean value of the specific electric moment produced by the action of the external wave. Let $|0\rangle$ be the wave function of the crystal in the absence of excitons.

*Strictly speaking, for a fixed value of N_3 , the crystal thickness $l = (N_3 - 1)a$. Hence, $L_0 = (N_3 + 1)a = l + 2a$.

Then the wave function of the crystal in the presence of a wave (9.7) having a frequency near that of the exciton states $\Omega(k_3) = E(k_3)/\hbar$, will have the following form in the first-order perturbation theory:

$$\psi = |0\rangle + \sum_{k_3} \frac{\omega e^{-i\omega t}}{\hbar \left[\Omega(k_3) - \omega - \frac{i}{2} \gamma(k_3) \right]} A^\dagger(k_3) |0\rangle, \quad (9.13)$$

where $\hbar\gamma$ is the width of the exciton state arising from interaction of the excitons with phonons.

If v is the volume of the unit cell of the crystal, then in the state ψ the mean value of the vector of the polarization per unit volume of the crystal at the site occupied by the lattice node \mathbf{m} is given by the equation

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

Substituting the values (9.9), (9.10), and (9.3) into this expression, and solving for the complex polarizability $\alpha(\omega)$, we obtain (for $k_3 \approx Q$, and $\Omega(k_3) = \omega$)

$$\alpha(\omega) = \frac{1}{v\hbar} \frac{\langle \varphi_f | \mathbf{er} | \varphi_0 \rangle^2 \Delta(k_3 - Q)}{\Omega(k_3) - \omega - \frac{i}{2} \gamma(k_3)}.$$

If ϵ_0 is the dielectric constant due to all the other electronic states of the crystal, then it follows from Maxwell's equations that the refractive index and the absorption coefficient η for a monochromatic light wave of frequency ω is given by the equation

$$(n + i\eta)^2 = \epsilon_0 + 4\pi\alpha(\omega),$$

which implies

$$n^2 = \frac{1}{2} (\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1), \quad \eta^2 = \frac{1}{2} (\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1),$$

where

$$\epsilon_1 = \epsilon_0 + \frac{4\pi}{\hbar v} \frac{\langle \varphi_f | \mathbf{er} | \varphi_0 \rangle^2 [\Omega(k_3 - \omega)] \Delta(k_3 - Q)}{[\Omega(k_3) - \omega]^2 + \frac{1}{4} \gamma^2(k_3)},$$

$$\epsilon_2 = \frac{2\pi\gamma(k_3)}{\hbar v} \frac{\langle \varphi_f | \mathbf{er} | \varphi_0 \rangle^2 \Delta(k_3 - Q)}{[\Omega(k_3) - \omega]^2 + \frac{1}{4} \gamma^2(k_3)}.$$

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

$$\omega = \Omega(k_3^0), \quad k_3^0 = \frac{\omega}{c} n. \quad (9.14)$$

Then, only the terms $k_3 = k_3^0$ will make an essential contribution to the summation in (9.13); for these, $\Delta(k_3^0 - Q) \approx 1$. When $\omega = \Omega(k_3^0)$, the imaginary component of the dielectric constant and the absorption coefficient will attain the values

$$\eta_{\max}^2 = \frac{1}{2} (\sqrt{\epsilon^2 + \Gamma^2} - \epsilon), \quad (\epsilon_2)_{\max} = \frac{8\pi \langle \varphi_f | \mathbf{er} | \varphi_0 \rangle^2}{\hbar v \gamma(k_3)} \equiv \Gamma. \quad (9.15)$$

Here the values of the refractive index n entering into (9.14) are given by the equation

$$n^2 = \frac{1}{2} (\sqrt{\epsilon^2 + \Gamma^2} + \epsilon), \quad (9.16)$$

while the values of $\epsilon \approx \epsilon_0$. The refractive index takes

on its maximum value when the following two conditions are simultaneously satisfied:

$$|\Omega(k_3^0) - \omega| = \frac{1}{2} \gamma(k_3^0), \quad k_3^0 = \frac{\omega}{c} n_{\max}. \quad (9.17)$$

In such a case,

$$(\epsilon_1)_{\max} = \epsilon + \frac{1}{2} \Gamma, \quad \epsilon_2 \approx \frac{1}{2} \Gamma,$$

$$n_{\max}^2 = \frac{1}{2} \left(\sqrt{\epsilon^2 + \epsilon \Gamma + \frac{1}{2} \Gamma^2 + \epsilon + \frac{1}{2} \Gamma} \right),$$

where Γ is given by (9.15).

