Polarization Dependence of Two-Photon
Absorption in Solids

by

Todd Richard Bader

Submitted in Partial Fulfillment
of the
Requirements for the Degree

DOCTOR OF PHILOSOPHY

Supervised by Professor Albert Gold

Institute of Optics

The University of Rochester
Rochester, New York

1969

Vita

The author was born in Albany, New York on February 12, 1943. He did his undergraduate work in physics at the State University of New York at Albany, where he received his bachelor's degree in 1965.

In 1965 the author began his graduate study at the Institute of Optics at the University of Rochester. During the academic years 1965-1967 and 1968-1969 he was a graduate teaching assistant. He served as a research assistant in 1967-1968.

Acknowledgments

The author would like to thank Professor Albert Gold for his suggestion of the problem and for his continuing interest and participation in this work. The interest of Professor Robert S. Knox and his critical reading of parts of the manuscript are greatly appreciated.

The author would like to thank Professor M. Inoue and Professor Y. Toyozawa for their most helpful correspondence.

Many stimulating and informative discussions, especially on the experimental aspects of two-photon absorption, with Mr. Terrence H. Reilly have been of invaluable aid throughout the course of this work.

The author would also like to thank his wife, Sharon, for her rather blind but stimulating interest, and for typing the thesis.

This research was supported in part by a grant from the National Science Foundation.

Abstract

The dependence of two-photon absorption in solids on the polarization of the exciting photons has recently been studied, both experimentally and theoretically, as a means of identifying electron state symmetries. Theoretically, polarization dependence has been calculated for allowed two-photon transitions at the Γ -point from a totally symmetric ground state to a final state of arbitrary symmetry for each of the thirty-two point groups and at other symmetry points for several crystal structures. More recently, polarization dependence has been studied for forbidden transitions in cubic structures in a two spherical band model with the inclusion of exciton effects in the intermediate and final states. In this model the polarization dependence was found to be independent of one-electron state symmetries or the orientation of photon polarizations with respect to the crystal axes.

This work extends the previous investigations in several respects. Mathematical expressions and tables are obtained for allowed Γ -point transitions between states of arbitrary symmetry for the thirty-two point groups and for transitions at other symmetry points in hexagonal close-packed and wurtzite structures. For

forbidden transitions a simpler band model is used neglecting exciton effects. This predicts a polarization dependence similar to, but more easily evaluated than, the earlier result; the ratio of maximum to minimum absorption predicted by the earlier calculation is a complicated function of the band gap and exciton binding energies, which usually are not precisely known, while in the simpler model this ratio is a simple function of the photon energies. The effects of $k \cdot p$ splitting of p-like valence bands is considered in this model, and it is found that only the ratio of maximum to minimum is altered. In addition the polarization dependence is calculated for forbidden X-point transitions in the two band model, but in which the ellipsoidal character of energy surfaces near this point are taken into account. The two-photon absorption is found to depend both on the symmetries of the initial and final states and on the orientation of the polarization vectors with respect to the crystal axes.

Table of Contents

Chapter	Page
I. Introduction	1
II. Two-Photon Absorption	7
A. Perturbation Theory	7
B. Application to Solids	16
III. Allowed Transitions	35
A. Formalism	36
B. Γ -Point Transitions	44
C. Transitions at Non-central Symmetry Points	62
IV. Forbidden Transitions	82
A. Mahan's Model	83
B. Band Model	92
C. p-like Valence Bands	97
D. X-Point Transitions	114
V. Application to Experiment	120
A. CuCl	121
B. ZnS	127
C. RbI	131
D. CsI	134
E. KI	137
F. TlCl	144

Chapter	Page
VI. Conclusion	146
Appendices	
A. $k \cdot p$ Perturbation Theory	149
B. Symmetry of $\Lambda(\omega)$	151
C. Derivation of Clebsch-Gordan Symmetry Relation	153
D. Table of Correspondence of Point Group Notations	156
E. Angular Functions for Symmetry Points in Face-Centered Cubic, Diamond, Zinc Blende and Simple Cubic Structures	158
References	164

List of Tables

Table No.		Page
3-1	Angular Dependence Functions for Γ -Point Transitions	46
3-2	Complete Character Table for the Double Group of A in Hexagonal Close-Packed Structures	66
3-3	Angular Dependence Functions for Hexagonal Close-Packed Structures	68
3-4	Angular Dependence Functions for Wurtzite Structures	76
D-1	Correspondence of Point Group Notations	156
E-1	Angular Dependence Functions for Face-Centered Cubic, Diamond, Zinc Blende and Simple Cubic Structures	158

List of Figures

Figure No.		Page
2-1	Paths of forbidden two-photon absorption	31
3-1	Definition of axes for point groups D_2 , D_{2h} , C_{2v} , D_4 , C_{4v} and D_{4h}	58
3-2	Definition of axes for point groups D_{2d} , D_3 , D_{3d} , C_{3v} and D_6	59
3-3	Definition of axes for point groups C_{6v} , D_{6h} and D_{3h}	60
3-4	Definition of axes for point groups T , T_d , T_h , O and O_h	61
3-5	Brillouin zone of hexagonal close-packed and wurtzite structures	75
4-1	Two-photon absorption for spherical p-like bands	105
4-2	Ratio of parallel to perpendicular polarization absorption for $\mu_1 > \mu_2$	112
4-3	Ratio of parallel to perpendicular polarization absorption for $\mu_2 > \mu_1$	113
4-4	Constant energy surfaces near X-point extremum	115
5-1	Band structure of CuCl	124
5-2	Two-photon absorption spectrum of CuCl	125
5-3	Polarization dependence of two-photon absorption in CuCl	126
5-4	Band structure of ZnS	129

Figure No.		Page
5-5	Polarization dependence of two-photon absorption in ZnS	130
5-6	Two-photon absorption in RbI.	133
5-7	Two-photon absorption in CsI	135
5-8	Band structure of CsI	136
5-9	Band structure of KI	141
5-10	Two-photon absorption spectrum of KI	142
5-11	Polarization dependence of two-photon absorption in KI	143
E-1	Brillouin zones of simple cubic, diamond, zinc blende, face-centered cubic and body-centered cubic structures	162

Chapter I

Introduction

Spectroscopy, the study of the interaction of light with matter, provides many useful methods of investigating the physical properties of atoms, molecules, and solids. In the study of insulators and semiconductors, with which this dissertation is concerned, substantial information on photon absorption (and hence, for example, exciton, impurity state and band energies) has been gained with the use of now commonplace spectroscopic techniques.¹ Response functions, such as the polarizability, in this ordinary spectroscopy are proportional to the electric field. Only with very large fields are nonlinear effects observable. Such light sources were not available until the early 1960's. With the advent of the laser nonlinear spectroscopy quickly became an area of wide interest.²

The nonlinear process of two-photon absorption was first discussed by Goeppert-Mayer³ long before the laser was developed. Two-photon absorption techniques were developed by Hopfield and Worlock⁴ for the study of solids. Such techniques are useful in studying the electronic states of solids in several ways. Suppose a crystal having inversion symmetry has a minimum vertical band gap E_g at

$\vec{k} = 0$. The shape of the absorption edge in this crystal is described approximately by $(\hbar\omega - E_g)^{3/2}$ for one-photon absorption and by $(\hbar\omega_1 + \hbar\omega_2 - E_g)^{1/2}$ for two-photon absorption, where $\hbar\omega$ is the energy of a photon, if the valence and conduction bands have the same parity. The two-photon process in this case allows a better examination of states having energy near E_g , and permits excitons constructed from states in these bands to be observed. In the more general case the two-photon absorption data provides a supplement to the one-photon data. The one-photon absorption coefficient is often so large that the experimentalist must employ reflectivity techniques⁵ or use a very thin crystalline sample,⁶ the results of which exhibit effects (though they are usually assumed to be small) due to the surface.⁷⁻⁹ Large samples can be used in the two-photon process; and the absorption takes place in the heart of the crystal, where the Born-von Karman boundary conditions used in band theory are better approximated.

Yet another premium can be placed on the utilization of two-photon spectroscopy in the study of solids. The dependence of the absorption coefficient on the directions of polarization of the two photons can provide useful information on the symmetries of the conduction and valence bands. Dresselhaus¹⁰ emphasized the fact that the anisotropic one-photon absorption in anisotropic crystals could be explained by group theoretical considerations. Consid-

erably more extensive information, however, can be obtained from the two-photon spectra of solids, including those which are one-photon isotropic, by examining the absorption coefficient as a function of the directions of polarization of two incident beams. The form of this angular dependence function will depend on the irreducible representations of the crystallographic point group to which the initial and final states belong. Inoue and Toyozawa¹¹ first drew attention to this fact and calculated the functions for all final crystal state symmetries for each of the thirty-two point groups. They also calculated the angular functions for transitions at points and on lines of symmetry in the Brillouin zone other than $\vec{k} = 0$ for NaCl, CsCl, diamond, and zinc blende structures. Their results give directly the angular function for a transition between one-electron states of arbitrary symmetry only in the case of allowed two-photon transitions in which either the valence band or the conduction band belongs to the identity representation of the group of the wave vector, and, in the case of excitons, when the envelope function belongs to the identity representation.

It often happens that one-electron transitions are forbidden (by parity, for example) at an energy band extremum. The "forbidden" transitions observed in the optical spectra take place on an energy surface in $\vec{k}$ -space enclosing the extremum. The two-photon absorption

coefficient for these transitions has been calculated by Mahan^{19, 20} in a two band model in which the valence and conduction bands are assumed to be spherical near the extremum. Exciton effects were explicitly included in his calculation. Mahan found that the absorption coefficient does not depend on the directions of polarization with respect to the crystal axes, but only on the angle between the two polarization vectors. The absorption coefficient has the form $a \cos^2 \theta + b \sin^2 \theta$. The ratio a/b is difficult to evaluate and it depends on quantities which are not always precisely known.

Angular dependence measurements¹²⁻¹⁸ have been made on crystals in which the observed transitions are of the allowed kind and on crystals in which the transitions are forbidden. These measurements have all been discussed by their investigators in the light of the theoretical works of Inoue and Toyozawa¹¹ and of Mahan.²⁰

In this dissertation the angular functions will be produced for transitions in which the conduction band and valence band at the center of the Brillouin zone are of arbitrary symmetry for each of the thirty-two point groups. A way of finding the angular dependence of transitions between states of arbitrary symmetry at other high symmetry points in the Brillouin zone will be given which utilizes the Γ -point tables and the tables of Inoue and Toyozawa for the non-central symmetry points. Also, the angular

functions for symmetry lines and points of the hexagonal close-packed and wurtzite structures will be calculated. The results will apply to band-to-band transitions and exciton transitions when the envelope function belongs to the identity representation. For forbidden transitions a simpler model will be considered in which exciton effects are ignored, but in which the restriction to two spherical bands is retained. It is shown that this model leads to a polarization dependence similar to that obtained by Mahan but for which the ratio a/b is a simple function of the photon energies only. The effect on the polarization dependence of $\vec{k} \cdot \vec{p}$ splitting near the Γ -point is considered in the particular case of p-like valence bands and a totally symmetric conduction band, and it is shown that this band splitting does not alter the form of the polarization dependence, but changes the expression for the ratio a/b . Finally, the polarization dependence will be determined for forbidden transitions at the X-point in simple cubic and face-centered cubic structures, about which the constant energy surfaces are ellipsoidal. For these transitions it is found that the absorption coefficient depends on the symmetries of the initial and final states and on the orientations of the polarization vectors with respect to the crystal axes.

In Chapter II a review of the perturbation treatment of two-photon absorption will be given with its application

to the process in solids. Chapter III contains the formalism used to obtain the angular functions for allowed transitions and includes the results for the Γ -point and non-central symmetry points. Chapter IV is devoted to forbidden transitions, containing a review of Mahan's²⁰ results and the calculations neglecting exciton effects. A discussion of some of the experimental work¹²⁻¹⁷ in terms of theoretical results is presented in Chapter V.

Chapter II

Two-Photon Absorption

A. Perturbation Theory

The process of two-photon absorption by an atomic system can be treated with the use of second order time-dependent perturbation theory.^{21,22} The specific process of interest is the following: we imagine that we have an atomic system, such as a crystalline solid, in its lowest energy state. Two linearly polarized light beams are incident on the system, each possessing a narrow spread in frequency. The atomic system is such that it has no excited states near energy $\hbar\omega_1$ or $\hbar\omega_2$ the photon energies of light beams one and two, respectively. But it does have an excited state near $\hbar\omega_1 + \hbar\omega_2$. In solids it is generally impossible to avoid a resonance at energy $2\hbar\omega_1$ or $2\hbar\omega_2$. We must therefore stipulate that in a two beam experiment, one beam must have insufficient power to cause detectable absorption of two photons from the same beam, say beam one. This will be accomplished with the use of a "conventional" light source. Beam two, a laser, must be sufficiently potent to allow the detection of absorption of two photons, one each from beams one and two, and hence it is imperative to avoid a

resonance at $2\hbar\omega_2$. This is generally accomplished by choosing the laser (or the crystal) such that $\hbar\omega_2$ is less than half the energy of the lowest excited state of the crystal.

The Hamiltonian of the entire system, in the coulomb gauge, is

$$H = \sum_{j=1}^N \frac{1}{2m} \left[\vec{p}_j - \frac{e}{c} \vec{A}(\vec{r}_j) \right]^2 + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) + H_F \quad (2-1)$$

$$= H_0 - \frac{e}{mc} \sum_j \vec{A}(\vec{r}_j) \cdot \vec{p}_j + \frac{e^2}{2mc^2} \sum_j A^2(\vec{r}_j)$$

where $H_0 = H_A + H_F$ and j runs over all electrons.

