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IDENTIFICATION OF EXCITONS WITH LIGHT WAVES IN A CRYSTAL AND THE MACROSCOPIC THEORY OF EXCITONS WITH AND WITHOUT ACCOUNT OF RETARDATION

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Excitons are identified with light waves in a crystal. The theory of excitons is reduced to the macroscopic theory of light waves. The energy bands, limiting energies for $\mathbf{k} \to 0$, effective masses etc. of excitons are expressed in terms of the dielectric constant tensor $\epsilon(\omega, \mathbf{k})$. In the limit $c \to \infty$, we obtain the results of the conventional exciton theory, based on the Schrödinger equation and neglecting retardation of interactions between particles. The results show that retardation can be neglected when the electromagnetic wave that accompanies an exciton is longitudinal. If, however, the wave possesses a rotational field, retardation considerably affects the results in regions where the refractive index is not very large. Exciton energies and effective masses then differ from those derived by means of the Schrödinger equation. Crystals of different symmetries are considered.

EXCITONS and light waves in crystals are physical concepts of entirely different origins and have been described mathematically in entirely different ways. Light waves are described by Maxwell's equations, with the mechanical motions of electrons and nuclei in a crystal taken into account entirely by the tensor form of the dielectric constant $\epsilon(\omega)$ (ω is the wave frequency). Beginning with Frenkel's first paper,[1] excitons have been described by the Schrödinger equation without allowing for retardation in the interactions between particles of a crystal.

Exciton absorption of light in a crystal has so far been treated as a quantum transition in which a photon is absorbed and an exciton is created. This procedure would be justified if light and molecules were two weakly interacting subsystems, as in the case of a gas. In a crystal, however, only the effect of the electromagnetic field on molecules can be regarded as a small perturbation, whereas the effect of the molecules on the field is not a small perturbation. There is a great difference between light waves in a crystal and in a vacuum; for the same frequency we find different wavelengths, different dispersion laws, etc. An exception occurs when the refractive index n in a crystal is very close to unity, but this is not usually the case in the absorption region.

The mechanical energy of crystal electrons and nuclei makes an important contribution to the energy of a light wave. We thus have a mixed "electromagnetic-mechanical" wave. However, the same can be said of an exciton wave, since it follows from references 2–6 that an exciton wave generates an accompanying electromagnetic wave that contributes greatly to the energy of the exciton. Excitons must therefore be identified with light waves in a crystal; both are small oscillations (excitations) of a system consisting of two strongly interacting parts — a crystal and an electromagnetic field.

As an illustration let us consider the optical vibration of an ionic lattice.[6] This vibration, when regarded as a mechanical phenomenon, is a typical exciton, but it is accompanied by the appearance in the crystal of fictitious charges and polarization currents that vary periodically in space and in time. The currents establish an electromagnetic field oscillating with the same frequency and wavelength. The amplitude of field oscillations is uniquely determined by the amplitude of normal ionic vibration, which can thus obviously be identified with an infrared light wave in the crystal.

As in our earlier papers,[2,4] we shall in general define an exciton as any excited state of the system that is characterized by a single wave vector $\mathbf{k}$ (with otherwise discrete quantum numbers). Regarding a crystal together with an electromagnetic field as a conservative system performing small quantized harmonic oscillations, we can identify the photon energy $\hbar\omega(\mathbf{k})$ with the exciton energy. The scattering of an exciton on lattice vibrations, accompanied by phonon creation or absorption, should be identified with the Raman scattering of a light quantum on the lattice vibrations.

Our earlier conclusion[3,4] that when the exciton lifetime is infinite no light is absorbed in a crystal, regardless of the magnitude of the phototransition oscillator strength per unit cell, now becomes trivial. Absorption becomes possible only as a result of exciton decay accompanied by a thermal transition of the system to excited states of another type.

For a quantitative study of excitons it is obviously just as necessary to consider the retardation of electromagnetic interactions as in the case of light waves. The Schrödinger equation is therefore, generally speaking, inadequate for excitons since it accounts only for instantaneous interactions between charges at all distances. There are two ways in which excitons can be studied while accounting for retardation in long-range interactions.

1) The Schrödinger Hamiltonian of the crystal should be supplemented by the energy of the rotational part of the field and by its interaction with particles. The latter is introduced into the Schrödinger problem of particle motion as a small external (classical) time-dependent perturbation. The rotational part of the field is determined self-consistently from the Maxwell equations, into the right-hand members of which we substitute the charges and currents that are derived from a solution of the Schrödinger problem.

The solution of the self-consistent problem as a whole enables us to determine the dispersion law for small vibrations of the entire conservative system, i.e., the dependence of ω on **k**. When these vibrations are quantized the energy of an exciton is given by

$$u_{\mathbf{k}} = \hbar\omega(\mathbf{k}). \tag{1}$$

We followed this first procedure in references 2, 4 and 7, where the above-mentioned dispersion law was derived.