In general, conditions (9.14) and (9.17) are satisfied at different crystal thicknesses. For small values of $\gamma(k_3^0)$, the refractive index given by conditions (9.14) and (9.16) differs little from n_{\max} , and hence the conditions (9.14) are more essential.

If we substitute the value k_3^0 into (9.14), we can convince ourselves that these conditions are satisfied when the crystal thickness takes on the values

$$L \equiv a(N_3 + 1) = \frac{\pi c \nu_3}{\omega n}, \quad \nu_3 = 1, 2, 3, \dots \quad (9.18)$$

We shall assume that the equation is satisfied for

$$L_0 = \frac{\pi c \nu_3^0}{\omega n}. \quad (9.19)$$

Then Eqs. (9.18) and (9.14) are also satisfied for crystal thicknesses that are multiples of L_0 (if $n = \text{const.}$).

The results given above have pertained to the case of weak absorption, in which we can neglect the decline in amplitude of the light wave as it passes through the crystal. Taking into account the decline in the amplitude of the light wave has the result that the wave vector of the wave within the crystal will not have a definite value. The value of the uncertainty is of the order of $(\omega/c)\eta$, where η is the absorption coefficient. In line with this, the conditions (9.14) can be satisfied to a precision of $(\omega/c)\eta$. In order that the discreteness of the values of k_3 be manifested, the following inequality must be satisfied:

$$\Delta k_3 \equiv \frac{\pi}{(N_3 + 1)a} > \frac{\omega}{c} \eta. \quad (9.20)$$

In order that the energy resonances be manifested, the distance between the levels of the exciton states for different values of k_3 must exceed the corresponding value of γ . This distance is of the order of magnitude of $\Delta L/N_3$, where ΔL is the width of the exciton band for a thick crystal. Consequently, the following inequality must be satisfied:

$$\frac{\Delta L}{N_3} > \gamma. \quad (9.21)$$

The satisfaction of the inequalities (9.20) and (9.21) is favored by small values of N_3 . However, at very small values of N_3 , the sharp maximum in the function (9.11) defining the resonance in terms of the wave numbers is smoothed out, and the picture of the macroscopic concepts for n and η fails to hold. At low temperatures (small γ), we might hope to observe changes in the values of n and η with varying thickness of crystals in the region of exciton bands having $\Delta L \sim 10^3 \text{ cm}^{-1}$ for crystals containing several hundred molecular layers.

An oscillation of the values of n and η with varying crystal thickness has been observed by Brodin^[47,48] in studying the passage of light polarized along the monoclinic axis through thin platy crystals of anthracene at a temperature of 20.4°K and frequency 25108 cm⁻¹.

Figures 12 and 13 show the results obtained by Brodin from measurements with variation of the crystal thickness from 0.07 to 0.3 μ , corresponding to a variation in N_3 from 74 to 300.

In anthracene the width of the exciton band is $\sim 10^3$ cm⁻¹. Hence, the spacing between the sublevels of the exciton band is of the order of magnitude of 3 cm⁻¹.

Hence, at low temperatures inequality (9.21) is satisfied. When $a(N_3 + 1) = 0.1 \mu$, the measured value of $\eta = 0.96$, and hence $(\omega/c)\eta = 1.5 \times 10^5$ cm⁻¹. Then, for crystal thicknesses less than 0.3 μ , inequality (9.20) is also satisfied.