$H_A \equiv \frac{1}{2m} P^2 + V$ is the energy of the unperturbed atomic system, with $\vec{P} \equiv \sum_j \vec{p}_j$. H_F is the free photon field Hamiltonian. It is not necessary to use the quantized field formalism for absorption processes,^{23,24} but we shall employ it here simply for convenience.²⁵ In this description the vector potential is given by

$$\vec{A}(\vec{r}_j) = c \sum_{\vec{k}, \sigma} \sqrt{\frac{2\pi\hbar}{\omega_k V \epsilon_{k\sigma}}} \hat{\epsilon}_{k\sigma} \left[a_{k\sigma} e^{i\vec{k} \cdot \vec{r}_j} + a_{k\sigma}^\dagger e^{-i\vec{k} \cdot \vec{r}_j} \right], \quad (2-2)$$

where $\vec{k} = \frac{2\pi}{v^{1/3}} (l_1 \hat{x} + l_2 \hat{y} + l_3 \hat{z})$ ($l_i = \text{integer}$) and σ runs over two polarizations. $H_F \equiv \sum_{\vec{k}, \sigma} \hbar\omega_k \left[a_{k\sigma}^\dagger a_{k\sigma} + \frac{1}{2} \right]$ is a sum of harmonic oscillator Hamiltonians, each of which has eigenstates such that

$$a_{k\sigma} |n_{k\sigma}\rangle = \sqrt{n_{k\sigma} + 1} |n_{k\sigma} + 1\rangle$$

and

$$a_{k\sigma}^{\dagger} |n_{k\sigma}\rangle = \sqrt{n_{k\sigma}} |n_{k\sigma}-1\rangle.$$

The energy of state $|n_{k\sigma}\rangle$ is $\hbar\omega_k(n_{k\sigma} + \frac{1}{2})$. $a_{k\sigma}$ and $a_{k\sigma}^{\dagger}$ are seen to be annihilation and creation operators, respectively, and hence will correspond respectively to absorption and emission of photons. The total field eigenstate can then be written $|n_1, n_2, \dots n_i \dots\rangle$, where n_i ($i \equiv k, \sigma$) represents the number of photons of type i which are present in the field. The eigenstates of H_0 can now be written in the form

$$|\alpha\rangle = |a\rangle |n_1, n_2, \dots n_i, \dots\rangle,$$

where $|a\rangle$ are eigenstates of H_R with energy E_a . $|\alpha\rangle$ has energy $E_{\alpha} = E_a + \sum_i \hbar\omega_i(n_i + \frac{1}{2})$.

As described earlier, light beam one is composed of photons having polarization $\hat{\epsilon}_1$, having direction of propagation very nearly $\hat{k}_1$, and having energy within a narrow envelope about $\hbar\omega_1$. Beam two is similarly described. Thus the initial state of the system can be written

$$|I\rangle \equiv |g; 0, 0, \dots n_{11}, n_{12}, \dots 0 \dots \dots n_{21}, n_{22}, \dots n_{2j} \dots 0 \dots\rangle$$

where n_{1i} is the number of photons with polarization having $\hat{k}_i$ and ω_i very nearly $\hat{k}_1$ and ω_1 , and similarly for n_{2j} . The final state is

$$|F\rangle \equiv |f; 0, 0, \dots n_{11}, n_{12}, \dots n_{1i}-1, \dots 0 \dots n_{21}, n_{22}, \dots n_{2j}-1, \dots 0 \dots\rangle$$

Following the standard time-dependent perturbation theory, the state of the entire system at a time t is

$$|\psi(t)\rangle = \sum_{\alpha} c_{\alpha}(t) e^{-i E_{\alpha} t / \hbar} |\alpha\rangle$$

$|\psi(t)\rangle$ satisfies

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = (H_0 + H') |\psi(t)\rangle$$

where H' is the last two terms of Eq.2-1. $C_{\alpha}(t)$ satisfies

$$i\hbar \frac{dc_{\alpha}}{dt} = \sum_{\beta} \langle \alpha | H' | \beta \rangle c_{\beta}(t). \quad (2-3)$$

$|c_{\alpha}(t)|^2$ is the probability of finding the system in state $|\alpha\rangle$ at time t , subject to the condition $c_{\alpha}(0) = \delta_{\alpha I}$.

Expanding $c_{\alpha}(t)$ in a power series in the perturbation constant λ , we have $c_{\alpha}(t) = \sum_{n=0}^{\infty} c_{\alpha}^{(n)}(t)$, where $c_{\alpha}^{(n)}(t)$ is of order λ^n . Substituting into Eq.2-3 and equating equal powers of λ , we obtain

$$i\hbar \frac{dc_{\alpha}^{(0)}}{dt} = 0$$

$$i\hbar \frac{dc_{\alpha}^{(n)}}{dt} = \sum_{\beta} \langle \alpha | H' | \beta \rangle e^{i\omega_{\alpha\beta}t} c_{\beta}^{(n-1)}(t), \quad n > 0.$$

We find immediately that

$$c_{\alpha}^{(0)}(t) = c_{\alpha}^{(0)}(0) = \delta_{\alpha I}$$

and

$$i\hbar \frac{dc_{\alpha}^{(1)}}{dt} = \langle \alpha | H' | I \rangle e^{i\omega_{\alpha I}t}$$

so that

$$c_{\alpha}^{(1)}(t) = -\frac{1}{\hbar \omega_{\alpha I}} \langle \alpha | H' | I \rangle [e^{i\omega_{\alpha I} t} - 1].$$

We will restrict ourselves to systems, or portions of systems, in which $e^{i\vec{k} \cdot \vec{r}_j} \approx 1$. Since we are interested in an absorption process, the vector potential becomes in the dipole approximation

$$\vec{A}(\vec{r}_j) = c \sum_{k\sigma} \sqrt{\frac{2\pi\hbar}{\omega_k V \kappa_{k\sigma}}} \hat{E}_{k\sigma} a_{k\sigma}.$$

In the case of a solid the dielectric constant κ will sometimes depend on the direction of polarization. We will make a requirement here that in an experiment $\hat{E}$ is to be chosen so that κ will remain constant. For example, in a hexagonal crystal $\hat{E}_1$ can be chosen to lie in the direction of the c-axis, while $\hat{E}_2$ may be varied in the plane perpendicular to the c-axis. The subscript σ will now be dropped from $\kappa_{k\sigma}$.

In H' the ratio of the term quadratic in A to the term linear in A is of the order $\frac{e}{c\rho} A$, which is small. The term quadratic in A cannot in this approximation connect states with different electronic states anyway. Therefore we will drop this term from H' , and the effective perturbation becomes

$$H' = -\frac{e}{mc} \vec{A} \cdot \vec{P} = -\frac{e}{m} \sum_{k\sigma} \sqrt{\frac{2\pi\hbar}{\omega_k V \kappa_k}} a_{k\sigma} \hat{E}_{k\sigma} \cdot \vec{P}. \quad (2-4)$$

From Eq.2-4 it is seen that $\langle \alpha | H' | I \rangle$ is non-zero only if a single photon is absorbed. Since there is no atomic state such that $E_a - E_i = \hbar \omega_1$ or $\hbar \omega_2$, then $\hbar \omega_{\alpha I} = E_a - E_i - \hbar \omega_1$ or $E_a - E_i - \hbar \omega_2$ is appreciably different from zero, and $|c_{\alpha}^{(1)}(t)|^2$ is very small, oscillating rapidly in time. We find

$$\begin{aligned} i\hbar \frac{d}{dt} c_F^{(2)}(t) &= \sum_M \langle F | H' | M \rangle e^{i\omega_{FM}t} c_M^{(1)}(t) \\ &= -\frac{1}{\hbar} \sum_M \langle F | H' | M \rangle \langle M | H' | I \rangle e^{i\omega_{FM}t} \frac{e^{i\omega_{MI}t} - 1}{\omega_{MI}} \end{aligned}$$

and

$$c_F^{(2)}(t) = \frac{1}{\hbar^2} \sum_M \frac{\langle F | H' | M \rangle \langle M | H' | I \rangle}{\omega_{MI}} \left[\frac{e^{i\omega_{FI}t} - 1}{\omega_{FI}} - \frac{e^{i\omega_{FM}t} - 1}{\omega_{FM}} \right].$$

By the hypothesis that $E_{fg} = \hbar \omega_1 + \hbar \omega_2$, $\omega_{FI} \approx 0$. We may neglect the second term in the brackets since it is never resonant.

$$|c_F^{(2)}(t)|^2 = \frac{1}{\hbar^2} \left| \sum_M \frac{\langle F | H' | M \rangle \langle M | H' | I \rangle}{E_M - E_I} \right|^2 \frac{\sin^2 \frac{1}{2} \omega_{FI} t}{(\frac{1}{2} \omega_{FI})^2} \quad (2-5)$$

The final state $|F\rangle$ has two photons less than the initial state $|I\rangle$, one from beam one, the other from beam two.

The intermediate state $|M\rangle$ must have one photon less than $|I\rangle$, but it can be one of energy near $\hbar \omega_1$ or near $\hbar \omega_2$.

Thus two terms of the sum in Eq.2-4 survive, and Eq.2-5 reduces to

$$|C_F^{(2)}(t)|^2 = \frac{1}{\hbar^2} \left(\frac{e}{m}\right)^4 \left(\frac{2\pi\hbar}{V}\right)^2 \frac{n_1(\hat{k}_1, \omega_1) n_2(\hat{k}_2, \omega_2)}{\omega_1 \omega_2 \kappa_1 \kappa_2} \\ \times |P_{fg}^{(2)}|^2 \frac{\sin^2 \frac{1}{2} [E_{fi}/\hbar - (\omega_1 + \omega_2)] t}{\frac{1}{4} [E_{fi}/\hbar - (\omega_1 + \omega_2)]^2}$$

where

$$P_{fg}^{(2)} \equiv \sum_m \left[\frac{\langle f | \hat{E}_1 \cdot \vec{P} | m \rangle \langle m | \hat{E}_2 \cdot \vec{P} | g \rangle}{E_m - E_g - \hbar\omega_2} + \frac{\langle f | \hat{E}_2 \cdot \vec{P} | m \rangle \langle m | \hat{E}_1 \cdot \vec{P} | g \rangle}{E_m - E_g - \hbar\omega_1} \right] \quad (2-6)$$

Here $|f\rangle$, $|m\rangle$ and $|g\rangle$ represent electronic states.

The transition rate for two-photon absorption is then

$$W^{(2)} = \frac{d}{dt} \sum_F |C_F^{(2)}(t)|^2 \\ = \frac{1}{\hbar^2} \left(\frac{e}{m}\right)^4 \left(\frac{2\pi\hbar}{V}\right)^2 \frac{1}{\kappa_1 \kappa_2} \sum_F \frac{d}{dt} \left(\left| \frac{n_1(\hat{k}_1, \omega_1) n_2(\hat{k}_2, \omega_2)}{\omega_1 \omega_2} |P_{fg}^{(2)}|^2 \right. \right. \\ \left. \left. \times \frac{\sin^2 \frac{1}{2} [E_{fg}/\hbar - (\omega_1 + \omega_2)] t}{\frac{1}{4} [E_{fg}/\hbar - (\omega_1 + \omega_2)]^2} \rho(\hbar\omega_1) \rho(\hbar\omega_2) d(\hbar\omega_1) d(\hbar\omega_2) \right. \right)$$

The density of states $\rho(\hbar\omega_i) = dN/d(\hbar\omega_i)$ is given by

$$\rho(\hbar\omega_i) = \frac{V}{(2\pi c)^3} \frac{\omega_i^2}{\hbar} d\Omega_i.$$

Here $d\Omega_i = \sin\theta_i d\theta_i d\phi_i$ and $\hat{k}_i = (\theta_i, \phi_i)$.

$$\frac{c}{V} n_i(\hat{k}_i, \omega_i) \rho(\hbar\omega_i) d(\hbar\omega_i) = \frac{c}{V} n_i(\hat{k}_i, \omega_i) \frac{V}{(2\pi c)^3} \frac{\omega_i^2}{\hbar} d(\hbar\omega_i) d\Omega_i$$

is the number of photons incident per unit area per second having energy within $d(\hbar\omega_i)$ and direction $\hat{k}_i$ of propagation within $d\Omega_i$.

$$f_i(\omega_i) d(\hbar\omega_i) \equiv \frac{c}{V} d(\hbar\omega_i) \int n_i(\hat{k}_i; \omega_i) \frac{V}{(2\pi c)^3} \frac{\omega_i^2}{\hbar} d\Omega_i$$

is the number of photons per unit area per second with energy between $\hbar\omega_i$ and $\hbar(\omega_i + d\omega_i)$.

$$F_i \equiv \int f_i(\omega_i) d(\hbar\omega_i)$$

is the total flux density of beam i .

We shall use the fact that $\sin^2 xt / x^2$ is strongly peaked about $x = 0$ for large t by extending the limits of integration over x to $\pm\infty$. In this case

$$\int_{-\infty}^{\infty} \frac{\sin^2 xt}{x^2} dx = 2\pi t$$

We assume that $|P_{fg}^{(2)}|^2$ varies slowly with ω_1 and ω_2 compared with f_1 and f_2 . The transition rate then becomes

$$W^{(2)} = \frac{2\pi}{\hbar} \left(\frac{e}{m}\right)^4 \left(\frac{2\pi\hbar}{c}\right)^2 \frac{1}{\kappa_1 \kappa_2} \sum_f |P_{fg}^{(2)}|^2 \int \frac{f_1(\omega) f_2(E_{fg}/\hbar - \omega)}{\omega (E_{fg}/\hbar - \omega)} d(\hbar\omega).$$

It has been stipulated that $n_i(\hat{k}_i; \omega)$ is a function strongly peaked about ω_i , so that f_1 and f_2 are narrow bands at ω_1 and ω_2 respectively, and hence

$$\int f_1(\omega) f_2(E_{fg}/\hbar - \omega) d\hbar\omega$$

is a narrow function of E_{fg} centered at $E_{fg} = \hbar\omega_1 + \hbar\omega_2$.

