| Semiconductor crystals: II. Optical absorption and excitons 12 h DIRECT OPTICAL TRANSITIONS	Các tinh thể bán dẫn: II. Hấp thụ quang học và các exciton DỊCH CHUYỂN QUANG HỌC TRỰC TIẾP (DỊCH CHUYỂN KHÔNG THÔNG QUA PHONON)
In the process of direct photon absorption a photon of energy « and wavevector K is absorbed by the crystal with the creation of an electron at kei in a conduction band and a hole at khoie in the valence band. The scale	Trong quá trình hấp thụ photon trực tiếp, một photon có năng lượng…và vector sóng K được hấp thụ bởi tinh thể đồng thời tạo ra một electron có vector sóng kei trong vùng dẫn và lỗ trống có khoie trong vùng hóa trị. Độ

of wavevectors of optical photons is of the order of 104 cm-1 and may almost always be neglected in comparison with the scale of wavevectors in the Brillouin zone, 108 cm-1. The conserva¬tion of wavevector in the absorption process requires

FIG. 1. Direct absorption processes in (a) and (6); the absorption process (c) is indirect and takes place with the emission or absorption of a phonon.

lớn của các vector sóng của các photon quang học vào cỡ 104 cm-1 và gần như có thể bỏ qua so với độ lớn của các vector sóng trong vùng Brillouin, 108 cm-1. Bảo toàn vector sóng trong quá trình hấp thụ đòi hỏi (buộc)

(1)
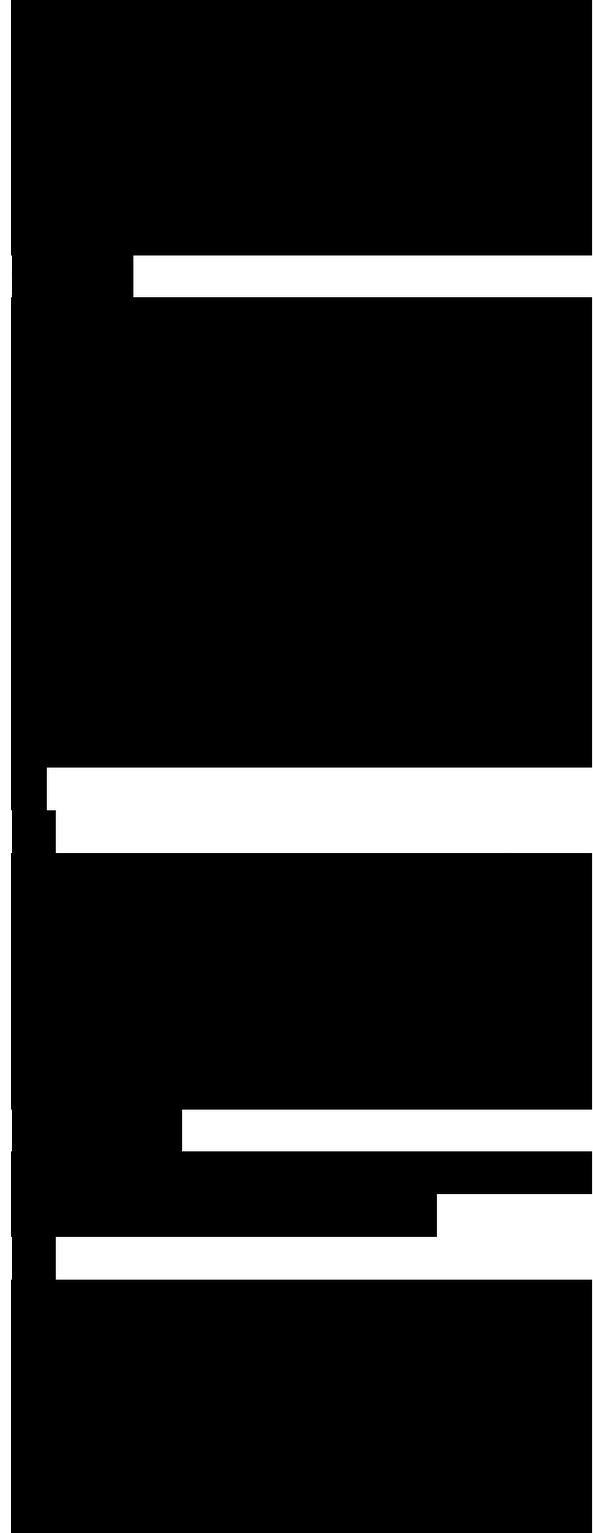
we may usually replace k' by k. Thus [<5h:fp|k-y)[2 determines the intensity of the transition; this same quantity

determines the mutual interaction of the two bands 7, 6 in the reciprocal effective mass tensors. We see that bands which perturb each other strongly are always connected by allowed optical transitions for the direct absorp¬tion or emission of a photon.