Brodin observed maxima in the absorption coefficient (Fig. 12) at crystal thicknesses of 0.105, 0.168, and 0.223 μ . Hence we can assume that the value of L_0 in (9.19) is $\sim 0.059 \mu$. According to (9.19), this

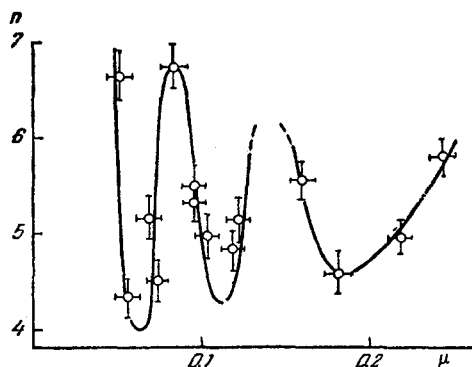


FIG. 12. Dependence of the refractive index on the thickness of a single crystal for light of frequency 25108 cm⁻¹ polarized along the monoclinic axis of the crystal.

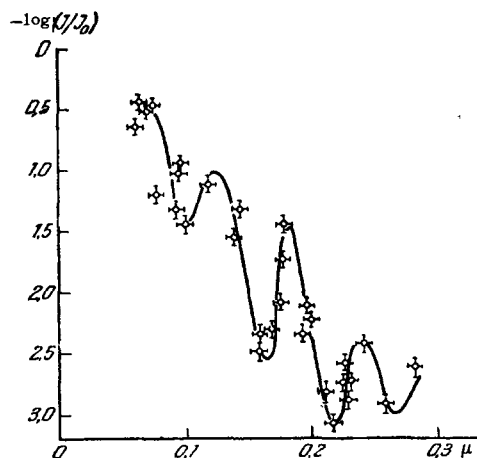


FIG. 13. Dependence of the absorption coefficient on the thickness of a single crystal for light of frequency 25108 cm⁻¹ polarized along the monoclinic axis of the crystal.

value of L_0 can correspond to values of $n = 3.38$ with $\nu_3 = 1$, or $n = 6.76$ with $\nu_3 = 2$. In Brodin's experiments the refractive index was as high as ~ 6.8 . Thus, the second variant of the values, $n = 6.76$ and $\nu_3 = 2$, agrees satisfactorily with experiment.

Thus, owing to the discreteness of the values of the energy and wave vectors of the exciton states in crystals of small thickness, in a certain range of variation of the thickness at low temperature, the coefficients n and η are not bulk characteristics of the substance, since they depend on the crystal thickness. As the temperature of the crystal is increased, inequality (9.21) ceases to be satisfied, and the discrete structure of the values of the energy and the wave vector in the exciton bands has no practical significance.

10. THE FORM OF ABSORPTION AND LUMINESCENCE BANDS DUE TO LOCALIZED EXCITATIONS

In Sec. 8, it was shown in discussing Fig. 11 that at low temperatures the width of absorption bands corresponding to transitions from vibrational sublevels of the ground state to the exciton band is basically determined by the width of this band. The width of the luminescence bands for the reverse transitions also depends on the probabilities of occupancy of the individual sublevels of the exciton band. For localized excitations and excitations of impurity molecules, both the widths of the absorption bands and those of the luminescence bands essentially depend on the interaction of the electronic excitation with the lattice vibrations. As a rule, these interactions are considerably larger than those of the exciton states with the lattice vibrations. This is so because a transition to an excited state in a local (or impurity) center involves a considerable tendency to local distortion of the crystal structure. However, in the exciton state, the excitation is distributed over a considerable region of the crystal, and hence, the local distortion of the structure will be small.

We shall now discuss a very simple theory permitting us to determine the form of absorption and luminescence bands of impurity molecules (or local excitations) and their temperature-dependence.*

We shall assume that the concentration of impurity centers is so small that we can neglect their mutual influence. Then we can study a system consisting of a single molecule and the crystal. We shall write the energy operator of this system in the form

$$H = H_{cr}(R) + H_{mol}(r) + V(r, R), \quad (10.1)$$

where R is the set of all degrees of freedom of the crystal, r is the set of internal degrees of freedom

*Such a theory has been developed by Davydov,^[92,93] Davydov and Lubchenko,^[94] Lubchenko,^[95-98] and Ratner and Zil'berman.^[99]

of the impurity molecule, and $V(r, R)$ is the operator for the interaction between the molecule and the crystal. In the adiabatic approximation, the energy state of the system is given by the equation

$$(\epsilon_l + V_{ll}(R) + H_{cr}(R) - E)\Phi(R) = 0, \quad (10.2)$$

where

$$V_{ll}(R) = \int \psi_l^* V(r, R) \psi_l d\tau, \quad (10.3)$$

and ψ_l and ϵ_l are the eigenfunctions and eigenvalues of the operator H_{mol} for the energy of the impurity molecule (or a molecule of the crystal when this state does not give rise to excitons). For the sake of definiteness, we shall speak below only of an impurity molecule.