Noting that

$$\iint f_1(\omega) f_2(E_{fg}/\hbar - \omega) d(\hbar\omega) dE_{fg} = F_1 F_2$$

we set

$$\int f_1(\omega) f_2(E_{fg}/\hbar - \omega) d(\hbar\omega) = F_1 F_2 \delta[E_{fg} - \hbar(\omega_1 + \omega_2)].$$

It follows that

$$W^{(2)} = \frac{2\pi}{\hbar} \left(\frac{e}{m}\right)^4 \left(\frac{2\pi\hbar}{c}\right)^2 \frac{F_1 F_2}{\kappa_1 \kappa_2 \omega_1 \omega_2} \sum_f |P_{fg}^{(2)}|^2 \delta[E_{fg} - \hbar(\omega_1 + \omega_2)].$$

A two-photon absorption coefficient can be defined to describe the attenuation of one of the beams:

$$\alpha^{(2)} \equiv \frac{W^{(2)}}{\frac{VF_1}{\sqrt{\kappa_1}}}$$

$$= \frac{(2\pi)^3 \hbar}{V} \left(\frac{e}{m}\right)^4 \frac{F_2}{\kappa_2 \sqrt{\kappa_1} \omega_1 \omega_2} \sum_f |P_{fg}^{(2)}|^2 \delta[E_{fg} - \hbar(\omega_1 + \omega_2)].$$

(2-7)

B. Application to Solids

In this section the form of the absorption coefficient will be obtained for electronic transitions in solids in which the ground state is described by a filled valence band and an empty conduction band separated by a forbidden energy gap. Effects of lattice vibrations will be neglected. Two general classifications of two-photon transitions, described as "allowed" and "forbidden" in analogy to Elliot's²⁶ classification of one-photon transitions, are discussed in the literature.²² This terminology is not really appropriate, however, for two reasons: first, it arose in the discussion of inter-band transitions to describe the fact that a two-photon transition between bands at a given point in the Brillouin zone was allowed at adjacent points; second, the excited electronic states of a crystal are more correctly described as excitons²⁷, which mix states of different $\vec{k}$, thus formally rendering the classification inappropriate. A distinction between two-photon "allowed" and "forbidden" transitions consistent with the usual terminology, however, is useful, especially when the electron-hole interaction effect is not too large. We will treat, therefore, the two cases defined as follows: let $|v(\vec{k}_0)\rangle$ and $|c(\vec{k}_0)\rangle$ be valence and conduction band states at $\vec{k}_0$, the point of an extremum of $E_c(\vec{k}) - E_v(\vec{k})$. Then if

$$\sum_n \frac{\langle c(k_0) | \hat{E} \cdot \vec{p} | n(k_0) \rangle \langle n(k_0) | \hat{E}_z \cdot \vec{p} | v(k_0) \rangle}{\Omega_n} = 0$$

for $\Omega_n = \text{constant}$, the transition is forbidden. An allowed transition is one which is not forbidden. The most common forbidden transition occurs when $|c(k_0)\rangle$ and $|v(k_0)\rangle$ are of opposite parity. In the discussion of forbidden transitions we will assume that this is the case; when some other symmetry property is responsible for the zero in the above equation, the treatment and results are exactly the same.

In order to describe the electronic states of the crystal we first establish the notation. Let $|n^+(k)\rangle$ label all conduction bands and $|n^-(k)\rangle$ all valence bands. Suppose the minimum vertical energy gap occurs at $\vec{k}_0$. Then $|v_j(k)\rangle$ and $|c_i(k)\rangle$ are those particular valence and conduction bands, respectively, such that the minimum vertical energy gap is $E_{c_i}(k_0) - E_{v_j}(k_0)$. That is, $\{|v_j(k_0)\rangle\}$ is a degenerate set, as is $\{|c_i(k_0)\rangle\}$.

The ground state of a crystal can be approximated as a determinant of one-electron Bloch states from the valence bands:

$$|g\rangle = A \prod_{n^-} \prod_{s=1}^N |n^-(k_s)\rangle.$$

$A \equiv \frac{1}{\sqrt{N!}} \sum_P (-1)^P P$, where p is the parity of permutation P .

If the electron-hole interaction is ignored, we can write an excited state as

$$\begin{aligned}
|m\rangle &= \mathcal{A} \prod_{s=1}^N |1^-(k_s)\rangle |2^-(k_s)\rangle \cdots \\
&\quad \cdots |n^-(k_1)\rangle |n^-(k_2)\rangle \cdots |n^+(k'')\rangle \cdots |n^-(k_N)\rangle \cdots \\
&\equiv |n^+(k''), n^-(k''')\rangle
\end{aligned}$$

where valence band state $|n^-(k''')\rangle$ has been replaced by some conduction band state $|n^+(k'')\rangle$.

The final state is

$$|f\rangle = |c_i(k), v_j(k')\rangle.$$

With these states we find

$$\begin{aligned}
\langle m | \hat{\epsilon}_2 \cdot \vec{p} | g \rangle &= \langle n^+(k'') | \hat{\epsilon}_2 \cdot \vec{p} | n^-(k''') \rangle \delta_{k'', k'''}
\end{aligned}$$

where $\delta_{k'', k'''}$ arises from conservation of momentum.

$$\begin{aligned}
\langle f | \hat{\epsilon}_1 \cdot \vec{p} | m \rangle &= \delta_{k, k''} \delta_{k', k'''} \begin{cases} \delta_{v_j n^-} \langle c_i(k'') | \hat{\epsilon}_1 \cdot \vec{p} | n^+(k'') \rangle & n^+ \neq c_i \\ -\delta_{c_i n^+} \langle n^-(k''') | \hat{\epsilon}_1 \cdot \vec{p} | v_j(k''') \rangle & n^- \neq v_j \\ \delta_{v_j n^-} \delta_{c_i n^+} [\langle c_i(k'') | \hat{\epsilon}_1 \cdot \vec{p} | c_i(k'') \rangle \\ - \langle v_j(k''') | \hat{\epsilon}_1 \cdot \vec{p} | v_j(k''') \rangle] \end{cases}
\end{aligned}$$

Substituting into Eq.2-6 we obtain

$$\begin{aligned}
P_{fg}^{(2)} &= \sum_n \left[\frac{\langle c_i(k) | \hat{\epsilon}_1 \cdot \vec{p} | n(k) \rangle \langle n(k) | \hat{\epsilon}_2 \cdot \vec{p} | v_j(k) \rangle}{E_n(k) - E_v(k) - \hbar\omega_2} \right. \\
&\quad \left. + \frac{\langle c_i(k) | \hat{\epsilon}_2 \cdot \vec{p} | n(k) \rangle \langle n(k) | \hat{\epsilon}_1 \cdot \vec{p} | v_j(k) \rangle}{E_n(k) - E_v(k) - \hbar\omega_1} \right] \quad (2-8)
\end{aligned}$$

where n runs over n^- and n^+ .

Let us consider the case in which the energy difference $E_{c_i}(\vec{k}) - E_{v_j}(\vec{k})$ has a minimum at some point $\vec{k}_0$.

in the Brillouin zone. Near $\vec{k} = \vec{k}_0$ state $|n(k)\rangle$ is given by $\vec{k} \cdot \vec{p}$ perturbation theory as²⁸ (see Appendix A)

$$|n(k)\rangle = |n(k_0)\rangle + \frac{\hbar}{m} \sum_{\ell}' \frac{\langle \ell(k_0) | \vec{k} \cdot \vec{p} | n(k_0) \rangle | \ell(k_0) \rangle}{E_n(k_0) - E_{\ell}(k_0)}.$$

$|c_i(k)\rangle$ and $|v_j(k)\rangle$ are given by similar expressions.

(Linear terms in the energy sometimes occurring in spin-orbit coupled bands will be neglected.) If $|c_i(k_0)\rangle$ and $|v_j(k_0)\rangle$ have the same parity or are of mixed parity, we can neglect the second term in the $\vec{k} \cdot \vec{p}$ expansions:

Allowed

$$P_{fg}^{(2)} = \sum_n \left[\frac{\langle c_i(k_0) | \hat{E}_1 \cdot \vec{p} | n(k_0) \rangle \langle n(k_0) | \hat{E}_2 \cdot \vec{p} | v_j(k_0) \rangle}{E_n(k_0) - E_v(k_0) - \hbar\omega_2} + \frac{\langle c_i(k_0) | \hat{E}_2 \cdot \vec{p} | n(k_0) \rangle \langle n(k_0) | \hat{E}_1 \cdot \vec{p} | v_j(k_0) \rangle}{E_n(k_0) - E_v(k_0) - \hbar\omega_1} \right] \quad (2-9)$$

If $|c_i(k_0)\rangle$ and $|v_j(k_0)\rangle$ are of opposite parity, we have:

Forbidden

$$P_{fg}^{(2)} = \frac{\hbar}{m} \sum_n \left[\sum_{\ell \neq c_i} \frac{\langle c_i | \vec{k} \cdot \vec{p} | \ell \rangle \langle \ell | \hat{E}_1 \cdot \vec{p} | n \rangle \langle n | \hat{E}_2 \cdot \vec{p} | v_j \rangle}{(E_c - E_{\ell})(E_n(k) - E_v(k) - \hbar\omega_2)} + \sum_{\ell \neq n} \frac{\langle c_i | \hat{E}_1 \cdot \vec{p} | \ell \rangle \langle \ell | \vec{k} \cdot \vec{p} | n \rangle \langle n | \hat{E}_2 \cdot \vec{p} | v_j \rangle}{(E_n - E_{\ell})(E_n(k) - E_v(k) - \hbar\omega_2)} + \sum_{\ell \neq n} \frac{\langle c_i | \hat{E}_1 \cdot \vec{p} | n \rangle \langle n | \vec{k} \cdot \vec{p} | \ell \rangle \langle \ell | \hat{E}_2 \cdot \vec{p} | v_j \rangle}{(E_n - E_{\ell})(E_n(k) - E_v(k) - \hbar\omega_2)} + \sum_{\ell \neq v} \frac{\langle c_i | \hat{E}_1 \cdot \vec{p} | n \rangle \langle n | \hat{E}_2 \cdot \vec{p} | \ell \rangle \langle \ell | \vec{k} \cdot \vec{p} | v_j \rangle}{(E_v - E_{\ell})(E_n(k) - E_v(k) - \hbar\omega_2)} \right] + \text{similar terms with subscripts 1 and 2 interchanged} \quad (2-10)$$

If the electron-hole interaction is not ignored, the form of the excited states of the crystal must be modified. In this case the crystal Hamiltonian

$$H = -\frac{\hbar^2}{2m} \sum_i [\nabla_i^2 + U(\vec{r}_i)] + H_{\text{spin}} + \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

is no longer diagonal with respect to the states $|\eta^+(k), \eta^-(k)\rangle$. The problem of finding correct linear combinations of these states which diagonalize H has received considerable attention, and the fruits of its study constitute the theory of excitons²⁷. Before returning to the discussion of two-photon absorption we will give a brief description of some of the results of exciton theory.

It is a good approximation for weakly bound excitons to construct the states from two bands, but we will retain more than two when several are degenerate at $\vec{k} = \vec{k}_0$. Thus, for example, we can write an excited crystal state

$$|c\nu, \mu \vec{K}\rangle = \sum_{\vec{k}, i, j} F_{c_i \nu_j}^{\mu}(\vec{k}, \vec{k}-\vec{K}) |c_i(\vec{k}), \nu_j(\vec{k}-\vec{K})\rangle$$

where $F_{c_i \nu_j}(\vec{k}, \vec{k}-\vec{K})$ satisfies

$$\sum_{\vec{k}', i', j'} \langle c_i(\vec{k}), \nu_j(\vec{k}-\vec{K}) | H | c_{i'}(\vec{k}'), \nu_{j'}(\vec{k}'-\vec{K}) \rangle F_{c_{i'} \nu_{j'}}^{\mu}(\vec{k}', \vec{k}'-\vec{K}) = E_{c\nu \vec{K}}^{\mu} F_{c_i \nu_j}^{\mu}(\vec{k}, \vec{k}-\vec{K})$$

$\vec{K}$ is the exciton momentum, the difference between the electron and hole momenta, and is one of the labels of the space group representation according to which $|c\nu, \mu \vec{K}\rangle$ transforms. Since the ground state and $\vec{P}$ transform

according to $\vec{K} = 0$ representations, the intermediate states and the final state must also. This is simply another way of saying that crystal momentum is conserved. We will therefore need only $\vec{K} = 0$ excitons, so we define

$$f_{c_i v_j}^{\mu}(\vec{k}) \equiv F_{c_i v_j}^{\mu}(\vec{k}, \vec{k}).$$

Then f must satisfy

$$\sum_{k' j'} \langle c_i(k), v_j(k) | H | c_{i'}(k'), v_{j'}(k') \rangle f_{c_{i'} v_{j'}}^{\mu}(k') = E_{c v o}^{\mu} f_{c_i v_j}^{\mu}(\vec{k}) \quad (2-11)$$

One can define the Fourier transform of f ,

$$U_{c_i v_j}^{\mu}(\vec{\beta}) \equiv N^{-\frac{1}{2}} \sum_{\vec{k}} e^{i \vec{k} \cdot \vec{\beta}} f_{c_i v_j}^{\mu}(\vec{k}) \quad (2-12)$$

where $\vec{\beta}$ is the separation of the localized (Wannier) electron state lattice site and the hole state lattice site.

These localized states $a_{nR}(\vec{r})$ are defined by the (unitary) Fourier transform of Bloch functions

$$a_{nR}(\vec{r}) \equiv a_n(\vec{r} - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i \vec{k} \cdot \vec{R}} \psi_{n\vec{k}}(\vec{r})$$

where $\vec{R}$ is a lattice site. The symmetry properties and degree of localization of $a_{nR}(\vec{r})$ about $\vec{R}$ are discussed by Slater,²⁹ Koster³⁰ and Kohn.³¹ $U_{c_i v_j}^{\mu}(\vec{\beta})$ is commonly known as the envelope function.