INDIRECT OPTICAL TRANSITIONS

Sometimes, as in Si and Ge, the minimum energy difference between the valence and conduction bands does not occur for Ak — 0, but the band minima fall at different k values and cannot be connected by an alowed optical transition. If this is true, the threshold of strong optical absorption will lie at a higher energy than the energy gap. But at energies slightly above the energy gap a weak absorption takes place with the emission or absorption of a phonon of wavevector q:

(4)   kel + khoIe + q^O.

If the conduction and valence band edges do not lie at the same point in k space, the indirect or nonvertical process will dominate the optical absorption over the appropriate energy interval. The energy balance

w = £(kc) - e(k,,) ± co¬

at absolute zero no phonon is available to be absorbed in the process and here the positive sign must be taken on the right-hand side. At higher temperatures there are thermal phonons available to be absorbed, and photon absorption may take place at an energy lower by 2o)phonon, where

the phonon has a wavevector of magnitude close to the difference $|k_c - k_v|$ at the band edges.

The intensity of the indirect transition[1] is determined by second-order matrix elements of the electron-phonon and electron-photon interactions. Second-order matrix elements for processes in which a phonon is absorbed involve

Here the c's are electron operators and the a's are phonon operators. The form of the electron-phonon interaction was discussed in Chapter 7. In the process described the electron is initially at $k - q$ in the valence band y and the phonon occupation number is n_q for wavevector q. In the final state the electron is at k in the conduction band 8 and the phonon occupation is $n_q - 1'$. The corresponding matrix element for emission of a phonon is written down by using the terms $c^{\dagger}_{q} c_{k} a^{\wedge}$ of the electron-phonon interaction.

Actually there will be a number of threshold energies because in principle every branch of the phonon spectrum will participate at the same wavevector, but at different frequencies. Optical measurements have been able in this way to determine directly the difference in thi wavevectors of the conduction and valence band edges, provided tha the phonon spectrum itself is known, as from inelastic neutron scatter¬ing studies.

OSCILLATORY MAGNETO ABSORPTION LANDAU TRANSITIONS

In the presence of a strong static magnetic field the optical absorp¬tion near the threshold of the direct transition in semiconductors is observed to exhibit oscillations. That is, at fixed H the absorption coefficient is periodic in the photon energy. In a magnetic field the interband transitions (Fig. 2) take place between the Landau magnetic levels in the valence band and the corresponding levels in the conduc-

1   See Bardeen, Blatt, and Hall, Proc. of Conf. on Photoconductivity, Atlantic City, 1954 (Wiley, 1956), p. 146.

Fig. 2. Schematic diagram showing the magnetic levels for kz = 0 as labeled by n (kz = 0) for two simple bands. The possible transitions are shown for the case in which the direct transition is allowed by parity.

tion band. Such transitions are called Landau transitions. In a magnetic field parallel to the z axis the energies in the two bands, if nondegenerate, are

where o>c, uv are the cyclotron frequencies and nc, nv are the anomalous magnetic moments. The spatial parts of the wavefunctions in each band are of the form \p{x} — u0(x)F(x), where UQ(X) is the Bloch function in the appropriate band for k = 0 and, from Eq. (11.13),

(7)   Fn(x)   =   ei(k«v+k^<pn(x - ckv/eH)

in the Landau gauge. Here Fn is the solution of the appropriate Wan¬nier equation and <pn is the harmonic oscillator wavefunction for the nth. excited state.
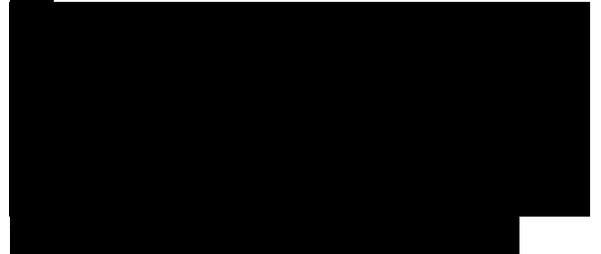
The matrix element for optical absorption is proportional to