Let $U(R)$ be the potential energy of the crystal without the impurity molecule, and R_0 the set of equilibrium positions of the molecules in this structure corresponding to the minimum of $U(R)$. Then for small deviations from these equilibrium values, we can write

$$W_l(R) \equiv V_{ll}(R) + U(R) = W_l(R_0) + V_{ll}^{(2)}(R - R_0) + \frac{1}{2} W_{ll}^{(2)}(R - R_0)^2. \quad (10.4)$$

We shall introduce normal coordinates ξ_a such that

$$\frac{1}{2} W_{ll}^{(2)}(R - R_0)^2 = \frac{\hbar}{2} \sum_s \omega_{sl} \left(\xi_s^2 - \frac{\partial^2}{\partial \xi_s^2} \right), \quad (10.5)$$

where the ω_{sl} are the lattice vibration frequencies of the system when the impurity molecule is in the l -th electronic state. The summation is performed over all possible lattice vibrations. Here the second term in (10.4) is expressed in terms of the normal coordinates ξ_s by using the equation

$$(R - R_0) V_{ll}^{(2)} = \sum_s a_{sl} \xi_s. \quad (10.6)$$

Substituting (10.4)–(10.6) into (10.2), we obtain the equation

$$\left\{ \frac{\hbar}{2} \sum_s \omega_{sl} \left[-\frac{\partial^2}{\partial \xi_s^2} + (\xi_s - \xi_{sl})^2 \right] - e \right\} \Phi^l(\xi) = 0, \quad (10.7)$$

where the quantities

$$\xi_{sl} = -\frac{a_{sl}}{\hbar \omega_{sl}} \quad (10.8)$$

give the displacements in the equilibrium positions of the molecules in the crystal structure when one adds to it an impurity molecule in the l -th quantum state,

$$e = E_l - \left\{ \epsilon_l + W_l(R_0) + \frac{\hbar}{2} \sum_s \omega_{sl} \xi_{sl}^2 \right\},$$

and E is the total energy of the system.

Equation (10.7) can be broken down into a set of independent Schrödinger equations for harmonic oscillators. Hence, we can write its solution directly:

$$\Phi_{\{n_s\}}^l(\xi) = \prod_s \varphi_{n_s}(\xi_s - \xi_{sl}), \quad (10.9)$$

where the $\{n_s\} \equiv \dots n_s, n_s', \dots$ are the sets of oscillator quantum numbers defining the vibrational state of the molecules of the crystal containing the impurity molecule in the l -th electronic state. Here the total energy of the system is

$$E_{l\{n_s\}} = \hbar \sum_s \omega_{sl} \left(n_s + \frac{1}{2} \right) + \epsilon_l + W_l(R_0) - \frac{\hbar}{2} \sum_s \omega_{sl} \xi_{sl}^2, \quad (10.10)$$

while the corresponding wave function is

$$\Psi_{l\{n_s\}}(r, \xi) = \psi_l(r) \Phi_{\{n_s\}}^l(\xi). \quad (10.11)$$

We shall be interested in the changes in the energy of the system when the impurity molecule undergoes a transition from the ground state $l = 0$ to the l -th excited state. If this transition occurs without change in the quantum numbers of the lattice vibrations (phononless electronic transition), the change in the energy of the system is

$$E_{l\{n_s\}} - E_{0\{n_s\}} \equiv \hbar \Omega_{l0}^{n_s} = \hbar \Omega_l + \sum_s (\omega_{sl} - \omega_{s0}) n_s, \quad (10.12)$$

where

$$\hbar \Omega_l \equiv \Delta \epsilon_l + V_{ll}(R_0) - V_{00}(R_0) + \frac{\hbar}{2} \sum_s (\omega_{s0} \xi_{s0}^2 - \omega_{sl} \xi_{sl}^2). \quad (10.13)$$

When $\omega_{s0} \neq \omega_{sl}$, the change in energy of the system in a phononless transition depends on the numbers n_s , i.e., on the vibrational state of the molecules in the crystal structure.