The solution of the unperturbed Schrödinger problem neglecting retardation is thus an auxiliary intermediate step. At this stage we can use the results given in numerous publications where excitons were considered on the basis of the Schrödinger equation. It must be emphasized, however, that the corresponding Schrödinger excited crystal states are not in general real excitons, and that the corresponding eigenenergies differ considerably from the energies of real excitons when retardation is taken into account, as we shall see below.

We shall avoid conflict with conventional terminology by applying the term "exciton" to states of the auxiliary Schrödinger problem which neglects retardation. For real states of the entire conservative system (crystal plus electromagnetic field) we now introduce the term "light-exciton." (The word "photon" would not adequately express the large contribution from the mechanical energy of the particles.)

2) A second method for studying light-excitons will be used in this paper. The macroscopic electromagnetic field accompanying a light-exciton wave is defined by Maxwell's equations and is treated as a light wave. When we confine ourselves to cases in which the wavelength is considerably greater than the lattice constant, this field can be calculated by conventional macroscopic crystal optics, retardation in long-range interactions now being taken into account immediately. The energy of this light wave as calculated from the equations of electrodynamics will, as we know, include the mechanical energy of motion of the particles (electrons and nuclei). The dispersion law $\omega = \omega(\mathbf{k})$ that is determined for the wave will then be identified with that for small harmonic vibrations of the entire conservative system mentioned above, whereupon (1) will give the energy of the light-exciton.

The advantage of this second procedure lies in the fact that it is now entirely unnecessary to formulate and solve an auxiliary Schrödinger problem. On the other hand, it is necessary to specify (borrow from some source) the dependence of the dielectric constant ϵ on frequency ω and on the wave vector **k**. The dependence of ϵ on **k** is called the spatial dispersion. The dependence of ϵ on ω and **k** reflects the specific character of mechanical particle motion in the crystal, and its theoretical derivation would, of course, require solving the Schrödinger problem for the crystal.

Thus, identifying light-excitons with light waves in the crystal and assuming the electric field **E**, induction **D**, and magnetic field **H** to be proportional to

$$\exp\{i(\mathbf{kr} - \omega t)\} \quad (\mathbf{k} = \omega n \mathbf{s}/c, \quad |\mathbf{s}| = 1), \tag{2}$$

we obtain for the amplitude of the electric field the well-known vector equation

$$\mathbf{D} = \varepsilon(\omega, \mathbf{k})\,\mathbf{E} = n^2[\mathbf{E} - \mathbf{s}(\mathbf{sE})], \tag{3}$$

which is equivalent to a system of three homogeneous scalar equations. When the determinant of this system is set equal to zero we obtain the familiar equation for n:

$$\bar{\varepsilon} n^4 + [\bar{\varepsilon}^2 - \bar{\varepsilon}\,\mathrm{Sp}\,\varepsilon]\,n^2 + \varepsilon_1\varepsilon_2\varepsilon_3 = 0. \tag{4}$$

It is assumed here that the Cartesian coordinates are taken along the principal axes of the tensor $\epsilon(\omega, 0)$. Then the determinant for ϵ equals $\epsilon_1\epsilon_2\epsilon_3$, to terms of order $\mathbf{k}^2$. In (4) we have

$$\bar{\varepsilon} = (\mathbf{s}, \varepsilon \mathbf{s}), \quad \overline{\varepsilon^2} = (\mathbf{s}, \varepsilon^2 \mathbf{s}), \quad \mathrm{Sp}\,\varepsilon = \sum_{j=1}^{3} \varepsilon_j, \tag{5}$$

where ϵ_j ($j = 1, 2, 3$) are the principal values of the tensor ϵ.

If the dependence of ϵ on ω and $\mathbf{k}$ is given, (4) is used to determine $n(\omega)$ for a given direction of $\mathbf{s}$, thus determining $\omega(\mathbf{k})$ and the light-exciton energy (1). The existence of spatial dispersion raises (4) to higher than the fourth power in n, and more than two branches of the dispersion $n(\omega)$ are therefore obtained. These branches for different special cases are considered in references 2 and 6—9.

We can speak of light-exciton energy bands u_k, in a rigorous sense, only when the light-exciton possesses a very long lifetime, i.e., when light absorption in the crystal is negligibly small, as will be assumed below. In an infinite crystal the allowed bands comprise the values of u_k that correspond to real values of n. The values of u_k [and, correspondingly, of $\omega(\mathbf{k})$] that correspond to complex values of n are forbidden. In addition to spatial energy bands, a finite crystal may have allowed surface bands representing waves for which only the projection of $\mathbf{k}$ perpendicular to the crystal surface is complex. In the present work we do not consider surface bands or finite crystals.