In the case of two non-degenerate bands Eq.2-11 can be written

$$\sum_{k'} \langle c(k), v(k) | H | c(k'), v(k') \rangle f_{c v}^{\mu}(k') = E_{c v}^{\mu} f_{c v}^{\mu}(k)$$

or

$$\begin{aligned}
& \{ \langle c(k) | H^e | c(k) \rangle - \langle v(k) | H^h | v(k) \rangle \} \\
& - \sum_{k'} \langle c(k), v(k) | \frac{e^2}{|\vec{r}_e - \vec{r}_h|} | c(k'), v(k') \rangle f_{cv}^H(k') \\
& = [E_{cv}^H - E_o - E_{gap}] f_{cv}^H(k') \quad (2-13)
\end{aligned}$$

where E_o is the crystal ground state energy and $E_{gap} = E_c(k_o) - E_v(k_o)$. When the electron-hole interaction is weak we expect the electron-hole separation to be, on the average, large, so that $f(k)$ is a narrow function centered at $\vec{k}_o$. We can therefore write Eq.2-13 in an effective mass approximation as

$$\begin{aligned}
& \frac{\hbar^2}{2} \left[\sum_{\lambda\lambda'} \left(\frac{1}{m_c^*} - \frac{1}{m_v^*} \right)_{\lambda\lambda'} (k - k_o)_\lambda (k - k_o)_{\lambda'} \right] f_{cv}^H(k) \\
& - \sum_{k'} \langle c(k), v(k) | \frac{e^2}{|\vec{r}_e - \vec{r}_h|} | c(k'), v(k') \rangle f_{cv}^H(k') \\
& = [E_{cv}^H - E_{gap} - E_o] f_{cv}^H(k') \quad (2-14)
\end{aligned}$$

In the case of spherical non-degenerate bands Wannier³² showed that Eq.2-14 leads to the hydrogenic equation

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\vec{\beta}}^2 - \frac{e^2}{\beta} \right] u_{cv}^H(\vec{\beta}) = [E_{cv}^H - E_o - E_{gap}] u_{cv}^H(\vec{\beta}) \quad (2-15)$$

Here the separation $|\vec{r}_e - \vec{r}_h|$ was, on the average, large, and it could be replaced by the separation of the electron and hole lattice sites $\vec{\beta} = |\vec{R}_e - \vec{R}_h| \approx |\vec{r}_e - \vec{r}_h|$. Since the electron-hole interaction varied slowly from lattice site

to lattice site, $\vec{\beta}$ is approximated to be a continuous variable. The energies of the two bands (assumed here to have extrema at $\vec{k} = 0$) near $\vec{k} = 0$ were given in the effective mass approximation by

$$E_{\alpha}(\vec{k}) = E_{\alpha}(0) + \frac{\hbar^2 k^2}{2m_{\alpha}^*}$$

$1/\mu \equiv 1/m_c^* - 1/m_v^*$ is the reduced inverse effective mass. Corrections which introduce a dielectric constant into the hydrogenic equation are discussed in the book by Knox.²⁷

The effective mass approximation is good for large-radius excitons, since in this case $f_{cv}^{\mu}(k)$ is a narrow function centered at $\vec{k} = 0$. This approximation is not suitable, however, when the electron and hole are strongly interacting.

When an extremum of $E_c(\vec{k}) - E_v(\vec{k})$ occurs at a point other than $\vec{k} = 0$, or in anisotropic crystals at $\vec{k} = 0$, one obtains from Eq.2-14 an equation somewhat more difficult than Eq.2-15:

$$\left\{ -\frac{\hbar^2}{2} \sum_{\lambda\lambda'} \left(\frac{1}{m_c^*} - \frac{1}{m_v^*} \right)_{\lambda\lambda'} \frac{\partial^2}{\partial \beta_{\lambda} \partial \beta_{\lambda'}} - \frac{e^2}{\beta} \right\} \mathcal{U}(\vec{\beta}) = [E - E_0 - E_{gap}] \mathcal{U}(\vec{\beta}) \quad (2-16)$$

It is worthwhile to note that the operator in braces is invariant under operations of the point group of the crystal, so that $\mathcal{U}(\vec{\beta})$ (and $f(k)$) must transform according to a representation of the point group.

In the case of degeneracy at band extrema, the matrix $\langle C_i(k), V_j(k) | H | C_{i'}(k'), V_{j'}(k') \rangle$ can be written

$$H_{ii'}^e \delta_{jj'} \delta_{kk'} + H_{jj'}^h \delta_{ii'} \delta_{kk'} + V_{ijk, i'j'k'}^{eh}$$

where

$$H^e = -\frac{\hbar^2}{2m} \nabla_{\vec{r}_e}^2 + U_e(\vec{r}_e), \quad H^h = -\frac{\hbar^2}{2m} \nabla_{\vec{r}_h}^2 + U_h(\vec{r}_h)$$

and

$$V^{eh} = -\frac{e^2}{|\vec{r}_e - \vec{r}_h|}.$$

Dresselhaus³³ has treated the case of large radius excitons, in which case $V_{ijk, i'j'k'}^{eh} = V_{k, k'}^{eh} \delta_{ii'} \delta_{jj'}$ and, in an effective mass approximation,

$$H_{ii'}^e = \frac{\hbar^2}{2} \sum_{\alpha\beta} \left(\frac{1}{m_e^*} \right)_{ii'}^{\alpha\beta} (k_e - k_e^0)_\alpha (k_e - k_e^0)_\beta + E_c(k_0) \delta_{ii'}$$

$$H_{jj'}^h = \frac{\hbar^2}{2} \sum_{\alpha\beta} \left(\frac{1}{m_h^*} \right)_{jj'}^{\alpha\beta} (k_h - k_h^0)_\alpha (k_h - k_h^0)_\beta + E_v(k_0) \delta_{jj'}$$

where

$$\left(\frac{1}{m_e^*} \right)_{ii'}^{\alpha\beta} \equiv \frac{1}{m} \delta_{ii'} \delta_{\alpha\beta} + \frac{1}{m^2} \sum_l \left[\frac{\langle C_i | p_\alpha | l \rangle \langle l | p_\beta | C_{i'} \rangle}{E_c - E_l} + \frac{\langle C_i | p_\beta | l \rangle \langle l | p_\alpha | C_{i'} \rangle}{E_c - E_l} \right]$$

etc.

If we had chosen initially the correct band states, H^e and H^h would be diagonal and the problem would reduce to several problems of two bands each. However, in this case the effective masses are functions of the direction in $\vec{k}$ space away from the extrema. An example of this will be given in Chapter IV. This warping of bands has an effect on the type of equation which must be solved for the coefficients f . Under these circumstances, Eq.2-14 cannot be reduced to an equation as simple as even Eq.2-16. One finds

$$\frac{\hbar^2}{2} \sum_{\beta'} G_{c,v_j}(\vec{\beta}-\vec{\beta}') \mathcal{U}_{c,v_j}^{\mu}(\vec{\beta}') - \frac{e^2}{\beta} \mathcal{U}_{c,v_j}^{\mu}(\vec{\beta}) = [E_{c,v_j}^{\mu} - E_o - E_{g,p}] \mathcal{U}_{c,v_j}^{\mu}(\vec{\beta})$$

where

$$G_{c,v_j}(\vec{\beta}-\vec{\beta}') \equiv N^{-1} \sum_k e^{i\vec{k} \cdot (\vec{\beta}-\vec{\beta}')} \sum_{\lambda\lambda'} \left[\frac{1}{\mu_{ij}(k_\theta, k_\phi)} \right]_{\lambda\lambda'} k_\lambda k_{\lambda'}$$

Again note that since $\sum_{\lambda\lambda'} [1/\mu(k_\theta, k_\phi)]_{\lambda\lambda'} k_\lambda k_{\lambda'}$ is totally symmetric with respect to the point group, U must transform under a representation of the point group.

In cases where the warping of the bands is slight,

$$\text{i. e., } \left[\frac{1}{\mu_{ij}(k_\theta, k_\phi)} \right]_{\lambda\lambda'} = \left[\frac{1}{\mu_{ij}(0,0)} \right]_{\lambda\lambda'} + \delta g(k_\theta, k_\phi)_{\lambda\lambda'}$$

where δ is small, one might first solve for zero-order wave functions by Eq.2-15 or Eq.2-16, and then treat the "integral operator"

$$\delta \frac{\hbar^2}{2} \sum_{\beta'} N^{-1} \sum_k e^{i\vec{k} \cdot (\vec{\beta}-\vec{\beta}')} \sum_{\lambda\lambda'} g(k_\theta, k_\phi)_{\lambda\lambda'} k_\lambda k_{\lambda'}$$

as a perturbation.

The correct states to use in the second-order matrix element $P_{fg}^{(2)}$, both in the final state and in the intermediate states, are the stationary states of the crystal, that is, exciton states. Elliot²⁶ and Dresselhaus³⁴ have given the form of the absorption coefficient for single-photon transitions to exciton states. For the two-photon absorption coefficient we will assume that we can work with excitons constructed from two bands. The

final state is

$$|c_i, v_j; \mu\rangle = \sum_k f_{c_i v_j}^\mu(k) |c_i(k), v_j(k)\rangle$$

and a typical intermediate state is

$$|n^+ n^-; \nu\rangle = \sum_k f_{n^+ n^-}^\nu(k) |n^+(k), n^-(k)\rangle.$$

The ground state to intermediate state matrix element of $P_{fg}^{(2)}$ is

$$\langle m | \hat{E}_2 \cdot \vec{P} | g \rangle = \sum_k f_{n^+ n^-}^\nu(k)^* \langle n^+(k) | \hat{E}_2 \cdot \vec{P} | n^-(k) \rangle \quad (2-17)$$

The intermediate state to final state matrix element is

$$\begin{aligned} & \langle f | \hat{E}_1 \cdot \vec{P} | m \rangle \\ &= \begin{cases} \delta_{v_j n^-} \sum_{k'} f_{c_i v_j}^\mu(k')^* f_{n^+ v_j}^\nu(k') \langle c_i(k') | \hat{E}_1 \cdot \vec{P} | n^+(k') \rangle & n^+ \neq c_i \\ -\delta_{c_i n^+} \sum_{k'} f_{c_i v_j}^\mu(k')^* f_{c_i n^-}^\nu(k') \langle n^-(k') | \hat{E}_1 \cdot \vec{P} | v_j(k') \rangle & n^- \neq v_j \\ \delta_{v_j n^-} \delta_{c_i n^+} \sum_{k'} f_{c_i v_j}^\mu(k')^* f_{c_i v_j}^\nu(k') \\ \quad \times [\langle c_i(k') | \hat{E}_1 \cdot \vec{P} | c_i(k') \rangle - \langle v_j(k') | \hat{E}_1 \cdot \vec{P} | v_j(k') \rangle] \end{cases} \end{aligned} \quad (2-18)$$

Unless the conduction and valence band are of opposite parity, the first term in the $\vec{k} \cdot \vec{p}$ expansions gives the dominant contribution. Then Eq. 2-17 becomes

$$\begin{aligned} \langle m | \hat{E}_2 \cdot \vec{P} | g \rangle &= \langle n^+(k_o) | \hat{E}_2 \cdot \vec{P} | n^-(k_o) \rangle \sum_k f_{n^+ n^-}^\nu(\vec{k})^* \\ &= \langle n^+(k_o) | \hat{E}_2 \cdot \vec{P} | n^-(k_o) \rangle N^{\frac{1}{2}} U_{n^+ n^-}^\nu(o)^* \end{aligned} \quad (2-19)$$

where the band extrema occur at $\vec{k}_o$. $U_{n^+ n^-}^\nu(\vec{\beta})$ must therefore have the total symmetry of the point group. If parity is well defined there are other possible terms arising from

Eq.2-17. If the valence and conduction bands have the same parity, then intermediate states of the same parity can contribute by keeping the cross terms of $\langle n^+(k) | \hat{\epsilon}_2 \cdot \vec{p} | n^-(k) \rangle$ when $\vec{k} \cdot \vec{p}$ expansions of $|n^+(k)\rangle$ and $|n^-(k)\rangle$ are supplied. In this case Eq.2-17 becomes

$$\begin{aligned} \langle m | \hat{\epsilon}_2 \cdot \vec{p} | g \rangle &= \sum_k f_{n^+n^-}^\nu(k)^* \frac{\hbar}{m} \sum_l' \left\{ \frac{\langle n^+(k_0) | \hat{\epsilon}_2 \cdot \vec{p} | l(k_0) \rangle \langle l(k_0) | \vec{k} \cdot \vec{p} | n^-(k_0) \rangle}{E_{n^+}(k_0) - E_l(k_0)} \right. \\ &\quad \left. + \frac{\langle n^+(k_0) | \vec{k} \cdot \vec{p} | l(k_0) \rangle \langle l(k_0) | \hat{\epsilon}_2 \cdot \vec{p} | n^-(k_0) \rangle}{E_{n^+}(k_0) - E_l(k_0)} \right\} \\ &= \sum_k f_{n^+n^-}^\nu(k)^* \hat{\epsilon}_2 \cdot \vec{M}_{n^+n^-} \cdot \hbar \vec{k} \end{aligned}$$

where

$$M_{n^+n^-}^{\alpha\beta} \equiv \frac{1}{m} \sum_l' \left\{ \frac{\langle n^+ | p_\alpha | l \rangle \langle l | p_\beta | n^- \rangle}{E_{n^+} - E_l} + \frac{\langle n^+ | p_\beta | l \rangle \langle l | p_\alpha | n^- \rangle}{E_{n^+} - E_l} \right\}$$

$\frac{1}{m} \vec{M}_{n^+n^-}$ is an "inverse interband effective mass" tensor which occurs in one-photon dipole forbidden transitions³⁵ and one-photon quadrupole allowed transitions.³⁶

$$\begin{aligned} \langle m | \hat{\epsilon}_2 \cdot \vec{p} | g \rangle &= N^{-\frac{1}{2}} \sum_{k,\beta} U_{n^+n^-}^\nu(\beta)^* \hat{\epsilon}_2 \cdot \vec{M}_{n^+n^-} \cdot \hbar \vec{k} e^{i\vec{k} \cdot \vec{\beta}} \\ &\cong \frac{N^{\frac{1}{2}}}{(2\pi)^3} \int d^3\beta d^3k U_{n^+n^-}^\nu(\beta)^* \hat{\epsilon}_2 \cdot \vec{M}_{n^+n^-} \cdot \frac{\hbar}{i} \nabla_\beta e^{i\vec{k} \cdot \vec{\beta}} \\ &= N^{\frac{1}{2}} \int d^3\beta U_{n^+n^-}^\nu(\beta)^* \hat{\epsilon}_2 \cdot \vec{M}_{n^+n^-} \cdot \frac{\hbar}{i} \nabla_\beta \delta(\vec{\beta}) \\ &= N^{\frac{1}{2}} \hat{\epsilon}_2 \cdot \vec{M}_{n^+n^-} \cdot \frac{\hbar}{i} \nabla_\beta U_{n^+n^-}^\nu(\beta)^* \Big|_{\beta=0} \quad (2-20) \end{aligned}$$

For hydrogenic excitons $U_{n^+n^-}^\nu(\vec{\beta})$ must be a p-state. This contribution to "allowed" excitation will be ignored for the present, but it will be returned to in Chapter III.

Eq.2-18 becomes

$$\langle f | \hat{\epsilon}_1 \cdot \vec{p} | m \rangle$$

$$= \begin{cases} \delta_{n^-v_j} \langle c_i(k_0) | \hat{\epsilon}_1 \cdot \vec{p} | n^+(k_0) \rangle \sum_{\beta} U_{c_i v_j}^{\mu}(\beta)^* U_{n^+ v_j}^{\nu}(\beta) & n^+ \neq c_i \\ -\delta_{n^+c_i} \langle n^-(k_0) | \hat{\epsilon}_1 \cdot \vec{p} | v_j(k_0) \rangle \sum_{\beta} U_{c_i v_j}^{\mu}(\beta)^* U_{c_i n^-}^{\nu}(\beta) & n^- \neq v_j \\ 0 & n^+ = c_i, n^- = v_j \end{cases} \quad (2-21)$$

It is seen that U^{ν} must belong to the same representation as U^{μ} .