If we write the operator for dipole interaction with an electromagnetic wave having an electric field intensity \mathcal{E}_0 in the form

$$H' = -e r \mathcal{E}_0 (e^{-i\omega t} + e^{i\omega t}),$$

then we can calculate the transition electric moment and complex-polarizability tensor of the impurity molecule in the first-order approximation of the perturbation theory (see [92,93]). If we assume that the x , y , and z coordinate axes are directed along the principal axes of the polarizability tensor β , we have

$$\beta_{xx} = \frac{|d_{l0}^x|^2}{\hbar} \overline{\sum_{\{n_s'\}} \frac{\prod_s |M_{n_s, n_s'}^{x,l}|^2}{\Omega + \sum_s (n_s' - n_s) \omega_{s0} - \omega - i\gamma}}, \quad (10.14)$$

where the bar over the summation sign indicates averaging over all the initial states $\{n_s\}$ of the lattice vibrations,

$$\Omega \equiv \Omega_{l0}^{n_s}, \quad (10.14a)$$

γ characterizes the width of the excited level in the free molecule, and

$$M_{n_s, n_s'}^{x,l} = \int \varphi_{n_s'}(\xi_s - \xi_{sl}) \varphi_{n_s}(\xi_s - \xi_{s0}) d\xi_s \quad (10.15)$$

is the overlap integral of the oscillator wave functions.

Using the values (10.15), and introducing the refractive index μ and the absorption coefficient η by means of the equation

$$(\mu + i\eta)^2 = \epsilon_0 + 4\pi\nu\beta,$$

we obtain (see [92,93]) for the simplest case of an isotropic crystal

$$\left. \begin{aligned} \mu^2 - \eta^2 &= \epsilon_0 + \frac{4\pi\nu}{\hbar} |d_{i0}^x|^2 F(\omega), \\ \mu\eta &= \frac{2\pi\nu}{\hbar} |d_{i0}^x|^2 S(\omega), \end{aligned} \right\} \quad (10.16)$$

where ϵ_0 is the dielectric constant of the crystal without the impurity molecule, ν is the number of impurity molecules per unit volume of crystal,

$$S(\omega) = \text{Re } \Lambda, \quad F(\omega) = \text{Im } \Lambda, \quad (10.17)$$

$$\Lambda = \int_0^\infty \exp\{i\xi(\Omega - \omega + i\gamma) + g(\xi)\} d\xi, \quad (10.18)$$

$$g(\xi) = \frac{1}{2} \sum_s \{(\bar{n}_s + 1) e^{i\xi\omega_s} + \bar{n}_s e^{-i\xi\omega_s} - (2n_s + 1)\} (\xi_{s0} - \xi_{sl})^2, \quad (10.19)$$

and

$$\bar{n}_s = (e^{\frac{\hbar\omega_s}{kT}} - 1)^{-1}$$

is the average number of phonons of type s at the temperature T .

At low impurity concentrations $\nu \ll 1$, Eqs. (10.16) can be considerably simplified:

$$\left. \begin{aligned} \mu &= \mu_0 + DF(\omega), \\ \eta &= DS(\omega), \end{aligned} \right\} \quad (10.20)$$

where

$$\mu_0^2 = \epsilon_0, \quad D = \frac{2\pi\nu |d_{i0}^x|^2}{\hbar|\mu_0|}.$$

Thus, the calculation of μ and η is reduced to calculating the integral (10.18). We shall discuss the limiting cases.

a) The case of "infinitesimally weak" interaction.