In order to consider extremely long light-exciton waves we must assume $n \to 0$ in the preceding equations. It then follows from (3) that at least one of the principal values of ϵ must equal zero and that the corresponding projection of $\mathbf{E}$ may differ from zero:

$$\varepsilon_j(\omega', 0) = 0, \qquad \mathbf{E}_j \neq 0. \tag{6}$$

Here ω' [the roots of (6)] are the frequencies of the limiting waves, which do not depend on the direction of wave propagation ($\mathbf{s}$). It will be shown below that for "purely mechanical" excitons the limiting frequencies and energies generally depend on $\mathbf{s}$. When crystal symmetry causes two or three principal values of ϵ to vanish at the same frequency ω', two or three projections of the electric vector may correspondingly differ from zero for the limiting wave. The trivial case of an extremely long radio wave with $\omega = 0$ will not be considered.

Equations (1)—(6) provide the basis for a macroscopic theory of real light-excitons in a crystal. It is interesting to determine the relationships between the properties of light-excitons and excitons. The latter are understood to be the corresponding excited crystal states calculated by means of the Schrödinger equation, neglecting retardation and the rotational part of the field accompanying the electromagnetic wave. Such calculations are very common in the literature. The exciton theory is obviously a limiting case of the light-exciton theory with retardation neglected (i.e., $c \to \infty$). At the same time, for a wave with given values of ω and $\mathbf{k}$, $\mathbf{k}$ could remain finite in (2) only with n also approaching infinity. Passing to this limit in (4), the dependence of ω on $\mathbf{k}$ becomes possible only through spatial dispersion. We thus find that the neglect of spatial dispersion in electrodynamics is equivalent to the assumption of an infinitely narrow exciton energy band.

For extremely long exciton waves we must assume $k \to 0$ in (1)—(5) in addition to the limit $n \to \infty$ discussed above. The frequencies ω_0 of limiting exciton waves will then differ greatly from the frequencies ω' of limiting light-exciton waves, as will be evident from the examples discussed below.

We shall consider different possible types of light-excitons and some of their properties. When it is necessary to assign a specific dependence of ϵ_j on ω and $\mathbf{k}$, this dependence will be assumed to have the form

$$\varepsilon_j(\omega, \mathbf{k}) = \varepsilon_{0j} + G_j / (\mathscr{E}_{0j} + F_j(\mathbf{k}) - \hbar\omega), \tag{7}$$

where ϵ_{0j}, G_j and $\mathscr{E}_{0j}$ are constants. We may assume $F_j(0) = 0$ for a suitable value of $\mathscr{E}_{0j}$. It has been shown in reference 4 that ϵ_j actually has the form (7) if ω is in the vicinity of an isolated exciton light-absorption band. In this frequency region we shall assume that the two other principal values of ϵ are constants: $\epsilon_{j'} = \epsilon_{0j'}$, $j' \neq j$.

Exceptions occur when different principal values of $\epsilon(\omega, 0)$ coincide because of crystal symmetry, as in the case of cubic crystals. In such instances two exciton energy levels which coincide for $\mathbf{k} = 0$ are separated when $\mathbf{k} \neq 0$,[9] giving rise to two close absorption bands, neither of which can be regarded as isolated. The expression for $\epsilon_j(\omega, \mathbf{k})$ then contains two fractions of the type seen in the right member of (7), with identical values of $\mathscr{E}_{0j}$ but different $F_j(\mathbf{k})$. Thus (7) represents ϵ_j only when $\mathbf{k} = 0$.

We shall hereinafter confine ourselves to crystals possessing an inversion center and not lower than rhombic symmetry. In such crystals $\epsilon(\omega, \mathbf{k})$ is an even function of $\mathbf{k}$; the principal axes of $\epsilon(\omega, 0)$ coincide with 2-fold or 4-fold crystallographic axes and are therefore independent of ω. It will also be of importance that in such crystals the principal axis of the $\epsilon(\omega, 0)$ tensor is also the principal axis of the $\epsilon(\omega, \mathbf{k})$ tensor when $\mathbf{k}$ is parallel or perpendicular to this axis.

Light-excitons of the following three types are possible in a crystal.

1. Longitudinal light-excitons, $\mathbf{E} \parallel \mathbf{s}$. The right member of (3) vanishes, so that $\epsilon \mathbf{E} = 0$, i.e., $\mathbf{E}$ and $\mathbf{k}$ can be oriented only in one of the principal polarization directions j and the corresponding principal value ϵ_j vanishes:

$$\mathbf{E} = \mathbf{E}_j, \qquad \varepsilon_j(\omega, \mathrm{k}) = 0. \tag{8}$$

The second of these equations determines the dependence of ω on $\mathbf{k}$, which is possible only because of spatial dispersion.

For this wave the induction $\mathbf{D}$, the magnetic field strength, and the rotational part of the electric field all vanish. Since n does not appear in (3) the limiting transition $n \rightarrow \infty$ is without effect. A longitudinal light-exciton is consequently identical with the corresponding exciton and can be calculated by means of the Schrödinger equation, neglecting retardation, as has usually been done.