Substitution of Eq.2-19 and Eq.2-21 into Eq.2-6 yields

Allowed

$$P_{fg}^{(2)} = N^{\frac{1}{2}} \sum_{\nu \beta} \left\{ \sum_{n^+} U_{c_i v_j}^{\mu}(\beta)^* U_{n^+ v_j}^{\nu}(\beta) U_{n^+ v_j}^{\nu}(0)^* \right. \\ \times \left[\frac{\langle c_i(k_0) | \hat{\epsilon}_1 \cdot \vec{p} | n^+(k_0) \rangle \langle n^+(k_0) | \hat{\epsilon}_2 \cdot \vec{p} | v_j(k_0) \rangle}{E_{n^+ v_j}(\nu) - \hbar \omega_2} \right] \\ - \sum_{n^-} U_{c_i v_j}^{\mu}(\beta)^* U_{c_i n^-}^{\nu}(\beta) U_{c_i n^-}^{\nu}(0)^* \\ \times \left[\frac{\langle c_i(k_0) | \hat{\epsilon}_1 \cdot \vec{p} | n^-(k_0) \rangle \langle n^-(k_0) | \hat{\epsilon}_2 \cdot \vec{p} | v_j(k_0) \rangle}{E_{c_i n^-}(\nu) - \hbar \omega_2} \right] \\ \left. + \text{terms with 1 and 2 interchanged} \right\} \quad (2-22)$$

The ground state energy is taken to be zero.

When the valence and conduction bands have opposite parity we must keep both parities of intermediate states.

When Eq.2-19 applies, Eq.2-18 becomes

$$\langle f | \hat{\mathbf{E}}_1 \cdot \vec{\mathbf{p}} | m \rangle = \sum_{\mathbf{k}} f_{c;v_j}^{\mu}(\mathbf{k})^* f_{n^+v_j}^{\nu}(\mathbf{k}) \\ \times \frac{\hbar}{m} \sum_l \left\{ \frac{\langle c_i(k_0) | \hat{\mathbf{E}}_1 \cdot \vec{\mathbf{p}} | l(k_0) \rangle \langle l(k_0) | \vec{\mathbf{k}} \cdot \vec{\mathbf{p}} | n^+(k_0) \rangle}{E_{n^+} - E_l} \right. \\ \left. + \frac{\langle c_i(k_0) | \vec{\mathbf{k}} \cdot \vec{\mathbf{p}} | l(k_0) \rangle \langle l(k_0) | \hat{\mathbf{E}}_1 \cdot \vec{\mathbf{p}} | n^+(k_0) \rangle}{E_c - E_l} \right\}$$

$$= \begin{cases} \frac{N}{V} \int d^3\beta \mathcal{U}_{c;v_j}^{\mu}(\beta)^* \hat{\mathbf{E}}_1 \cdot \vec{\mathbf{M}}_{c;n^+} \cdot \frac{\hbar}{i} \nabla_{\beta} \mathcal{U}_{n^+v_j}^{\nu}(\beta) & \begin{cases} n^- = v_j \\ n^+ \neq c_i \end{cases} \\ -\frac{N}{V} \int d^3\beta \mathcal{U}_{c;v_j}^{\mu}(\beta)^* \hat{\mathbf{E}}_1 \cdot \vec{\mathbf{M}}_{n^-v_j} \cdot \frac{\hbar}{i} \nabla_{\beta} \mathcal{U}_{c;n^-}^{\nu}(\beta) & \begin{cases} n^- \neq v_j \\ n^+ = c_i \end{cases} \\ \frac{N}{V} \int d^3\beta \mathcal{U}_{c;v_j}^{\mu}(\beta)^* \hat{\mathbf{E}}_1 \cdot \left(\frac{\vec{m}}{\mu_{ij}} \right) \cdot \frac{\hbar}{i} \nabla_{\beta} \mathcal{U}_{c;v_j}^{\nu}(\beta) & \begin{cases} n^- = v_j \\ n^+ = c_i \end{cases} \end{cases}$$

$$\left(\frac{\vec{1}}{\mu_{ij}} \right) = \frac{1}{m} \vec{\mathbf{M}}_{c;c_i} - \left(\frac{1}{m} \vec{\mathbf{M}}_{v_jv_j} \right)$$

is the reduced reciprocal effective mass tensor.

When Eq.2-20 applies for $\langle m | \hat{\mathbf{E}}_2 \cdot \vec{\mathbf{p}} | q \rangle$, Eq.2-21 gives

$\langle f | \hat{\mathbf{E}}_1 \cdot \vec{\mathbf{p}} | m \rangle$. With these matrix elements we have

Forbidden

$$P_{fg}^{(2)} =$$

$$\left\{ N^{\frac{1}{2}} \sum_{\nu} \left[\sum_{n^+} \mathcal{U}_{n^+v_j}^{\nu}(0)^* \frac{\hat{\mathbf{E}}_1 \cdot \vec{\mathbf{M}}_{c;n^+} \cdot \langle \mathcal{U}_{c;v_j}^{\mu} | \vec{\mathbf{p}} | \mathcal{U}_{n^+v_j}^{\nu} \rangle}{E_{n^+v_j}(\nu) - \hbar \omega_2} \langle n^+(k_0) | \hat{\mathbf{E}}_2 \cdot \vec{\mathbf{p}} | v_j(k_0) \rangle \right. \right. \\ \left. \left. - \sum_{n^-} \mathcal{U}_{c;n^-}^{\nu}(0)^* \frac{\hat{\mathbf{E}}_1 \cdot \vec{\mathbf{M}}_{n^-v_j} \cdot \langle \mathcal{U}_{c;v_j}^{\mu} | \vec{\mathbf{p}} | \mathcal{U}_{c;n^-}^{\nu} \rangle}{E_{c;n^-}(\nu) - \hbar \omega_2} \langle c_i(k_0) | \hat{\mathbf{E}}_2 \cdot \vec{\mathbf{p}} | n^-(k_0) \rangle \right] \right\}$$

$$\begin{aligned}
& + N^{\frac{1}{2}} \sum_{\nu} \sum_{n^+} \langle c_i(k_0) | \hat{E}_i \cdot \vec{p} | n^+(k_0) \rangle \frac{\langle u_{c_i\nu_j}^{\mu} | u_{n^+\nu_j}^{\nu} \rangle \hat{E}_2 \cdot \vec{M}_{n^+\nu_j} \cdot \frac{\hbar}{i} \nabla_{\beta} u_{n^+\nu_j}^{\nu}(\beta) |_0}{E_{n^+\nu_j}(\nu) - \hbar \omega_2} \\
& - \sum_{n^-} \langle n^-(k_0) | \hat{E}_i \cdot \vec{p} | \nu_j(k_0) \rangle \frac{\langle u_{c_i\nu_j}^{\mu} | u_{c_i n^-} \rangle \hat{E}_2 \cdot \vec{M}_{c_i n^-} \cdot \frac{\hbar}{i} \nabla_{\beta} u_{c_i n^-}^{\nu}(\beta) |_0}{E_{c_i n^-}(\nu) - \hbar \omega_2} \\
& \left. \begin{aligned} & + \text{terms with subscripts 1 and 2 interchanged} \end{aligned} \right\} \quad (2-23)
\end{aligned}$$

Here

$$\langle u_{c_i\nu_j}^{\mu} | \vec{p} | u_{n^+\nu_j}^{\nu} \rangle \equiv \frac{N}{V} \int u_{c_i\nu_j}^{\mu}(\beta)^* \frac{\hbar}{i} \nabla_{\beta} u_{n^+\nu_j}^{\nu}(\beta) d^3\beta \quad (2-24)$$

and

$$\langle u_{c_i\nu_j}^{\mu} | u_{n^+\nu_j}^{\nu} \rangle \equiv \frac{N}{V} \int u_{c_i\nu_j}^{\mu}(\beta)^* u_{n^+\nu_j}^{\nu}(\beta) d^3\beta .$$

Let us now consider the significance of the terms in Eq.2-23. Each line represents a class of paths followed in the two-photon absorption process. Fig.2-1 is a schematic diagram of these paths with (a), (b), (c) and (d) indicating representatives of paths corresponding to the first, second, third and fourth lines, respectively, of Eq.2-23. In Fig.2-1 the vertical lines represent the initial, intermediate and final states as indicated at the top of each diagram. The horizontal dashes label conduction and valence band states. The parity of the bands is indicated by g or u. (When we speak of the parity of a band we will mean the parity of the band at the extremum.) Circles and crosses represent holes and

Fig.2-1. Paths of forbidden two-photon absorption

electrons, respectively, and ν and μ label envelope functions of the electron-hole pair. Note that ν is always totally symmetric and, in a cubic crystal, μ must have T_{1u} symmetry.

Referring again to Eq.2-23, the first line represents a path in which a photon raises an electron from the valence band v_j to a conduction band of opposite parity, the position of the electron with respect to the hole being described by a totally symmetric envelope. The other photon forces the electron to the final state with the electron in band c_i , its position with respect to the hole then given by envelope function ν . The second line describes the path in which the final state is reached via the intermediate state in which an electron in band c_i moves, with respect to a hole in a valence band of parity opposite to that of c_i , according to a totally symmetric envelope. In the third line the intermediate state consists of an electron in an upper conduction band having the same parity as v_j , the band of the hole, the envelope function having the same symmetry as that of the final state. The envelope also has the same symmetry in the intermediate state of the fourth line, where the electron in band c_i moves with respect to the hole in a lower valence band having parity the same as the conduction band. Notice that the final exciton envelope function $U_{c_i v_j}^{\mu}$ in all terms must be a p-state in the

hydrogenic model.

In this section we have given analytic expressions for the second-order matrix element $P_{fg}^{(2)}$, and hence the absorption coefficient by Eq.2-7, for allowed and forbidden transitions both in the simple band approximation and in an approximation to include exciton effects. To conclude this chapter we will give a brief description of relevant theoretical work which has appeared in the literature.

Braunstein³⁷ and Braunstein and Ockman³⁸ have given the form of the two-photon absorption coefficient in a three-band model neglecting exciton effects. They have characterized transitions by the behavior of the matrix elements $\langle n(k_0) | \hat{E} \cdot \vec{p} | v(k_0) \rangle$ and $\langle c(k_0) | \hat{E} \cdot \vec{p} | n(k_0) \rangle$, "allowed-forbidden", for example, meaning that $\langle n(k_0) | \hat{E} \cdot \vec{p} | v(k_0) \rangle \neq 0$ and $\langle c(k_0) | \hat{E} \cdot \vec{p} | n(k_0) \rangle = 0$. Both their allowed-allowed case and forbidden-forbidden case correspond to our allowed case. $P_{fg}^{(2)}$ in this model is obtained from Eq.2-8 by retaining a single intermediate band n , different from v and c and keeping the terms of order l , k , and k^2 for allowed-allowed, allowed-forbidden, and forbidden-forbidden, respectively. The first two are special cases of Eq.2-9 and Eq.2-10. We have assumed in deriving Eq.2-9 that when $|c(k_0)\rangle$ and $|v(k_0)\rangle$ have the same parity there will be opposite parity intermediate states $|n(k_0)\rangle$ whose contribution to $P_{fg}^{(2)}$ is much larger than the con-

tribution of order k^2 of the same parity intermediate states.

Loudon³⁹ and Inoue and Toyozawa¹¹ have given the form of the two-photon absorption coefficient in the allowed case when the final states are excitons, but have neglected to use excitons in the intermediate states. Their result for $P_{fg}^{(2)}$ was

$$P_{fg}^{(2)} = \mathcal{U}_{c,v_i}^H(o)^* \sum_n \left\{ \frac{\langle c_i(k_o) | \hat{E}_1 \cdot \vec{p} | n(k_o) \rangle \langle n(k_o) | \hat{E}_2 \cdot \vec{p} | v_j(k_o) \rangle}{E_n(k_o) - E_v(k_o) - \hbar\omega_2} + \frac{\langle c_i(k_o) | \hat{E}_2 \cdot \vec{p} | n(k_o) \rangle \langle n(k_o) | \hat{E}_1 \cdot \vec{p} | v_j(k_o) \rangle}{E_n(k_o) - E_v(k_o) - \hbar\omega_1} \right\} \quad (2-25)$$

We find a similar expression for the forbidden case:

$$P_{fg}^{(2)} = N^{\frac{1}{2}} \sum_n \frac{\hat{E}_1 \cdot \vec{M}_{c,n} \cdot \frac{\hbar}{i} \nabla_\beta \mathcal{U}_{c,v_i}^H(\beta)^* |_o \langle n(k_o) | \hat{E}_2 \cdot \vec{p} | v_j(k_o) \rangle}{E_n(k_o) - E_v(k_o) - \hbar\omega_2} + N^{\frac{1}{2}} \sum_n \frac{\langle c_i(k_o) | \hat{E}_1 \cdot \vec{p} | n(k_o) \rangle \hat{E}_2 \cdot \vec{M}_{n,v_j} \cdot \frac{\hbar}{i} \nabla_\beta \mathcal{U}_{c,v_i}^H(\beta) |_o}{E_n(k_o) - E_v(k_o) - \hbar\omega_2}$$

+ terms with subscripts 1 and 2 interchanged

We will make no more use of this expression.

Mahan^{19,20} has calculated the form of the absorption coefficient for the allowed and forbidden cases in a two-band model, using excitons in the final and intermediate states. His calculations will be discussed in Chapter IV.

Chapter III

Allowed Transitions

The usefulness of studying the dependence of the two-photon absorption coefficient on the directions of polarization of the incident light beams was first pointed out by Inoue and Toyozawa,¹¹ who calculated the angular dependence functions for a transition in which the initial state had the total symmetry of the symmetry group. When considered from the point of view of Bloch functions, one might ask what the polarization dependence is for a transition between a valence band and a conduction band for an arbitrary symmetry of either. In this chapter we will derive a mathematical expression for the polarization dependence of such a transition at the Γ -point and tabulate the angular dependences as a supplement to the tables of Inoue and Toyozawa. In addition we will obtain angular functions for transitions taking place at points and on lines of high symmetry in the Brillouin zone for hexagonal close-packed and wurtzite structures.