(8)   (nckcykcz\p\nvkvykvz) = / d3x u*c (x)puov(x) f dzxF*c(x)Fnv(x), crystal

where we have broken up the integral by treating the F's as essentially constant over a cell. The integral involving the F's will vanish unless k°y = kvy\ k\ = k\\ and nc = nv. This is analogous to the selection rules conserving k in the absence of a magnetic field. The equality of the n's follows by the orthogonality property of harmonic oscillator wavefunctions, noting that these do not depend on the effective mass. The allowed transitions have An = 0, as indicated in Fig. 2. After integrating the transition probability over the density of states for 2, it is found that the absorption coefficient is proportional to

The theory of oscillatory magnetoabsorption for degenerate bands and also for indirect transitions has been given by Roth, Lax, and Zwerdling, Phys. Rev. 114, 90 (1959). We note that magnetoabsorption experiments are particularly valuable in determining the param¬eters of a direct conduction-band energy surface which, because it is not the band edge, cannot be kept populated sufficiently to permit a cyclotron resonance experiment to be made; further, the experiments involve the anomalous magnetic moments or g factors.

EXCITONS

An exciton is defined as a nonconducting excited electronic state in a perfect insulator, usually a

nonmagnetic insulator. It is usual to speak of two types of excitons: a tightly bound or Frenkel exciton and a weakly bound or Mott exciton. Both types of excitons may be thought of as bound states of an electron and a hole; there is no sharp division between the two types. In a Frenkel exciton there is a high probability of finding the electron and hole on the same atom in the crystal; in a Mott exciton the wavefunction in the relative coordinate extends over many atoms. Frenkel excitons are realized in alkali-halide crystals and in many crystals of aromatic molecules; Mott excitons are found in semiconductor crystals having small energy gaps and high dielectric constants.

The machinery we developed for the inpurity-state problem may be taken over directly to the discussion of weakly bound excitons, of radii large in comparison with a lattice constant. For this reason, and because their experimental picture is richer, we limit ourselves here to the discussion of weakly bound excitons.

If both the conduction and valence band edges are spherical, nondegenerate, and are located at k = 0, the exciton spectrum and wavefunctions are obtained readily by an extension of the result found above for electrons bound in impurity states. We introduce the rela¬tive and center-of-mass coordinates

where both me and m* are usually positive. The effective hamiltonian in a cubic crystal is

The part of the wavefunction in X

must contain a factor etK'x; the part in the relative coordinates contains a factor Fn(x), where

(12) (ipl

is the hydrogenic wave equation with the reduced mass

(13)

and dielectric constant e. In direct analogy to the treatment of impurity states in Chapter 14, the total exciton wavefunction is

(14) #ic»(X,x) = eiKXF n (x) <pc(xe)<pv(xh),

where <pc(xe) is the Bloch function at $k = 0$ in the conduction band and <Pv(Xh) is the valence band function at $k = 0$. The excitation is propagated in the crystal as a wave of momentum K.

The energy of the state (14) is

(15)

referred to the conduction band edge. For bound states En is negative and the total exciton energy at low K is negative with respect to a separated hole-electron pair. For the hydrogenic hamiltonian (12) the energy is, with % restored,

(16)

for e = 5 and /i = 0.5m the ionization energy (n = 1) of the exciton is about i ev. We note that the minimum energy required to create an exciton starting from the ground state of the crystal is

(17)   A' = K ~

where Eg is the energy gap.

Excitons created by photon absorption from the ground state of the crystal are created near $K = 0$; therefore the direct exciton absorption spectrum is a series of sharp lines below the optical

absorption edge of the crystal. It is somewhat unusual to find a crystal in which there are two spherical band edges at k = 0, but this is apparently the situation in CU2O, for which the exciton spectrum is closely hydrogenic.