Here, when the impurity molecule is excited the equilibrium positions of the molecules in the crystal do not change; $(\xi_{s0} - \xi_{sl}) = 0$. In this case, $g(\xi) = 0$, and

$$\mu = \mu_0 - \frac{D(\omega - \Omega)}{(\Omega - \omega)^2 + \gamma^2}, \quad \eta = \frac{\gamma D}{(\Omega - \omega)^2 + \gamma^2}.$$

Hence, the curves for the dispersion and the absorption coefficient in this limiting case coincide in form with the corresponding curves for free molecules. There is only a shift in the resonance frequency. This shift is

$$\Delta \equiv \Omega - \frac{\Delta\epsilon_l}{\hbar} = \frac{V_{ll} - V_{00}}{\hbar} + \sum_s (\omega_{s0} - \omega_{sl}) \bar{n}_s.$$

At temperatures above the Debye temperature, i.e., when $kT > \hbar\omega_s$, we have

$$\hbar\Delta = (V_{ll} - V_{00}) + kT \sum_s \frac{\omega_{s0} - \omega_{sl}}{\omega_{s0}}.$$

b) The case of strong interaction. Let $\omega_s \leq \omega_0$; then function (10.19) for values $\xi < 1/\omega_0$ can be transformed into the form

$$g(\xi) = i\xi A - \xi^2 B^2, \quad (10.21)$$

where

$$A \equiv \frac{1}{2} \sum_s \omega_s (\xi_{s0} - \xi_{sl})^2, \quad (10.22)$$

$$B^2 \equiv \frac{1}{2} \sum_s (2\bar{n}_s + 1) \omega_s^2 (\xi_{s0} - \xi_{sl})^2. \quad (10.23)$$

If the following inequality is satisfied:

$$B^2 > \omega_0^2 \geq \omega_s^2 \quad (10.24)$$

the interaction of the electronic excitation with the lattice vibrations is said to be strong. The higher the temperature is, the greater the values of \bar{n}_s and B^2 , and the better inequality (10.24) is satisfied.

Under the condition (10.24), the integral of (10.18) acquires (see [93]) the form

$$\Lambda = \frac{\gamma\sqrt{\pi}}{2B} [1 - \Phi(z)] e^{z^2}, \quad (10.25)$$

where

$$z \equiv \frac{\gamma - i[\Omega_r - \omega]}{2B}, \quad \Omega_r = \Omega + A$$

is the resonance frequency, and $\Phi(z)$ is a Gaussian error function defined by the integral

$$\Phi(z) \equiv \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy = \begin{cases} \frac{2}{\sqrt{\pi}} \left(z - \frac{z^3}{3} + \dots \right), & \text{if } z < 1, \\ 1 - \frac{e^{-z^2}}{z\sqrt{\pi}} \left(1 - \frac{1}{2z^2} + \dots \right), & \text{if } z > 1. \end{cases} \quad (10.26)$$

In the region near the resonance frequency ($|\Omega_r - \omega|/2B < 1$), we can separate the real and imaginary components in (10.25) and use (10.20) and (10.17) to obtain:

$$\mu = \mu_0 + \frac{D}{B^2} (\Omega_r - \omega) \exp \left[\frac{\gamma^2 - (\Omega_r - \omega)^2}{4B^2} \right], \quad (10.27)$$

$$\eta = \frac{D}{B} \exp \left[\frac{\gamma^2 - (\Omega_r - \omega)^2}{4B^2} \right]. \quad (10.28)$$

In a region far from the resonance frequency, we have

$$\mu = \mu_0 + \frac{D(\Omega_r - \omega)}{(\Omega_r - \omega)^2 + \gamma^2}, \quad \eta = \frac{D\gamma}{(\Omega_r - \omega)^2 + \gamma^2}. \quad (10.29)$$

Thus, when inequality (10.24) is satisfied, the absorption curve near the resonance frequency has the form of a Gaussian curve (Pekar^[100] has also obtained this result). Here the dispersion curve is given by Eq. (10.28), which characterizes a sharper variation in the refractive index as one goes away from the resonance frequency, than is given by the ordinary dispersion curve for free molecules.

When the values of z are not very small, we must take into account also the cubic term in the expansion in (10.26). Then the absorption curve (10.27) will also contain a cubic term in addition to the linear term $(\Omega_r - \omega)$. Consequently, the absorption and dispersion curves will become asymmetric with respect to the resonance frequency, i.e., they will vary more rapidly

on the red side than on the blue:

$$\mu = \mu_0 + \frac{D}{B^2} (\Omega_r - \omega) \left[1 - \frac{(\Omega_r - \omega)^2}{12B^2} \right] \exp \left[\frac{\gamma^2 - (\Omega_r - \omega)^2}{4B^2} \right]$$

Finally, far from the resonance frequency, when $z > 1$, the μ and η curves will go over into the ordinary dispersion formulas (10.29).