A. Formalism

Let us first consider the sum over intermediate states in Eq.2-22. Here we must make some simplifying assumptions. If several bands are degenerate at $\vec{k} = \vec{k}_0$, we will assume that the difference in the effective masses of these bands at $\vec{k}_0$ is sufficiently small that

$$N^{\frac{1}{2}} \sum_{\nu\beta} \frac{\mathcal{U}_{c_i v_j}^{\mu}(\vec{\beta})^* \mathcal{U}_{n_l^+ v_j}^{\nu}(\vec{\beta}) \mathcal{U}_{n_l^+ v_j}^{\nu}(0)^*}{E_{n_l^+ v_j}(\nu) - \hbar\omega}$$

and

$$N^{\frac{1}{2}} \sum_{\nu\beta} \frac{\mathcal{U}_{c_i v_j}^{\mu}(\vec{\beta})^* \mathcal{U}_{c_i n_l^-}^{\nu}(\vec{\beta}) \mathcal{U}_{c_i n_l^-}^{\nu}(0)^*}{E_{c_i n_l^-}(\nu) - \hbar\omega}$$

are approximately independent of i, j and l , where $\{|c_i(k_0)\rangle\}$, $\{|v_j(k_0)\rangle\}$ and $\{|n_l^{\pm}(k_0)\rangle\}$ are degenerate sets. The second-order matrix element, excluding or including exciton effects, can then be written

$$P_{fg}^{(2)} = \langle c_i(k_0) | \hat{E}_1 \cdot \vec{p} \Lambda(\omega_2) \vec{p} \cdot \hat{E}_2 | v_j(k_0) \rangle \\ + \langle c_i(k_0) | \hat{E}_2 \cdot \vec{p} \Lambda(\omega_1) \hat{E}_1 \cdot \vec{p} | v_j(k_0) \rangle$$

where we define

$$\Lambda(\omega_m) =$$

$$\left\{ \begin{aligned} & \sum_n \frac{|n(k_0)\rangle \langle n(k_0)|}{E_n(k_0) - E_v(k_0) - \hbar\omega_m} && \text{in Eq.2-9 or Eq.2-25} \\ & N^{\frac{1}{2}} \sum_{n^+} \sum_{\nu\beta} \mathcal{U}_{cv}^\mu(\vec{\beta})^* \mathcal{U}_{n^+\nu}^\nu(\vec{\beta}) \mathcal{U}_{n^+\nu}^\nu(0)^* \frac{|n^+(k_0)\rangle \langle n^+(k_0)|}{E_{n^+\nu}(\nu) - \hbar\omega_m} \\ & + N^{\frac{1}{2}} \sum_{n^-} \sum_{\nu\beta} \mathcal{U}_{cv}^\mu(\vec{\beta})^* \mathcal{U}_{cn^-}^\nu(\vec{\beta}) \mathcal{U}_{cn^-}^\nu(0)^* \frac{|n^-(k_0)\rangle \langle n^-(k_0)|}{E_{cn^-}(\nu) - \hbar\omega_m} \end{aligned} \right.$$

in Eq.2-22

$\Lambda(\omega_m)$ has the total symmetry of the group of $\vec{k}_0$ (see Appendix B). Following Inoue and Toyozawa¹¹ we define

$$\begin{aligned} \Lambda_+ &= \Lambda(\omega_2) + \Lambda(\omega_1) \\ \Lambda_- &= \Lambda(\omega_2) - \Lambda(\omega_1). \end{aligned} \quad (3-1)$$

The two-photon absorption coefficient is proportional to

$$\sum_f |P_{fg}^{(2)}|^2 = \sum_{\vec{k}_0, ij} \left| \langle C_i(k'_0) | [\hat{\epsilon}_1 \cdot \vec{p} \Lambda(\omega_2) \vec{p} \cdot \hat{\epsilon}_2 + \hat{\epsilon}_2 \cdot \vec{p} \Lambda(\omega_1) \vec{p} \cdot \hat{\epsilon}_1] | V_j(k'_0) \rangle \right|^2$$

where $\vec{k}'_0$ runs over the star $\vec{k}_0$.⁴⁰

Using Eqs.3-1 the operator in square brackets becomes

$$\begin{aligned} & \frac{1}{2} \hat{\epsilon}_1 \cdot \vec{p} (\Lambda_+ + \Lambda_-) \vec{p} \cdot \hat{\epsilon}_2 + \frac{1}{2} \hat{\epsilon}_2 \cdot \vec{p} (\Lambda_+ - \Lambda_-) \vec{p} \cdot \hat{\epsilon}_1 \\ &= \frac{1}{2} \left\{ \hat{\epsilon}_1 \cdot \vec{p} \Lambda_+ \vec{p} \cdot \hat{\epsilon}_2 + \hat{\epsilon}_2 \cdot \vec{p} \Lambda_+ \vec{p} \cdot \hat{\epsilon}_1 \right\} \\ & \quad + \frac{1}{2} \left\{ \hat{\epsilon}_1 \cdot \vec{p} \Lambda_- \vec{p} \cdot \hat{\epsilon}_2 - \hat{\epsilon}_2 \cdot \vec{p} \Lambda_- \vec{p} \cdot \hat{\epsilon}_1 \right\} \end{aligned}$$

$$= \hat{\epsilon}_1 \cdot \{ (\vec{p} \wedge_+ \vec{p})_S + (\vec{p} \wedge_- \vec{p})_{AS} \} \cdot \hat{\epsilon}_2$$

where S and AS mean the symmetric and antisymmetric parts.

The tensor in braces, which will be labeled $\overleftrightarrow{T}$, can be written in matrix form as

$$\overleftrightarrow{T} = \begin{bmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{xy} & A_{yy} & A_{yz} \\ A_{xz} & A_{yz} & A_{zz} \end{bmatrix} + \begin{bmatrix} 0 & B_z & -B_y \\ -B_z & 0 & B_x \\ B_y & -B_x & 0 \end{bmatrix}$$

Here

$$B_x \equiv \frac{1}{2} (p_y \wedge_- p_z - p_z \wedge_- p_y)$$

and

$$B_y \equiv \frac{1}{2} (p_z \wedge_- p_x - p_x \wedge_- p_z)$$

$$B_z \equiv \frac{1}{2} (p_x \wedge_- p_y - p_y \wedge_- p_x)$$

transform as components of an axial vector (or pseudovector),

and

$$A_{ij} \equiv \frac{1}{2} (p_i \wedge_+ p_j + p_j \wedge_+ p_i)$$

transform as the product ij (e. g., A_{xy} transforms as xy). Recalling the notation for the polarization vectors,

$\hat{\epsilon}_1 = (l_1, m_1, n_1)$ and $\epsilon_2 = (l_2, m_2, n_2)$, the tensor operator is written in expanded form as

$$\hat{\epsilon}_1 \cdot \overleftrightarrow{T} \cdot \hat{\epsilon}_2 = l_1 l_2 A_{xx} + m_1 m_2 A_{yy} + n_1 n_2 A_{zz} \quad (3-2)$$

$$+ (n_1 l_2 + n_2 l_1) A_{xz} + (m_1 n_2 + m_2 n_1) A_{yz} + (l_1 m_2 + l_2 m_1) A_{xy}$$

$$+ (n_1 l_2 - n_2 l_1) B_y + (m_1 n_2 - m_2 n_1) B_x + (l_1 m_2 - l_2 m_1) B_z$$

For a given point group each term in this equation will not necessarily transform under an irreducible representation of the point group. For example, A_{xx} does not transform within a single representation of the cubic group, but $A_{xx} + A_{yy} + A_{zz}$ transforms according to the representation A_1 of group O . Therefore the terms in Eq.3-2 must be rearranged so as to be a sum of terms which transform according to specific rows of irreducible representations of the given point group; i. e.,

$$\hat{\epsilon}_1 \cdot \vec{T} \cdot \hat{\epsilon}_2 = \sum_{\mu n q} a_{nq}^{\mu} T_{nq}^{\mu}$$

where T_{nq}^{μ} transforms according to row n of representation Γ^{μ} . The index q distinguishes terms belonging to the same row of the same representation if more than one term occurs in the decomposition of $\hat{\epsilon}_1 \cdot \vec{T} \cdot \hat{\epsilon}_2$. The coefficients a_{nq}^{μ} are functions of $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$. (Henceforth representations will be labeled by Greek letters and rows by Latin letters.)

Let us relabel the valence and conduction band states in order to make their symmetry explicit; $|c_i(k_o)\rangle \equiv |\lambda i\rangle$ and $|v_j(k_o)\rangle \equiv |\nu j\rangle$, where λ and ν are irreducible representations of the group of $\vec{k}_o$, and i and j are rows. The absorption coefficient is now proportional to

$$\sum_{k_o, i, j} |\langle \lambda i | \hat{\epsilon}_1 \cdot \vec{T} \cdot \hat{\epsilon}_2 | \nu j \rangle|^2 = \sum_{k_o, i, j} \left| \sum_{\mu n q} a_{nq}^{\mu} \langle \lambda i | T_{nq}^{\mu} | \nu j \rangle \right|^2.$$

The following mathematical theorem will be proven. If an operator T can be decomposed into a sum of terms T_{nq}^{μ} which transform according to rows n of representation Γ^{μ} of a group, i. e., $T = \sum_{\mu nq} a_{nq}^{\mu} T_{nq}^{\mu}$, then

$$\sum_{ij} \left| \sum_{\mu nq} a_{nq}^{\mu} \langle \lambda i | T_{nq}^{\mu} | \nu j \rangle \right|^2 = \sum_{\mu \tau_{\mu}} \gamma(\mu, \tau_{\mu}), \quad (3-3)$$

where the sum over μ on the right extends only over those representations contained in the direct product $\Gamma^{\lambda*} \times \Gamma^{\nu}$, and

$$\gamma(\mu, \tau_{\mu}) \equiv \sum_s \left| \langle \Gamma' | \sum_{\sigma nq} a_{nq}^{\sigma} T_{nq}^{\sigma} | \mu \tau_{\mu} s \rangle \right|^2. \quad (3-4)$$

Γ' is the totally symmetric representation, and τ_{μ} distinguishes occurrences of Γ^{μ} if it occurs more than once in the decomposition of $\Gamma^{\lambda*} \times \Gamma^{\nu}$. The theorem says that the angular function for a transition between states of symmetries Γ^{λ} and Γ^{ν} is a linear combination of angular functions characteristic of transitions of the type $\Gamma' \rightarrow \Gamma^{\mu}$ for all Γ^{μ} contained in the decomposition of $\Gamma^{\lambda*} \times \Gamma^{\nu}$, and that the function for a transition of the type $\Gamma' \rightarrow \Gamma^{\mu}$ will occur as many times as Γ^{μ} is contained in $\Gamma^{\lambda*} \times \Gamma^{\nu}$.

Eq. 3-4 can be written

$$\begin{aligned} \gamma(\mu, \tau_{\mu}) &= \sum_s \left| \sum_{\sigma nq} a_{nq}^{\sigma} \langle \Gamma' | \sum_{r \tau_r} [A_{r, ns}^{\tau_r, \sigma}]^* | r \tau_r; \tau_{\mu} q \rangle \right| \\ &= \sum_s \left| \sum_q a_{nq}^{\mu} f_q^{\mu \tau_{\mu}} \right|^2, \end{aligned}$$

where⁴¹ we have used the fact that $\langle \Gamma' | r \tau_r; \tau_{\mu} q \rangle = 0$

unless $\Gamma^r = \Gamma^i$, in which case Γ^σ must be equal to Γ^M .
 $f_q^{\mu\tau_\mu}$ are complex constants, and $A^{\tau_\tau, \sigma\mu}_{r, ns}$ are the
 Clebsch-Gordan coefficients defined by

$$\Psi_r^{\tau_\tau} = \sum_{ns} [A^{\tau_\tau, \sigma\mu}_{r, ns}] \psi_n^\sigma \phi_s^\mu. \quad (3-5)$$

To prove the theorem we write

$$\begin{aligned} & \sum_{ij} \left| \sum_{\mu n q} a_{nq}^\mu \langle \lambda i | T_{nq}^\mu | \nu j \rangle \right|^2 \\ &= \sum_{ij} \left| \sum_{\mu n q} a_{nq}^\mu \sum_{\sigma \tau_\sigma s} [A^{\sigma \tau_\sigma, \mu \nu}_s, n_j]^* \langle \lambda i | \sigma \tau_\sigma s; i \rangle \right|^2 \\ &= \sum_{ij} \left| \sum_{\mu n q} a_{nq}^\mu \sum_{\tau_\lambda} [A^{\lambda \tau_\lambda, \mu \nu}_i, n_j]^* \eta_{q}^{\tau_\lambda} \right|^2, \end{aligned} \quad (3-6)$$

where $\eta_q^{\tau_\lambda}$ are complex constants. At this point we use
 a symmetry property of Clebsch-Gordan coefficients derived
 in Appendix C:

$$A^{\lambda \tau_\lambda, \mu \nu}_i, n_j = \sum_{\tau_\mu} C[(\lambda \mu) \bar{\nu}; \tau_\lambda \tau_\mu] [A^{\mu \tau_\mu, \lambda \bar{\nu}}_n, i j]^*.$$

$C[(\lambda \mu) \bar{\nu}; \tau_\lambda \tau_\mu]$ is a complex constant, and $\bar{\nu}$ denotes the
 representation which is complex conjugate to representation
 ν . Continuing, Eq.3-6 becomes

$$\sum_{ij} \left| \sum_{\mu n q} a_{nq}^\mu \sum_{\tau_\lambda \tau_\mu} C[(\lambda \mu) \bar{\nu}; \tau_\lambda \tau_\mu]^* [A^{\mu \tau_\mu, \lambda \bar{\nu}}_n, i j] \eta_q^{\tau_\lambda} \right|^2$$

$$\begin{aligned}
&= \sum_{ij} \sum_{\mu n q} \sum_{\mu' n' q'} \sum_{\tau_\lambda \tau_\mu} \sum_{\tau_{\lambda'} \tau_{\mu'}} (a_{nq}^\mu) (a_{n'q'}^{\mu'})^* \\
&\quad \times C[(\lambda\mu)\bar{\nu}; \tau_\lambda \tau_\mu]^* C[(\lambda\mu')\bar{\nu}; \tau_{\lambda'} \tau_{\mu'}] (\eta_{\bar{q}}^{\tau_\lambda}) (\eta_{\bar{q}'}^{\tau_{\lambda'}})^* \\
&\quad \times [A_{n, ij}^{\mu \tau_\mu, \lambda \bar{\nu}}] [A_{n', ij}^{\mu' \tau_{\mu'}, \lambda' \bar{\nu}}]^*
\end{aligned}$$

The Clebsch-Gordan coefficients are elements of a unitary matrix, so that when the sum over i and j is performed (see Appendix C) we obtain

$$\begin{aligned}
&\sum_{ij} \left| \sum_{\mu n q} a_{nq}^\mu \langle \lambda i | T_{nq}^\mu | \nu j \rangle \right|^2 \\
&= \sum_{\mu \tau_\mu n} \left| \sum_q a_{nq}^\mu \sum_{\tau_\lambda} C[(\lambda\mu)\bar{\nu}; \tau_\lambda \tau_\mu]^* \eta_{\bar{q}}^{\tau_\lambda} \right|^2 \\
&= \sum_{\mu \tau_\mu n} \left| \sum_q a_{nq}^\mu f_q^{\mu \tau_\mu} \right|^2 \\
&= \sum_{\mu \tau_\mu} \gamma(\mu, \tau_\mu),
\end{aligned}$$

which completes the proof.