For general energy surfaces the exciton problem is best formulated using the coordinate transformation
(18)   p = i(xe + xfc); x = xe - xfcj

rather than with the transformation (10). It is instructive to reexam¬ine the problem we have just solved. The hamiltonian (11) is trans¬formed with the use of
Thus, if II, p are the momenta conjugate to p, x, we have for the special case of spherical surfaces

If we look for a wavefunction of the form

the equation for Fn(x) is

The eigenvalue of (12) to second order in K is found by K • p perturbation theory:
(24)   g + 1 g + 1 (-1 - -1V g H*- Pi
v   8ju 4 \me mh/ i En — Ei

But by the atomic /-sum rule on the hydrogenic states I, n,
2   v, {n\v»\l)(l\p>\n) ,,
(25)
whence (24) becomes
<26> + 2(S^)**-
in agreement with (15).
The extension of the present treatment in the coordinate system (18)   to

ellipsoidal band edges follows directly on using the components of the reciprocal mass tensors in (19) and (20). The further extension to degenerate band edges is complicated in practice, but follows by using matrix operators for the multicomponent state functions at each band edge; see G. Dresselhaus, Phys. Chem. Solids 1, 14 (1956). In practice various approximate dodges are often employed to avoid confronting the complexity of the multicomponent equations.

We now discuss the intensity of optical absorption for a process in which an allowed (electric dipole) transition creates an exciton from a filled valence band. We take the bands to be spherical about $k = 0$ arid nondegenerate. From (14) the exciton wavefunction at $K = 0$ is

(27) $\#0n(x) = Fn(xe \sim xh)<pc(xe)<pv(xh),$

and in this scheme the wavefunction of the initial state is simply unity.

This is not the clearest way to treat a many-electron problem; it is better to use the formalism of second quantization, as in Chapter 5. We denoted the filled valence band by $i>o!$ then we define

this is a state in which an electron has been raised to the conduction band at k, leaving a hole in the valence band at — k. The nth exciton state for $K = 0$ may be written

$\#n = 2\#k(k|n) = T a^ik\#o(k|n), k k$

The electric dipole absorption is determined by the matrix element $(ck|p|ki>)$ of the momentum p between

the state k in the valence band and the state k in the conduction band. In second quantization the momentum operator is

P = X Cki'Ck* / d*x ^k{'(x)p^ki(x),

or, with I denoting the valence band v and V the conduction band c,

(30)   P = J af/3+k<ck|p|k!;).
k

Then the matrix element of p between the vacuum and the nth exciton state is

(31)   <$n|p|$0>   =   J (n|k'X^O10_k'ttk'ak"0—
k|^oXc^lp|kv>
k'k

= 2 (n|k)(ck|p[kw). k

The transition probability is proportional to

(32) |<$n|p|$o)|2   = |(c|p|i>)|2   (2 <n|k)) (J (k'|n)),
k k'

if (ck|p|kv) = (c|p|i>) over the range of k involved. But the (k|n) are such that in (32)

F,,(x) = X e*k'r(k[n);
F,,(0) - 2<k|»>,

and thus the transition probability involves

l(f.|p|*o)|2 ££ |<c|p|c>|2|F,,(0)|2.

For spherical masses Fn(0) is nonzero only for s states; for hydrogenic s states |^n(0)|2 « n" 3, if n is the principal quantum number.

"First forbidden" electric dipole transitions arise when the transition probability is proportional to \dFn(0)/dx\2, which is nonzero only for p states. Thus when electric dipole transitions are forbidden, with Fn(0) = 0, we may still observe excitons

because (ckjp|kv) j* 0, but the n — 1 exciton will be absent. There are no p-states for n = 1. This appears to be the picture in Cu20. The n = 1 line can actually be seen very faintly; Elliott [Phys. Rev. 124, 340 (1961); 108,1384 (1957)] suggests the weak transition is by electric quadrupole radiation.

Longitudinal and Transverse Excitons. We have seen in Chapter 3 that the dielectric polarization field of a cubic crystal has longitudinal and transverse modes, with a frequency splitting determined by the polarizability. In a covalent crystal the polarizability is determined by the excited electronic states of the crystal; that is, the polarizability depends on the nature of the exciton states. An exciton is in fact the quantum unit of the polarization field. The polarization splitting of longitudinal and transverse excitons was derived in Chapter 3 on the assumption that the wavevector of the excitation was small so that the dispersion of the uncoupled polarization could be neglected. At the same time we supposed the wavelength was small in comparison with the dimensions of the crystal, so that shape effects could be neglected. We continue here to make the same approximation; although the wave¬vector of the incident photon is very small compared with the extent of the first Brillouin zone, the crystal is supposed to be large in com¬parison with a wavelength.