Gorban' and Shishlovskii^[101,102] have made experimental studies (at room temperature) of the curves for absorption and dispersion of light by localized centers. In Fig. 14, taken from^[101,102], the solid line 1 indicates the experimental curve for absorption of light in an NaCl crystal in which absorption centers have been produced by x-irradiation. The peak of this curve is Gaussian in nature, in agreement with theory. We observe asymmetry as we go away from the resonance frequency: on the red side the curve falls off more quickly than on the blue side. The circles in Fig. 14 indicate the experimental points for the measured values of the refractive index. The solid curve 2 has been drawn according to Eq. (10.27); the dotted curve in Fig. 14 corresponds to the ordinary dispersion curve for free molecules having a very large extinction. We see from Fig. 14 that the experimental points fall rather well on the theoretical curve of (10.27). Kizel' and Rubinov^[103] have also conducted theoretical studies of light-absorption curves of impurity molecules at room temperature. They also remark that Eq. (10.28) satisfactorily agrees with experiment.

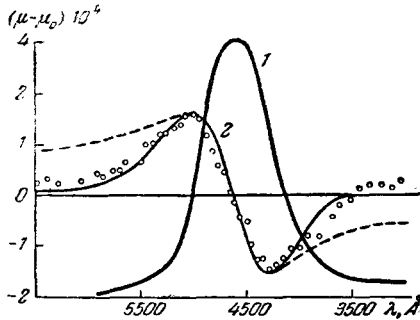


FIG. 14. Solid curve 1—experimental absorption curve for light in a NaCl crystal; solid curve 2—theoretical dispersion curve. Dotted curve—ordinary dispersion curve for free molecules having a very large extinction. Circles—experimental dispersion measurements.

c) The case of weak interaction. In the low-temperature case, inequality (10.24) is not satisfied for all lattice-vibration frequencies. In studying this case, we shall represent the function (10.19) in the form

$$g(\xi) = -g_0 + \sum_s (b_s e^{i\xi\omega_s} + c_s e^{-i\xi\omega_s}), \quad (10.30)$$

where

$$b_s = \frac{\bar{n}_s + 1}{2} (\xi_{s0} - \xi_{sl})^2, \quad c_s = \frac{\bar{n}_s}{2} (\xi_{s0} - \xi_{sl})^2, \quad g_0 = \sum_s (b_s + c_s). \quad (10.31)$$

Substituting (10.30) into the integral of (10.18), we transform it into the form

$$\Lambda = e^{-g_0} \int_0^\infty \exp\{i\xi[\Omega - \omega + i\gamma]\} \sum_{n,m} I_{n,m}(\xi) d\xi, \quad (10.32)$$

where

$$I_{n,m}(\xi) \equiv \frac{1}{n!m!} \left(\sum_s b_s e^{i\xi\omega_s} \right)^n \left(\sum_s c_s e^{-i\xi\omega_s} \right)^m,$$

and n and m take on positive integral values from zero to infinity.

Let the molecular excitation interact only with the lattice vibrations (one of the optical branches) such that $\omega_s \approx \omega_0$; then the integral in (10.32) can be easily calculated:

$$\Lambda = e^{-g_0} \sum_{n,m} \frac{b^n c^m \{\gamma + i[\Omega + (n-m)\omega_0 - \omega]\}}{n!m! \{[\Omega - \omega + (n-m)\omega_0]^2 + \gamma^2\}}, \quad (10.33)$$

where $b = \sum_s b_s$, $c = \sum_s c_s$, and Ω is given by (10.14a).