Before proceeding to the angular functions for the point groups, some comments must be made about the paths followed for allowed two-photon absorption. The preceding formalism was based on the assumption that only bands having parity opposite to that of the highest valence and lowest conduction bands entered into the intermediate states. This is an approximation, of course; all bands participate to some degree. Mahan²⁰ has considered

allowed two-photon absorption as being well-described within the framework of the two band model, thereby requiring that the bands in the intermediate states have the same parity as the valence and conduction bands. By proceeding with Eq.2-20 with $n^+ = c$ and $n^- = v$, Mahan showed that final state excitons could be s- or d-states, and indicated that the s-states had been considered earlier by Inoue and Toyozawa.¹¹ It is apparent, however, that the s-states considered by Inoue and Toyozawa are reached by different paths. The transitions of Inoue and Toyozawa are analogous to the allowed-allowed transitions of Braunstein and Ockman,^{37,38} while Mahan's transitions are analogous to the forbidden-forbidden type. Our assumption, then, is that the probability amplitudes for s-exciton transitions via opposite parity intermediate bands are considerably larger than the probability amplitudes for s- and d-exciton transitions described in the two-band model.

B. Γ -point Transitions

The angular dependence functions for all possible band-to-band transitions occurring at $\vec{k} = 0$ and to excitons of Γ' symmetry (when the stated assumptions are valid) are given in Table 3-1, where λ_i are real constants and c_i are real positive constants. As we have said before, transitions are not allowed between states of opposite parity, and so we have written $\Gamma_{\pm}^{\mu} \longleftrightarrow \Gamma_{\pm}^{\nu}$, meaning $\Gamma_{-}^{\mu} \longleftrightarrow \Gamma_{-}^{\nu}$ or $\Gamma_{+}^{\mu} \longleftrightarrow \Gamma_{+}^{\nu}$, when the point group contains the inversion. When two representations are given in parentheses they are degenerate by time reversal.⁴¹ The symbols used for the single-valued representations are those common in molecular applications (A, B, E and T) and the symbols used for the double-valued representations (Γ^{μ}) are defined in the book by Koster, Dimmock, Wheeler and Statz.⁴² To minimize the possibility of confusion in the notation, Appendix D provides a table of correspondence between the notation used here and the notation of Koster, et al. The definitions of the axes used for some of the point groups are given in Fig. 3-1 through Fig. 3-4. For the remaining groups- C_n , S_n and C_{nh} -the z axis is the axis of rotation, and x and y are arbitrary. Note that for some groups one can make an unambiguous choice of axes, while for others (e. g. D_{3d}) one must be more careful, for the angular functions for these are not invariant under a coordinate rotation of 90° .

In compiling Table 3-1 the angular functions for transitions of the type $\Gamma' \longleftrightarrow \Gamma''$ have been recalculated and agree with those reported by Inoue and Toyozawa except for the following cases: transitions of the type $\Gamma' \longrightarrow \Gamma^E$, where E denotes a pair of complex conjugate representations, for the groups C_4 , C_{4h} , S_4 , C_3 , S_6 , C_6 , C_{6h} and C_{3h} . The disagreement appears to be due to an algebraic error in the earlier calculation.

It is important to make some comments concerning the application of the angular functions in Table 3-1 in experiments. First, we point out the restriction placed on the directions of polarization made in part A of Chapter II. Second, it must be noted that Λ_+ and Λ_- are functions of ω_1 and ω_2 ; when $\omega_1 = \omega_2$, Λ_- is zero. Of course, this must be avoided in a two-beam experiment, as was stated in Chapter II. However, if the two frequencies are close, the two-photon absorption coefficient and polarization dependence can be strongly dependent on the frequency of the tunable light source. In the tables this fact is hidden in the constants; one needs only to remember that the components (and only the components) of $(\hat{e}_1 \times \hat{e}_2)$, e. g. $(l_1 m_2 - l_2 m_1)$, have coefficients dependent on Λ_- .

Table 3-1
Angular Dependence Functions

The group(s) are given at the heads of the left hand columns. Other symbols are defined in the text.

C_1	S_2	
$A \leftrightarrow A$	$A_{\pm} \leftrightarrow A_{\pm}$	$[l_1 l_2 + \lambda_1 m_1 m_2 + \lambda_2 n_1 n_2 + \lambda_3 (l_1 m_2 + l_2 m_1) + \lambda_4 (n_1 l_2 + n_2 l_1) + \lambda_5 (m_1 n_2 + m_2 n_1) + \lambda_6 (l_1 m_2 - l_2 m_1) + \lambda_7 (n_1 l_2 - n_2 l_1) + \lambda_8 (m_1 n_2 - m_2 n_1)]^2$
$\Gamma^2 \leftrightarrow \Gamma^2$	$\Gamma_{\pm}^2 \leftrightarrow \Gamma_{\pm}^2$	

C_2	C_{1h}	C_{2h}	
$A \leftrightarrow A$	$A' \leftrightarrow A'$	$A_{\pm} \leftrightarrow A_{\pm}$	$[l_1 l_2 + \lambda_1 m_1 m_2 + \lambda_2 n_1 n_2 + \lambda_3 (l_1 m_2 + l_2 m_1) + \lambda_4 (l_1 m_2 - l_2 m_1)]^2 \equiv A(\epsilon_1 \epsilon_2)$
$B \leftrightarrow B$	$A'' \leftrightarrow A''$	$B_{\pm} \leftrightarrow B_{\pm}$	
$A \leftrightarrow B$	$A' \leftrightarrow A''$	$A_{\pm} \leftrightarrow B_{\pm}$	$[(m_1 n_2 - m_2 n_1) + \lambda_5 (n_1 l_2 - n_2 l_1) + \lambda_6 (n_1 l_2 + n_2 l_1) + \lambda_7 (m_1 n_2 + m_2 n_1)]^2 \equiv B(\epsilon_1 \epsilon_2)$
$(\Gamma^3 \Gamma^4) \leftrightarrow (\Gamma^3 \Gamma^4)$	$(\Gamma^3 \Gamma^4) \leftrightarrow (\Gamma^3 \Gamma^4)$	$(\Gamma_{\pm}^3 \Gamma_{\pm}^4) \leftrightarrow (\Gamma_{\pm}^3 \Gamma_{\pm}^4)$	$A(\epsilon_1 \epsilon_2) + cB(\epsilon_1 \epsilon_2)$

Table 3-1 (Contd.)

D_2	C_{2v}	D_{2h}	
$A \leftrightarrow A$ $B_1 \leftrightarrow B_1$ $B_2 \leftrightarrow B_2$ $B_3 \leftrightarrow B_3$	$A_1 \leftrightarrow A_1$ $A_2 \leftrightarrow A_2$ $B_1 \leftrightarrow B_1$ $B_2 \leftrightarrow B_2$	$A_{\pm} \leftrightarrow A_{\pm}$ $B_{1\pm} \leftrightarrow B_{1\pm}$ $B_{2\pm} \leftrightarrow B_{2\pm}$ $B_{3\pm} \leftrightarrow B_{3\pm}$	$[l_1 l_2 + \lambda_1 m_1 m_2 + \lambda_2 n_1 n_2]^2 \equiv A(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \leftrightarrow B_1$ $B_2 \leftrightarrow B_3$	$A_1 \leftrightarrow A_2$ $B_1 \leftrightarrow B_2$	$A_{\pm} \leftrightarrow B_{1\pm}$ $B_{2\pm} \leftrightarrow B_{3\pm}$	$[(l_1 m_2 + l_2 m_1) + \lambda_3 (l_1 m_2 - l_2 m_1)]^2 \equiv B_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \leftrightarrow B_2$ $B_1 \leftrightarrow B_3$	$A_1 \leftrightarrow B_1$ $A_2 \leftrightarrow B_2$	$A_{\pm} \leftrightarrow B_{2\pm}$ $B_{1\pm} \leftrightarrow B_{3\pm}$	$[(n_1 l_2 + n_2 l_1) + \lambda_4 (n_1 l_2 - n_2 l_1)]^2 \equiv B_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \leftrightarrow B_3$ $B_1 \leftrightarrow B_2$	$A_1 \leftrightarrow B_2$ $A_2 \leftrightarrow B_1$	$A_{\pm} \leftrightarrow B_{3\pm}$ $B_{1\pm} \leftrightarrow B_{2\pm}$	$[(m_1 n_2 + m_2 n_1) + \lambda_5 (m_1 n_2 - m_2 n_1)]^2 \equiv B_3(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^5 \leftrightarrow \Gamma^5$	$\Gamma^5 \leftrightarrow \Gamma^5$	$\Gamma_{\pm}^5 \leftrightarrow \Gamma_{\pm}^5$	$A(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 B_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 B_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 B_3(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-1 (Contd.)

C_{4h}, S_4	C_{4h}	
$A \leftrightarrow A$ $B \leftrightarrow B$	$A_{\pm} \leftrightarrow A_{\pm}$ $B_{\pm} \leftrightarrow B_{\pm}$	$[(l_1 l_2 + m_1 m_2) + \lambda_1 n_1 n_2 + \lambda_2 (l_1 m_2 - l_2 m_1)]^2 \equiv A(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \leftrightarrow B$	$A_{\pm} \leftrightarrow B_{\pm}$	$[(l_1 l_2 - m_1 m_2) + \lambda_3 (l_1 m_2 + l_2 m_1)]^2 \equiv B(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \leftrightarrow E$ $B \leftrightarrow E$	$A_{\pm} \leftrightarrow E_{\pm}$ $B_{\pm} \leftrightarrow E_{\pm}$	$\begin{aligned} & [(n_1 l_2 + n_2 l_1) + \lambda_4 (m_1 n_2 - m_2 n_1) + \lambda_5 (n_1 l_2 - n_2 l_1)]^2 \\ & + [(m_1 n_2 + m_2 n_1) + \lambda_4 (n_1 l_2 - n_2 l_1) - \lambda_5 (m_1 n_2 - m_2 n_1)]^2 \\ & E(\hat{\epsilon}_1 \hat{\epsilon}_2) \end{aligned}$
$E \leftrightarrow E$	$E_{\pm} \leftrightarrow E_{\pm}$	$A(\hat{\epsilon}_1 \hat{\epsilon}_2) + cB(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(\Gamma^5 \Gamma^6) \leftrightarrow (\Gamma^5 \Gamma^6)$ $(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^7 \Gamma^8)$	$(\Gamma_{\pm}^5 \Gamma_{\pm}^6) \leftrightarrow (\Gamma_{\pm}^5 \Gamma_{\pm}^6)$ $(\Gamma_{\pm}^7 \Gamma_{\pm}^8) \leftrightarrow (\Gamma_{\pm}^7 \Gamma_{\pm}^8)$	$A(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(\Gamma^5 \Gamma^6) \leftrightarrow (\Gamma^7 \Gamma^8)$	$(\Gamma_{\pm}^5 \Gamma_{\pm}^6) \leftrightarrow (\Gamma_{\pm}^7 \Gamma_{\pm}^8)$	$B(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-1 (Contd.)

D_4, C_{4d}, D_{4h}	D_{4h}	
$A_1 \leftrightarrow A_1$ $A_2 \leftrightarrow A_2$ $B_1 \leftrightarrow B_1$ $B_2 \leftrightarrow B_2$	$A_{1\pm} \leftrightarrow A_{1\pm}$ $A_{2\pm} \leftrightarrow A_{2\pm}$ $B_{1\pm} \leftrightarrow B_{1\pm}$ $B_{2\pm} \leftrightarrow B_{2\pm}$	$[(l_{12} + m_{12}) + \lambda_1 n_{12}]^2 \equiv A_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \leftrightarrow A_2$ $B_1 \leftrightarrow B_2$	$A_{1\pm} \leftrightarrow A_{2\pm}$ $B_{1\pm} \leftrightarrow B_{2\pm}$	$(l_{12} - l_{21})^2 \equiv A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \leftrightarrow B_1$ $A_2 \leftrightarrow B_2$	$A_{1\pm} \leftrightarrow B_{1\pm}$ $A_{2\pm} \leftrightarrow B_{2\pm}$	$(l_{12} - m_{12})^2 \equiv B_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \leftrightarrow B_2$ $A_2 \leftrightarrow B_1$	$A_{1\pm} \leftrightarrow B_{2\pm}$ $A_{2\pm} \leftrightarrow B_{1\pm}$	$(l_{12} + l_{21})^2 \equiv B_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \leftrightarrow E$ $A_2 \leftrightarrow E$ $B_1 \leftrightarrow E$ $B_2 \leftrightarrow E$	$A_{1\pm} \leftrightarrow E_{\pm}$ $A_{2\pm} \leftrightarrow E_{\pm}$ $B_{1\pm} \leftrightarrow E_{\pm}$ $B_{2\pm} \leftrightarrow E_{\pm}$	$\begin{aligned} & [(m_{12} + m_{21}) + \lambda_2 (m_{12} - m_{21})]^2 \\ & + [(n_{12} + n_{21}) - \lambda_2 (n_{12} - n_{21})]^2 \\ & \equiv E(\hat{\epsilon}_1 \hat{\epsilon}_2) \end{aligned}$
$E \leftrightarrow E$	$E_{\pm} \leftrightarrow E_{\pm}$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 B_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 B_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-1 (Contd.)