When ϵ_j is represented by (7), we obtain from (1) and (8)

$$u_{\mathrm{k}}^{\parallel} = \hbar\omega(\mathrm{k}) = \mathscr{E}_{0j} + G_j/\varepsilon_{0j} + F_j(\mathrm{k}). \tag{9}$$

Here the dependence of G_j and ϵ_{0j} on $\mathbf{k}$ must also be taken into account.

2. Tranverse light-excitons, $\mathbf{E} \perp \mathbf{s}$. According to (3) $\mathbf{E}$ can only have one of the principal polarization directions ($\mathbf{E} = \mathbf{E}_j$), while the dependence of ω on $\mathbf{k}$ is given by*

$$n^2 \equiv (c\mathrm{k}/\omega)^2 = \varepsilon_j(\omega, \mathrm{k}). \tag{10}$$

The frequencies ω' of long light-exciton waves are in the limit the same as for longitudinal light-excitons, and are determined by (6). It follows from (10) that in those frequency regions where spatial dispersion can be neglected, ω must be a monotonic function of $|\mathbf{k}|$ since $\epsilon_j(\omega)$ is a single-valued increasing function of ω. Thus the limiting long wave $(\mathbf{k} = 0)$ corresponds to the lower boundary of the light-exciton energy band. Moreover, ω does not depend on the direction of $\mathbf{k}$ so long as this remains perpendicular to $\mathbf{E}$.

It should not be concluded from the monotonic dependence of ω on $|\mathbf{k}|$ that the second boundary of the allowed light-exciton energy band corresponds to extremely short waves. With decreasing wavelength the existing macroscopic theory becomes invalid, but not before spatial dispersion becomes important, thus complicating (10) and, in general, destroying the monotonic dependence of ω on $|\mathbf{k}|$. Thus in the second quadrant of Fig. 2 in reference 7 the abscissa of the extreme right-hand point of the dispersion curve corresponds to the upper boundary of the allowed frequency band. At the same time the refractive index of the wave is approximately 15, so that the wave is neither extremely long nor extremely short.

In the present case of a transverse light-exciton, we shall now pass to the limit of a "purely mechanical" exciton. For this purpose we let $c \rightarrow \infty$ in (10), thus obtaining

$$\varepsilon_j(\omega, \mathrm{k}) = \infty. \tag{11}$$

This determines the dependence of ω on $\mathbf{k}$ for a transverse exciton and is quite different from (10), which determines $\omega(\mathbf{k})$ for a light-exciton. (10) leads to the essential dependence of ω on $\mathbf{k}$ even in the case of negligible spatial dispersion, whereas in (11) such dependence is possible only as a result of spatial dispersion. When, for example, ϵ_j is given by (7), Eq. (11) leads to

$$u_{\mathrm{k}}^{\perp}(\mathrm{exc}) = \hbar\omega(\mathrm{k}) = \mathscr{E}_{0j} + F_j(\mathrm{k}). \tag{12}$$

A comparison with (9) shows that for $\mathbf{k} = 0$ the energy of a transverse exciton is diminished relative to that of a longitudinal exciton by the amount G_j/ϵ_{0j}:

$$u_0^{\parallel} - u_0^{\perp}(\mathrm{exc}) = G_j/\varepsilon_{0j}. \tag{13}$$

It was shown above that $\mathbf{E}$ for longitudinal and transverse light-excitons must have one of the principal directions of polarization. The converse is easily derived from (3): If $\mathbf{E}$ has one of the principal polarization directions, the light-exciton must be either longitudinal or transverse. It can also be shown that if $\mathbf{s}$ is parallel to a principal polarization direction, $\mathbf{E}$ must be either parallel to $\mathbf{s}$ or parallel to one of the principal polarization axes that are perpendicular to $\mathbf{s}$. Consequently, only longitudinal or transverse light-excitons are possible.

In order to exhaust the possible types of light-excitons we need only to consider those for which $\mathbf{E}$ and $\mathbf{s}$ are neither parallel nor perpendicular.

3. Light-excitons with $\mathbf{E}$ and $\mathbf{s}$ neither parallel nor perpendicular. It follows from the foregoing discussion that now neither $\mathbf{E}$ nor $\mathbf{s}$ is parallel to one of the principal polarization axes. We shall first consider the case in which $\mathbf{s}$ is perpendicular to one of the principal polarization directions (j). (3) and (4) now have two solutions, one of which is for transverse light-excitons:

$$n^2 = (c\mathrm{k}/\omega)^2 = \varepsilon_j(\omega, \mathrm{k}), \quad \mathbf{E} = \mathbf{E}_j. \tag{14}$$

This type has already been considered.

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*Since k will be perpendicular to the principal polarization direction j, the latter will be a principal axis of the two tensors $\varepsilon(\omega, \mathrm{k})$ and $\varepsilon(\omega, 0)$, thus coinciding with one of the Cartesian coordinate axes.