Photons are transverse and in cubic crystals couple only with transverse excitons. That is, a photon with k || z in a crystal with an s conduction band edge and an x, y, z degenerate valence band edge will couple with the exciton

bands made up from hole wavefunctions in the xoiy bands and electron wavefunctions in the s band; there is no $A_z p_z$ term in the interaction. To see this we work in the gauge div A = 0 and consider the electromagnetic wave

(35)   A =

Then the wave is polarized in the y direction:

H = curl A = — $ik_\pm e^{\sim i(at \sim kz)}$;

(36)   1 3A . a) A . . ,

E   i-

c dt c

and (36) has A • p coupling only with s_y excitons. The polarization associated with these excitons is purely transverse for k ‖ z; only s_z excitons have a longitudinal polarization for this direction of k.

In uniaxial crystals the dielectric polarizability is anisotropic and a purely longitudinal exciton mode exists only in special symmetry directions of k. We must consider depolarization effects on the exciton spectrum. Let $P_\pm$, P n denote polarization components normal and parallel, respectively, to the c axis in a uniaxial crystal; $/3j\_$, $(3\backslash\backslash$ are the static polarizabilities and $coj\_$, con are the resonance frequencies for transverse waves. We are particularly interested in the special case $(3 n «/3\pm$; that is, we consider an exciton of frequency near and neglect the contribution to the polarizability of the oscillators at $cot|$. Now

where $E_\pm$ is the _L component of the depolarization field of a polariza¬tion wave.

We find $E_\pm$ from div D = 0, exactly as in Chapter 4 we found the demagnetization field of a magnon.

Let k be the unit vector in the direction of k. The projection of P_l on the wave normal is k • Pj_ and the depolarization field is

(39) E = — 4-rk • Pj_; E± — — 47r(k • P±) sin 0k,

where 0k is the angle between k and the c axis. Then
 (40)
co_]_ dt This has two solutions:
(41) k • P± = 0;
(42) k • P± = P± sin dk;
co2 = coj_2; transverse mode; w2 = coj_2(l + 4x/3j_ sin2 dk);
mixed mode.

We have neglected e, the contribution to the dielectric properties from other modes; otherwise 4w would be replaced by 4w/(. These results are due to J. J. Hopfield and D. G. Thomas, Phys. Chem. Solids 12, 276 (1960).

The mixed mode is purely longitudinal for dk = t/2 and it is asymptotically transverse for 0k = 0 on our assumption y3‖ = 0. The photon coupling to the longitudinal or mixed mode therefore vanishes for 0k = t/2, but increases sharply as 0k is varied from this orientation. This effect has been observed in ZnO. The observation of an energy difference between transverse and longitudinal excitons is evidence that the exciton is mobile in the sense that there is a wavevector k associated with the exciton.

We now discuss observations of excitons in several crystals which have been studied in detail.

Germanium. Both direct and indirect excitons have been studied in

germanium. The direct excitons are formed at k = 0 by the absorp¬tion of one photon. The direct band gap is between the r8 valence band edge and the r2 band; the energy of the direct gap is 0.898 ev. The effective mass of the spherical r2 band edge is known to be m*/m 0. 037 from experiments on Landau transitions. An approximate effective hole mass can be defined as the mass which reproduces the binding energy of the lowest acceptor state when calculated from the hydrogenic relation; this mass is 0.20m. Thus the exciton effective n.ass M is given by

The calculated ground-state exciton energy referred to the r'2 edge is

using e = 16. The observed value is — 0.0025 ev.

The indirect excitons are excited across the indirect gap with the emission of a phonon of energy 0.0276 ev. The observed binding energy of the indirect exciton is 0.002(5) ev.

Cadmium Sulfide. The exciton spectrum of this crystal, including fine structure and magneto-optic effects, has been investigated rather fully; see, for example, J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961). The crystal is hexagonal and has the wurtzite struc¬ture; the energy band structure of wurtzite-type crystals is discussed by R. C. Casella, Phys. Rev. 114, 1514 (1959); Phys. Rev. Letters 5, 371 (1960). It is believed that the band edges in CdS, CdSe, and ZnO are similar and lie at or very near to k = 0. The energy gap in CdS is 2.53 ev.

The valence band is split at k = 0 into three twofold degenerate states, transforming in order of increasing energy as r7, r7, and F§, with separations of 0.057 and 0.016 ev, respectively. The con¬duction band edge transforms as r7. For r7 the energy has the form

$$s(k) = A\{kx2 + ky2) + Bk* \pm C(kx2 + K$$

as in Problem 14.4. Note that the third term is linear in k, but this term has never been detected. In CdS the conduction band edge is almost isotropic, with m* = 0.20m. The hole masses for the top valence band are m± = 0.7m and my « 5m; the band edge is ellipsoidal. The electronic g value is —1.8 and is very nearly isotropic; the holes

(r9) have 011 = —1.15 and g± = 0.