In the limiting case of low temperatures, $c \approx 0$. Hence, on summing over m in (10.33), only the term having $m = 0$ is retained, and here

$$\Lambda = e^{-g_0} \sum_{n=0}^{\infty} \frac{b^n \gamma + i[\Omega + n\omega_0 - \omega]}{n! \{[\Omega + n\omega_0 - \omega]^2 + \gamma^2\}}, \quad \text{if } T \approx 0. \quad (10.34)$$

By substituting (10.33) or (10.34) into (10.17) and (10.20), we can determine the relation of the refractive index and the absorption coefficient to ω . The absorption band consists of a set of equidistant bands shifted from the frequency Ω by distances of $(n-m)\omega_0$. With varying temperature, the position of the frequency Ω shifts slightly, since according to (10.14a) and (10.12), the value of Ω depends on \bar{n}_s . At the same time, the intensity distribution of the bands corresponding to different n and m also varies. Each term in (10.33) corresponds to the excitation of an impurity molecule with simultaneous creation of n phonons and annihilation of m phonons.

At very low temperatures, the ratio of the maxima of two consecutive absorption bands will be

$$\frac{b^n (n+1)!}{b^{n+1} n!} = \frac{n+1}{b}. \quad (10.35)$$

If

$$b = \sum_s \frac{\bar{n}_s + 1}{2} (\xi_{s0} - \xi_{sl})^2 < 1,$$

then each successive maximum will be lower than the previous one. The maximum absorption will correspond to a phononless transition, for which

$$\Lambda_0 = \frac{\gamma + i(\Omega - \omega)}{(\Omega - \omega)^2 + \gamma^2} e^{-g_0}$$

and the absorption coefficient

$$\eta(\omega) \approx \frac{\gamma D \exp(-g_0)}{(\Omega - \omega)^2 + \gamma^2}, \quad (10.36)$$

where

$$g_0 = \sum_s \left(\bar{n}_s + \frac{1}{2} \right) (\xi_{s0} - \xi_{s1})^2.$$

Hence, with increasing temperature, the maximum for the phononless transition will diminish. Here the values of b will increase, and when b becomes greater than unity, according to (10.35), among certain of the first absorption bands the subsequent maxima will be greater than the previous ones. Figure 15 shows the qualitative intensity variation of the successive absorption bands as one goes from $b = \frac{4}{5}$ to $b = 4$. With increasing temperature, the deformation of the absorption spectrum due to increase in b is supplemented by the superposition of new absorption bands belonging to various values of $m \neq 0$ in (10.33). Here absorption bands appear, distributed to the left of the frequency Ω of the phononless transition, and belonging to negative values of $n - m$. Owing to the increase in the values of b and c , the region encompassed by the absorption bands expands, while the intensity of each band diminishes owing to the presence of the factor $e^{-\xi_0}$.

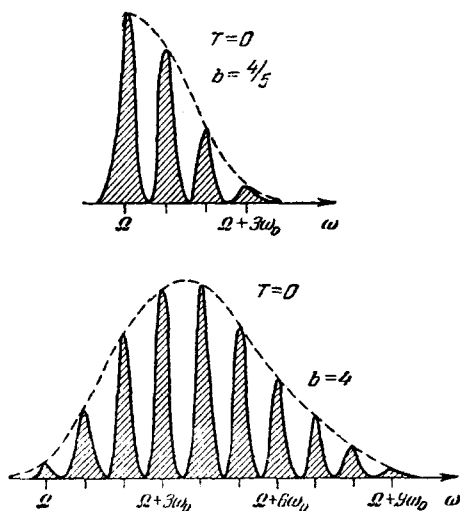


FIG. 15. Qualitative change in the nature of the absorption for various values of the parameter b determining the amount of coupling of the electronic excitation with the lattice vibrations.

The case discussed above involving interaction with phonons of only one optical branch of the vibrations is an idealization. In addition to the phonons of frequency ω_0 , phonons of other frequencies can also be created and absorbed. The systems of bands belonging to such transitions will be superimposed on the pattern shown in Fig. 15. In addition, owing to the interaction with phonons of the acoustic vibrations, whose frequencies are small and as a rule satisfy the inequality (10.24), each of the absorption bands will be broadened (this is already taken into account in Fig. 15) in correspondence to the above-discussed case of strong interaction. The half-widths of these bands will be determined by the values of B_i , which can be calculated using the formulas (10.23), provided that we take into account only the acoustic phonons in performing the summation.

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