The other solution is

$$n^2 = \left(\frac{ck}{\omega}\right)^2 = \frac{\varepsilon_i\varepsilon_l - \varepsilon_{il}\varepsilon_{li}}{s_i^2\varepsilon_i + s_l^2\varepsilon_l + s_i s_l(\varepsilon_{il} + \varepsilon_{li})},$$

$$i \neq l \neq j, \tag{15}$$

with **E** lying in a plane perpendicular to the j axis, while its direction is determined by $(\mathbf{s}, \mathbf{D}) = 0$, i.e.,

$$E_i(s_i\varepsilon_i + s_l\varepsilon_{li}) + E_l(s_i\varepsilon_{il} + s_l\varepsilon_l) = 0. \tag{16}$$

Here the subscripts i and *l* denote the two principal axes of $\epsilon(\omega, 0)$ perpendicular to j.

In the frequency region where spatial dispersion may be neglected $|\mathbf{k}|$ is a single-valued function of ω. Consequently, ω is a monotonic function of $|\mathbf{k}|$ for the given direction of **s**, and limiting long waves correspond to the boundaries of the energy band. This does not apply to the case in which spatial dispersion is taken into account, since **k** then appears in the right member of (15); this equation then is not of the first degree in $\mathbf{k}^2$ and has several roots of $\mathbf{k}^2$ for a given frequency. We shall now pass to the limit of a "purely mechanical" exciton in (15) and (16). Setting $c \to \infty$ in (15), we obtain (since $\epsilon_i \neq \epsilon_l$)

$$s_i^2\varepsilon_i(\omega, \mathbf{k}) + s_l^2\varepsilon_l(\omega, \mathbf{k}) + s_i s_l[\varepsilon_{il}(\omega, \mathbf{k}) + \varepsilon_{li}(\omega, \mathbf{k})] = 0. \tag{17}$$

This equation determines the dependence of ω on **k** for the exciton.

In the final case **s** is perpendicular to none of the principal polarization directions. (4) now splits into the two equations

$$n_\alpha^2 \equiv \left(\frac{ck_\alpha}{\omega}\right)^2 = \frac{1}{2}\left\{\frac{\Omega}{\bar{\varepsilon}} - \left[\left(\frac{\Omega}{\bar{\varepsilon}}\right)^2 - 4\frac{\varepsilon_1\varepsilon_2\varepsilon_3}{\bar{\varepsilon}}\right]^{1/2}\right\}, \tag{18}$$

$$n_\beta^2 \equiv \left(\frac{ck_\beta}{\omega}\right)^2 = \frac{1}{2}\left\{\frac{\Omega}{\bar{\varepsilon}} + \left[\left(\frac{\Omega}{\bar{\varepsilon}}\right)^2 - 4\frac{\varepsilon_1\varepsilon_2\varepsilon_3}{\bar{\varepsilon}}\right]^{1/2}\right\}. \tag{19}$$

Here $\Omega = \bar{\epsilon}\,\mathrm{Sp}\,\epsilon - \bar{\epsilon}^2$.

The direction of **E** is determined from (3) and is not perpendicular to that of **s**. When spatial dispersion exists each of these equations determines more than one dispersion branch of $\omega(\mathbf{k})$, which could be investigated only for a definite dependence of ϵ on **k**.

The frequency region in which spatial dispersion may be neglected can be investigated qualitatively. In this case

$$\Omega = \varepsilon_1\varepsilon_2(1 - s_3^2) + \varepsilon_1\varepsilon_3(1 - s_2^2) + \varepsilon_2\varepsilon_3(1 - s_1^2),$$

$$\varepsilon_{il} = 0, \quad i \neq l. \tag{19a}$$

For $\mathbf{k}_\beta^2 \geq \mathbf{k}_\alpha^2$ the solutions (18) and (19) will be called long-wave and short-wave light-excitons, respectively. Allowed frequency and energy bands for these light-excitons are determined from the condition that the radicands and the right members of (18) and (19) be positive. The same qualitative statements can be made concerning the dependence of ω on **k** for each of these light-excitons as in the case of a transverse light-exciton, with the following addition. For all ω for which n_α is real, n_β is also real. But it is also possible to have ω for which only n_β is real, but not n_α. This means that every allowed energy band of light-exciton (18) must be inside the band of light-exciton (19). The latter band is therefore wider than the former.

If for some frequency $\bar{\omega}$ we have $\Omega^2 = 4\bar{\epsilon}\epsilon_1\epsilon_2\epsilon_3$ and $\Omega/\bar{\epsilon} > 0$, then $\bar{\omega}$ is the common boundary of α and β (the sign of the radicand reverses when $\omega = \bar{\omega}$). When $\omega = \bar{\omega}$, $(d\omega/d|\mathbf{k}|)_{\bar{\omega}} = 0$ for both light-excitons. These relationships are shown approximately in the figure. For ω' determined from (6) the limiting long wave will be either the α wave (if $(\Omega/\bar{\epsilon})_{\omega'} > 0$) or the β wave (if $(\Omega/\bar{\epsilon})_{\omega'} < 0$). ω' is the boundary of the allowed band and, unlike $\bar{\omega}$, does not depend on the direction of **s**. The figure shows that the allowed bands may be entirely within the region of such long waves that macroscopic considerations and the neglect of spatial dispersion are possible for the entire band.