There are three series of exciton lines, each series associated with one of the three valence bands at k = 0.

Perhaps the most interesting feature of the exciton spectrum in CdS is its dependence on the sense of a magnetic field perpendicular to the c axis, with the photon wavevector _LH and _Lc. It is found that the intensities of the exciton lines vary markedly when H is reversed in sign, everything else remaining unchanged. That is, the effect depends on the sign of q X H, where q is the photon wavevector. Such an effect is impossible for a free electron, but the absence of a center of symmetry in the crystal allows it to occur. In the reference system of the exciton wavepacket the magnetic field appears as an electric field. The observations are analyzed in the paper
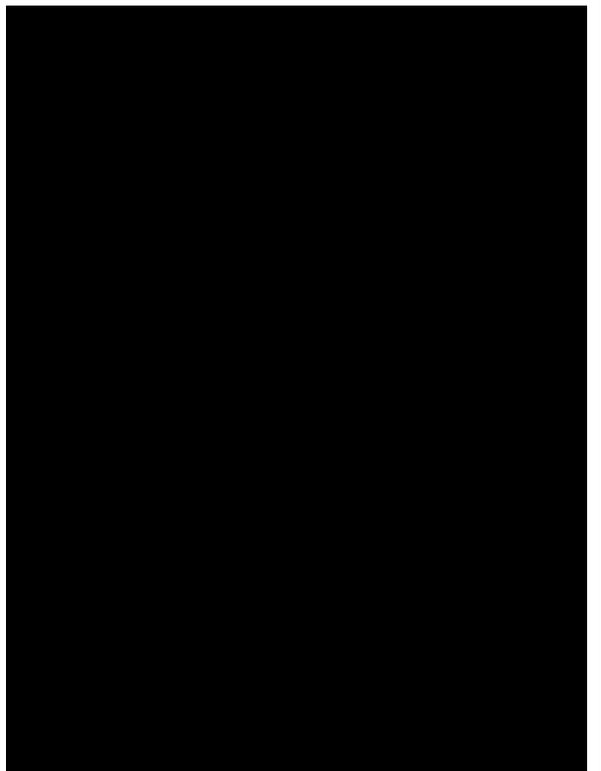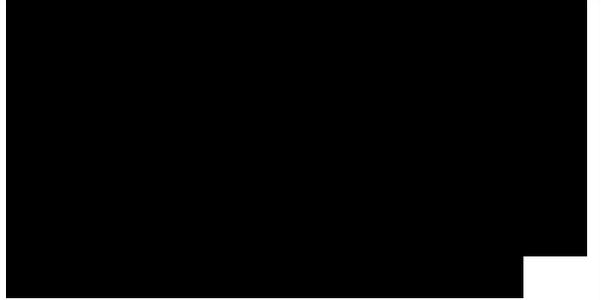
by Hopfield and Thomas cited previously. Only a moving exciton could experience such an effect. It would not occur for impurity absorption lines.

Cuprous Oxide. This cubic crystal exhibits beautiful hydrogenic excitons, which have been extensively studied, particularly by E. F. Gross and his school.3 It is unfortunate that the structure of the band edges are not yet known from cyclotron resonance or other independent studies, but some strong inferences can be made from the exciton results. A striking feature of the exciton spectrum is that the optical transition from the ground state of the crystal to the Is exciton state is very weak, as discussed previously.

For a discussion of excitons in ionic crystals, see D. L. Dexter, Nuovo cimento supplemento 7, 245-286 (1958).

PROBLEMS

1.Discuss for a direct optical transition the dependence of the absorption coefficient on the energy difference of the photon energy from the threshold energy.

2. Show that in a uniaxial crystal with nondegenerate band edges at $k = C$ the exciton wave equation may be written as

where

………..

3. Treat the term in y in Problem 2 as a small perturbation. Show that to first order in y the energies of the $n = 1$ and $n = 2$ states are, with Et as the effective rydberg,

4. In the magnetostark effect as

discussed above for CdS, estimate the magnitude of the quasielectric field for a magnetic field of 30 kilo-oersteds.

6. Show that the transition probability for a "first forbidden" electric dipole process creating an exciton is proportional to $|(dFn/dx)x=,0|2$.

r=0