In (18) and (19) we now make the limiting transition from light-excitons to excitons, for which purpose we set $c \to \infty$. In (18) only directions of **s** perpendicular to one of the principal polarization directions are then possible, resulting in a transverse exciton which is represented by (11) and (12).

In (19) the same limiting transition leads to

$$\bar{\varepsilon} \equiv \sum_{i=1}^{3} s_i^2\varepsilon_i(\omega, \mathbf{k}) = 0, \tag{20}$$

which extends (17) to the case in which all three projections of **s** differ from zero. (20) is fulfilled when all three principal values ϵ_i are finite. Consequently, putting $n \to \infty$ in (3), we obtain $\mathbf{E} \parallel \mathbf{s}$. The exciton is thus longitudinal although the original light-exciton (19) was not longitudinal. This result as well as the freedom for the direction of **s** distinguishes the present case from the previously considered longitudinal light-exciton. According to (20) the dependence of ω on k_1, k_2, k_3 is discontinuous at $\mathbf{k} = 0$. Assuming $\mathbf{k} \to 0$ in (20), we obtain

$$\sum_{i=1}^{3} s_i^2\varepsilon_i(\omega, 0) = 0, \tag{21}$$

which determines the frequencies of long exciton waves in the limit. These frequencies, i.e., the roots of (21), depend on **s**. The limiting value of the exciton energy therefore depends on the direction of **k** when its modulus approaches zero.

If, for example, in the given frequency region the principal contribution to the dielectric constant ϵ_j comes from the term associated with a virtual transition of the system to a single exciton state, while transitions to other states make negligibly small contributions, we have

$$\varepsilon_j = 1 + G_j / [\mathscr{E}_{0j} + F_j(\mathbf{k}) - \hbar\omega], \quad \varepsilon_l = \varepsilon_i = 1; \quad l, i \neq j. \quad (22)$$

In this case (20) leads to

$$u_{\mathbf{k}}(\mathrm{exc}) = \hbar\omega(\mathbf{k}) = \mathscr{E}_{0j} + G_j s_j^2 + F_j(\mathbf{k}). \quad (23)$$

In a crystal for which $\epsilon_1 = \epsilon_2 \neq \epsilon_3$ the aforementioned principal contribution is received by both ϵ_1 and ϵ_2, so that

$$\varepsilon_1 = \varepsilon_2 = 1 + G / [\mathscr{E}_0 + F(\mathbf{k}) - \hbar\omega], \qquad \varepsilon_3 = 1. \quad (24)$$

In this case (20) leads to

$$u_{\mathbf{k}}(\mathrm{exc}) = \hbar\,\omega(\mathbf{k}) = \mathscr{E}_0 + G(s_1^2 + s_2^2) + F(\mathbf{k}). \quad (25)$$

(13), (23) and (25) for limiting small values of $|\mathbf{k}|$ agree with the direct calculation of exciton energy by means of the Schrödinger equation.[3] (13) also agrees with calculations of particular exciton modes—polarized lattice vibrations.[6,10-13]

EXCITON EFFECTIVE MASSES

For the purpose of determining the effective mass of a light-exciton, u_k is expanded in powers of $\mathbf{k}$ near $\mathbf{k} = 0$. In the case of a strictly longitudinal light-exciton retardation may be neglected, as has been shown above, and the dependence of u_k on $\mathbf{k}$ can be calculated by means of the Schrödinger equation, as is customary in the literature. The macroscopic theory discussed above then yields no new results, particularly for the effective mass. We shall consider a non-longitudinal light-exciton, for which, when retardation is taken into account, very different results are obtained.

The dependence of ω on $\mathbf{k}$ is determined by (4), in which spatial dispersion may be disregarded since we are now considering the region of limiting long light-exciton waves.

There is no special reason why $d\epsilon_j/d\omega$ should vanish at the same frequency ω' at which ϵ_j vanishes. Therefore, excluding unlikely chance coincidences, we shall assume that in the region $\omega \approx \omega'$ we have

$$\varepsilon_j = g_j\hbar(\omega - \omega') + \ldots, \quad \hbar g_j \equiv (d\varepsilon_j/d\omega)_{\omega'}. \quad (26)$$

When ϵ_j in (4) is expanded in powers of $\omega - \omega'$ and only first-degree terms are retained, we obtain the following expressions for the effective mass: in crystals where $\epsilon_1 = \epsilon_2 = \epsilon_3$,

$$u_{\mathbf{k}} = \hbar\omega(\mathbf{k}) = \hbar\omega' + \hbar^2\mathbf{k}^2/2\mathfrak{m} + \ldots, \quad \mathfrak{m} = g(\hbar\omega')^2/2c^2; \quad (27)$$

in crystals where $\epsilon_1 = \epsilon_2 \neq \epsilon_3$, for an ordinary ray which is a transverse light-exciton of the type represented by (14) at frequencies where $\epsilon_h \equiv \epsilon_1 = \epsilon_2 \approx 0$, $\epsilon_3 \neq 0$,

$$u_{\mathbf{k}} = \hbar\omega(\mathbf{k}) = \hbar\omega' + \hbar^2\mathbf{k}^2/2\mathfrak{m}_h + \ldots, \quad \mathfrak{m}_h = g\ (\hbar\omega')^2/2c^2. \quad (28)$$

For an extraordinary ray which is a light-exciton of the type represented by (15) at frequencies where $\epsilon_3 \approx 0$, $\epsilon_h \equiv \epsilon_1 = \epsilon_2 \neq 0$,

$$u_{\mathbf{k}} = \hbar\omega(\mathbf{k}) = \hbar\omega' + \hbar^2(k_1^2 + k_2^2)/2\mathfrak{m} + \ldots,$$

$$\mathfrak{m} = g_3(\hbar\omega')^2/2c^2. \quad (29)$$

This equation shows that the light-exciton effective mass becomes infinite in direction 3. With spatial dispersion taken into account it would be finite but relatively very large. This means that for an extraordinary long-wave ray the projection of the group velocity is very much smaller in direction 3 than in other directions for the same values of the wave-vector projections.

At frequencies where $\epsilon_h \equiv \epsilon_1 = \epsilon_2 \approx 0$, $\epsilon_3 \neq 0$, for an extraordinary ray we obtain

$$u_{\mathbf{k}} = \hbar\omega(\mathbf{k}) = \hbar\omega' + \hbar^2 k_3^2 / 2\mathfrak{m} + \ldots, \quad \mathfrak{m} = g_h(\hbar\omega')^2 / 2c^2. \quad (30)$$

Here the light-exciton effective mass is infinite in directions 1 and 2, while the group velocity is very small.

For crystals with all three ϵ_j different, at frequencies for which one of the principal values of ϵ, such as ϵ_3, vanishes, (29) is obtained.

The effective mass of a light-exciton can be very much smaller than the mass m of a free electron. For example, if the frequency dependence of ϵ_j is represented by (7), we have

$$g_j = \varepsilon_{0j}^2 / G_j. \quad (31)$$

In order to estimate the parameter G_j we assume that dispersion results from electron polarization and that the electron state of the crystal can be considered on the basis of the Heitler-London-Heisenberg approximation (which assumes weak interactions between electrons belonging to different unit cells). Then

$$G_j = \frac{2\pi e^2 N\hbar^2 f_j}{m\mathscr{E}_{0j}} = \frac{2\pi I^2 f_j}{\mathscr{E}_{0j}}\left(\frac{a_0}{d}\right)^3, \quad (32)$$

where $a_0 = \hbar^2/me^2 = 0.529$ A, $I = e^2/a_0 = 27.1$ ev, f_j is the oscillator strength per unit cell for a phototransition from the ground state to the exciton state in question, $N = 1/d^3$ is the number of cells per unit volume, and d is the cubic-lattice constant. Let us, for example, consider a crystal with $d = 10a_0$, $\epsilon_{0j} = 2$, $\mathscr{E}_{0j} = 2$ ev. Assuming $f_j = 0.1$, we obtain $G_j = 0.23$ ev, $g_j = 17.4\ \mathrm{ev}^{-1}$, $\mathfrak{m}/m = 7.5 \times 10^{-5}$.

So small a value of the light-exciton effective mass corresponds, for the given kinetic energy, to a large value of its group velocity, which can considerably exceed the velocity of mechanical electron motion. It is thus shown that in the long-wave region a light-exciton is much more an electromagnetic than a mechanical phenomenon. According to (31) and (32), when the oscillator strength f_j is reduced $\mathfrak{m}$ increases but remains considerably smaller than m even for very small f_j. Thus in the crystal considered above $\mathfrak{m} = m$ only for $f_j = 7.5 \times 10^{-6}$. The light-exciton retains its predominantly electromagnetic character down to such small oscillator strengths. The foregoing numerical example shows that the properties of an exciton, particularly its effective mass, are strongly modified when retardation is taken into account.

It is important to estimate how far from the boundary of the allowed energy band the quadratic approximation for the dependence of u_k on **k** and the above-discussed effective masses still remain valid. The error of the approximation arises from the neglect of higher powers of $\omega - \omega'$ in (26). With (7) used for $\epsilon_j(\omega)$, (26) can be written as

$$\varepsilon_j(\omega) = \frac{\varepsilon_{0j}^2}{G_j}\hbar(\omega-\omega') - \frac{\varepsilon_{0j}^3}{G_j^2}\hbar^2(\omega-\omega')^2 + \ldots \qquad (33)$$

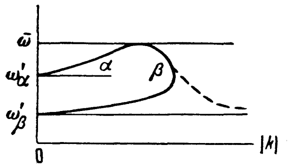
It thus appears that the quadratic term may be dropped if

$$|\hbar\omega - \hbar\omega'| = |u_{\mathbf{k}} - u_0| \ll G_j/\varepsilon_{0j}. \qquad (34)$$

In our numerical example above this means that $|u_k - u_0| \ll 0.115$ ev. Therefore at room temperature light-excitons possessing moderate quasi-kinetic thermal energy $u_k - u_0$ are still characterized by the aforementioned effective masses. In the study of such phenomena as light-exciton scattering by lattice vibrations and by impurities, light-exciton diffusion, collisions of light-excitons with current carriers etc., one should use the energies, effective masses and other light-exciton properties that really exist in crystals, rather than those of "purely mechanical" excitons.

We have considered the effective masses of light-excitons at the boundaries of the allowed energy bands corresponding to limiting long waves. Effective masses can also be introduced at other band boundaries corresponding in **k** space to the point $\mathbf{k} = \mathbf{k}^0 \neq 0$. The energy u_k is then expanded in powers of the differences $k_i - k_i^0$. For instance, it has been noted above that the frequency $\bar{\omega}$ (see the figure) is not the absolute band boundary but is the boundary only for waves having a given direction of **s**. But when **s** is chosen so that $\bar{\omega}$ as a function of **s** is an extremum (a maximum or a minimum when ω is the upper or lower band boundary, respectively) this frequency is the absolute boundary of bands α and β. Effective masses can be introduced at the corresponding point $\mathbf{k}^0$ since the expansion of $\omega - \bar{\omega}$ in powers of $k_i - k_i^0$ begins with quadratic terms. The results, which are easily obtained from (18) and (19), will not be given here.

Energy bands of light-excitons in biaxial crystals for a given direction of **k**. $\bar{\omega}$, but not ω'_α or ω'_β, depends on the direction of **k**.



A frequency region where spatial dispersion is important may also contain band boundaries near which effective masses can be introduced. For example, in Fig. 2 of our reference 7, corresponding to negative exciton effective mass M, the extreme right-hand point of the dispersion branch in the second quadrant is the upper boundary of the allowed band (as already mentioned above). At this point the expansion of the light-exciton energy is

$$u_{\mathbf{k}} = \mathscr{E}_0 + \hbar^2 q^2/M + \hbar^2(|\mathbf{k}| - q)^2/2\mathfrak{m} + \ldots,$$

$$\mathfrak{m} = {}^1/_4 M, \quad q^2 = \mathscr{E}_0\sqrt{2MG}/c\hbar^2. \qquad (35)$$

Here $\mathscr{E}_0$ and G are the parameters of (7). (35) was derived for an isotropically polarized crystal where the effective mass M of a "purely mechanical" exciton is also isotropic; it is also assumed that at the boundary in question we have $n^2 \gg \epsilon_0$. The boundary of the light-exciton energy band in **k** space is the sphere $|\mathbf{k}| = q$, along the radii of which the light-exciton effective mass $\mathfrak{m}$ is one-fourth the exciton effective mass. The light-exciton mass becomes infinite along tangents to the sphere.

When the same dispersion branch, represented in Fig. 2 of reference 7, enters the region of very large n, where $|\mathbf{k}| \gg q$ and where the dispersion curve merges with its rectilinear asymptote, we obtain for this region

$$u_{\mathbf{k}} = \mathscr{E}_0 + \hbar^2 k^2/2M + \ldots, \qquad (36)$$

i.e., the light-exciton acquires the properties of a mechanical exciton and is characterized by the effective mass of the latter. This follows naturally, since for $n \gg 1$ we should obtain results close to those for the limiting case $n \to \infty$. (36) is valid for values of $|\mathbf{k}|$ that are fairly large but still considerably smaller than π/d. The exciton band boundary $\mathscr{E}_0$ is not the boundary of the light-exciton band.

Equation (36) is also obtained for very large n in the case of $M > 0$, which is represented in Fig. 1 of reference 7. The lower boundary of the allowed light-exciton band will be the closest root ω' of (6) on the lower-frequency side of $\omega_0 = \mathscr{E}_0/\hbar$. When this band lies lowest so that the root does not exist, the lower boundary will be $\omega = 0$, at which

$$n = \sqrt{\varepsilon_{\text{stat}}} \neq 0, \quad \omega(\mathbf{k}) = c|\mathbf{k}|/\sqrt{\varepsilon_{\text{stat}}} + \ldots, \tag{36a}$$

i.e., an effective mass cannot be introduced.

It must be remembered that a crystal in thermal equilibrium contains mainly low-energy light excitons such as phonons, which have an allowed band width of the order kT. In this case the great majority of light-excitons will be associated with very large refractive indices n since there will be very many more large values than small values of $|\mathbf{k}|$ in $\mathbf{k}$ space. These light-excitons can therefore be regarded as mechanical excitons. For this reason retardation may be neglected in connection with such properties as exciton specific heat and thermal conductivity.

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