$\Gamma^6 \leftrightarrow \Gamma^6$ $\Gamma^7 \leftrightarrow \Gamma^7$	$\Gamma_{\pm}^6 \leftrightarrow \Gamma_{\pm}^6$ $\Gamma_{\pm}^7 \leftrightarrow \Gamma_{\pm}^7$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^6 \leftrightarrow \Gamma^7$	$\Gamma_{\pm}^6 \leftrightarrow \Gamma_{\pm}^7$	$B_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 B_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E(\hat{\epsilon}_1 \hat{\epsilon}_2)$

C_3	S_6	
$A \leftrightarrow A$ $\Gamma^6 \leftrightarrow \Gamma^6$	$A_{\pm} \leftrightarrow A_{\pm}$ $\Gamma_{\pm}^6 \leftrightarrow \Gamma_{\pm}^6$	$[(l_1 l_2 + m_1 m_2) + \lambda_1 n_1 n_2 + \lambda_2 (l_1 m_2 - l_2 m_1)]^2 \equiv A(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \leftrightarrow E$ $(\Gamma^4 \Gamma^5) \leftrightarrow \Gamma^6$	$A_{\pm} \leftrightarrow E_{\pm}$ $(\Gamma_{\pm}^4 \Gamma_{\pm}^5) \leftrightarrow \Gamma_{\pm}^6$	$[(n_1 l_2 + n_2 l_1) + \lambda_3 (l_1 m_2 + l_2 m_1) + \lambda_4 (l_1 l_2 - m_1 m_2) + \lambda_5 (m_1 n_2 - m_2 n_1) + \lambda_6 (n_1 l_2 - n_2 l_1)]^2 + [(m_1 n_2 + m_2 n_1) + \lambda_3 (l_1 l_2 - m_1 m_2) - \lambda_4 (l_1 m_2 + l_2 m_1) + \lambda_5 (n_1 l_2 - n_2 l_1) - \lambda_6 (m_1 n_2 - m_2 n_1)]^2 \equiv E(\hat{\epsilon}_1, \hat{\epsilon}_2)$
$E \leftrightarrow E$ $(\Gamma^4 \Gamma^5) \leftrightarrow (\Gamma^4 \Gamma^5)$	$E_{\pm} \leftrightarrow E_{\pm}$ $(\Gamma_{\pm}^4 \Gamma_{\pm}^5) \leftrightarrow (\Gamma_{\pm}^4 \Gamma_{\pm}^5)$	$A(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-1 (Contd.)

D_3, C_{3v}	D_{3d}	
$A_1 \longleftrightarrow A_1$ $A_2 \longleftrightarrow A_2$	$A_{1\pm} \longleftrightarrow A_{1\pm}$ $A_{2\pm} \longleftrightarrow A_{2\pm}$	$[(l_1 l_2 + m_1 m_2) + \lambda_1 n_1 n_2]^2 \equiv A_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \longleftrightarrow A_2$	$A_{1\pm} \longleftrightarrow A_{2\pm}$	$(l_1 m_2 - l_2 m_1)^2 \equiv A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \longleftrightarrow E$ $A_2 \longleftrightarrow E$ $\Gamma^4 \longleftrightarrow (\Gamma^5 \Gamma^6)$	$A_{1\pm} \longleftrightarrow E_{\pm}$ $A_{2\pm} \longleftrightarrow E_{\pm}$ $\Gamma_{\pm}^4 \longleftrightarrow (\Gamma_{\pm}^5 \Gamma_{\pm}^6)$	$[(m_1 n_2 - m_2 n_1) + \lambda_2 (m_1 n_2 + m_2 n_1) + \lambda_3 (l_1 l_2 - m_1 m_2)]^2$ $+ [(n_1 l_2 - n_2 l_1) - \lambda_2 (n_1 l_2 + n_2 l_1) - \lambda_3 (l_1 m_2 + l_2 m_1)]^2$ $\equiv E(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$E \longleftrightarrow E$ $\Gamma^4 \longleftrightarrow \Gamma^4$	$E_{\pm} \longleftrightarrow E_{\pm}$ $\Gamma_{\pm}^4 \longleftrightarrow \Gamma_{\pm}^4$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(\Gamma^5 \Gamma^6) \longleftrightarrow (\Gamma^5 \Gamma^6)$	$(\Gamma_{\pm}^5 \Gamma_{\pm}^6) \longleftrightarrow (\Gamma_{\pm}^5 \Gamma_{\pm}^6)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-1 (Contd.)

C_6	C_{3h}	C_{6h}	
$A \longleftrightarrow A$ $B \longleftrightarrow B$	$A' \longleftrightarrow A'$ $A'' \longleftrightarrow A''$	$A_{\pm} \longleftrightarrow A_{\pm}$ $B_{\pm} \longleftrightarrow B_{\pm}$	$\left[(l_1 l_2 + m_1 m_2) + \lambda_1 n_1 n_2 + \lambda_2 (l_1 m_2 - l_2 m_1) \right]^2$ $\equiv A(\epsilon_1 \epsilon_2)$
$A \longleftrightarrow B$	$A' \longleftrightarrow A''$	$A_{\pm} \longleftrightarrow B_{\pm}$	forbidden
$A \longleftrightarrow E'$ $B \longleftrightarrow E''$ $E' \longleftrightarrow E''$	$A' \longleftrightarrow E''$ $A'' \longleftrightarrow E'$ $E' \longleftrightarrow E''$	$A_{\pm} \longleftrightarrow E'_{\pm}$ $B_{\pm} \longleftrightarrow E''_{\pm}$ $E'_{\pm} \longleftrightarrow E''_{\pm}$	$\left[(n_1 l_2 + n_2 l_1) + \lambda_3 (m_1 n_2 - m_2 n_1) + \lambda_4 (n_1 l_2 - n_2 l_1) \right]^2$ $+ \left[(m_1 n_2 + m_2 n_1) + \lambda_3 (n_1 l_2 - n_2 l_1) - \lambda_4 (m_1 n_2 - m_2 n_1) \right]^2$ $\equiv E'(\epsilon_1, \epsilon_2)$
$A \longleftrightarrow E''$ $B \longleftrightarrow E'$	$A' \longleftrightarrow E'$ $A'' \longleftrightarrow E''$	$A_{\pm} \longleftrightarrow E''_{\pm}$ $B_{\pm} \longleftrightarrow E'_{\pm}$	$(1 - n_1^2)(1 - n_2^2) \equiv E'(\epsilon_1 \epsilon_2)$
$E' \longleftrightarrow E'$ $E'' \longleftrightarrow E''$	$E' \longleftrightarrow E'$ $E'' \longleftrightarrow E''$	$E'_{\pm} \longleftrightarrow E'_{\pm}$ $E''_{\pm} \longleftrightarrow E''_{\pm}$	$A(\epsilon_1 \epsilon_2) + cE''(\epsilon_1 \epsilon_2)$

Table 3-1 (Contd.)

$(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^7 \Gamma^8)$ $(\Gamma^9 \Gamma^{10}) \leftrightarrow (\Gamma^9 \Gamma^{10})$	$(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^7 \Gamma^8)$ $(\Gamma^9 \Gamma^{10}) \leftrightarrow (\Gamma^9 \Gamma^{10})$	$(\Gamma_{\pm}^7 \Gamma_{\pm}^8) \leftrightarrow (\Gamma_{\pm}^7 \Gamma_{\pm}^8)$ $(\Gamma_{\pm}^9 \Gamma_{\pm}^{10}) \leftrightarrow (\Gamma_{\pm}^9 \Gamma_{\pm}^{10})$	$A(\hat{\epsilon}_1, \hat{\epsilon}_2) + cE'(\hat{\epsilon}_1, \hat{\epsilon}_2)$
$(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^9 \Gamma^{10})$	$(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^9 \Gamma^{10})$	$(\Gamma_{\pm}^7 \Gamma_{\pm}^8) \leftrightarrow (\Gamma_{\pm}^9 \Gamma_{\pm}^{10})$	$E''(\hat{\epsilon}_1, \hat{\epsilon}_2)$
$(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^{11} \Gamma^{12})$ $(\Gamma^9 \Gamma^{10}) \leftrightarrow (\Gamma^{11} \Gamma^{12})$	$(\Gamma^7 \Gamma^8) \leftrightarrow (\Gamma^{11} \Gamma^{12})$ $(\Gamma^9 \Gamma^{10}) \leftrightarrow (\Gamma^{11} \Gamma^{12})$	$(\Gamma_{\pm}^7 \Gamma_{\pm}^8) \leftrightarrow (\Gamma_{\pm}^{11} \Gamma_{\pm}^{12})$ $(\Gamma_{\pm}^9 \Gamma_{\pm}^{10}) \leftrightarrow (\Gamma_{\pm}^{11} \Gamma_{\pm}^{12})$	$E'(\hat{\epsilon}_1, \hat{\epsilon}_2) + cE''(\hat{\epsilon}_1, \hat{\epsilon}_2)$
$(\Gamma^{11} \Gamma^{12}) \leftrightarrow (\Gamma^{11} \Gamma^{12})$	$(\Gamma^{11} \Gamma^{12}) \leftrightarrow (\Gamma^{11} \Gamma^{12})$	$(\Gamma_{\pm}^{11} \Gamma_{\pm}^{12}) \leftrightarrow (\Gamma_{\pm}^{11} \Gamma_{\pm}^{12})$	$A(\hat{\epsilon}_1, \hat{\epsilon}_2)$

D_6, C_{6v}	D_{3h}	D_{6h}	
$A_1 \leftrightarrow A_1$ $A_2 \leftrightarrow A_2$ $B_1 \leftrightarrow B_1$ $B_2 \leftrightarrow B_2$	$A'_1 \leftrightarrow A'_1$ $A'_2 \leftrightarrow A'_2$ $A''_1 \leftrightarrow A''_1$ $A''_2 \leftrightarrow A''_2$	$A_{1\pm} \leftrightarrow A_{1\pm}$ $A_{2\pm} \leftrightarrow A_{2\pm}$ $B_{1\pm} \leftrightarrow B_{1\pm}$ $B_{2\pm} \leftrightarrow B_{2\pm}$	$[(l_1 l_2 + m_1 m_2) + \lambda_1 n_1 n_2]^2 \equiv A_1(\hat{\epsilon}_1, \hat{\epsilon}_2)$
$A_1 \leftrightarrow A_2$ $B_1 \leftrightarrow B_2$	$A'_1 \leftrightarrow A'_2$ $A''_1 \leftrightarrow A''_2$	$A_{1\pm} \leftrightarrow A_{2\pm}$ $B_{1\pm} \leftrightarrow B_{2\pm}$	$(l_1 m_2 - l_2 m_1)^2 \equiv A_2(\hat{\epsilon}_1, \hat{\epsilon}_2)$

Table 3-1 (Contd.)

$A_1 \leftrightarrow B_1$ $A_1 \leftrightarrow B_2$ $A_2 \leftrightarrow B_1$ $A_2 \leftrightarrow B_2$	$A'_1 \leftrightarrow A''_1$ $A'_1 \leftrightarrow A''_2$ $A'_2 \leftrightarrow A''_1$ $A'_2 \leftrightarrow A''_2$	$A \leftrightarrow B_{1\pm 1\pm}$ $A \leftrightarrow B_{1\pm 2\pm}$ $A \leftrightarrow B_{2\pm 1\pm}$ $A \leftrightarrow B_{2\pm 2\pm}$	forbidden
$A_1 \leftrightarrow E_1$ $A_2 \leftrightarrow E_1$ $B_1 \leftrightarrow E_2$ $B_2 \leftrightarrow E_2$ $E_1 \leftrightarrow E_2$	$A'_1 \leftrightarrow E''_1$ $A'_2 \leftrightarrow E''_2$ $A''_2 \leftrightarrow E'_1$ $A''_1 \leftrightarrow E'_1$ $E'_1 \leftrightarrow E''_2$	$A \leftrightarrow E_{1\pm 1\pm}$ $A \leftrightarrow E_{2\pm 1\pm}$ $B \leftrightarrow E_{1\pm 2\pm}$ $B \leftrightarrow E_{2\pm 2\pm}$ $E \leftrightarrow E_{1\pm 2\pm}$	$\begin{aligned} & \left[(m_{12} n_{21} - m_{21} n_{12}) + \lambda_2 (m_{12} n_{21} + m_{21} n_{12}) \right]^2 \\ & + \left[(n_{12} l_{21} - n_{21} l_{12}) - \lambda_2 (n_{12} l_{21} + n_{21} l_{12}) \right]^2 \\ & \equiv E_1 (\hat{\epsilon}_1 \hat{\epsilon}_2) \end{aligned}$
$A_1 \leftrightarrow E_2$ $A_2 \leftrightarrow E_2$ $B_1 \leftrightarrow E_1$ $B_2 \leftrightarrow E_1$	$A'_1 \leftrightarrow E'_1$ $A'_2 \leftrightarrow E'_1$ $A''_2 \leftrightarrow E''_1$ $A''_1 \leftrightarrow E''_1$	$A \leftrightarrow E_{1\pm 2\pm}$ $A \leftrightarrow E_{2\pm 2\pm}$ $B \leftrightarrow E_{1\pm 1\pm}$ $B \leftrightarrow E_{2\pm 1\pm}$	$(1 - n_1^2)(1 - n_2^2) \equiv E_2 (\hat{\epsilon}_1 \hat{\epsilon}_2)$
$E_1 \leftrightarrow E_1$ $E_2 \leftrightarrow E_2$	$E'' \leftrightarrow E''$ $E' \leftrightarrow E'$	$E \leftrightarrow E_{1\pm 1\pm}$ $E \leftrightarrow E_{2\pm 2\pm}$	$A_1 (\hat{\epsilon}_1 \hat{\epsilon}_2) + c_{12} A_2 (\hat{\epsilon}_1 \hat{\epsilon}_2) + c_{22} E_2 (\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-1 (Contd.)

$\Gamma^7 \longleftrightarrow \Gamma^7$ $\Gamma^8 \longleftrightarrow \Gamma^8$	$\Gamma^7 \longleftrightarrow \Gamma^7$ $\Gamma^8 \longleftrightarrow \Gamma^8$	$\Gamma_{\pm}^7 \longleftrightarrow \Gamma_{\pm}^7$ $\Gamma_{\pm}^8 \longleftrightarrow \Gamma_{\pm}^8$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^7 \longleftrightarrow \Gamma^8$	$\Gamma^7 \longleftrightarrow \Gamma^8$	$\Gamma_{\pm}^7 \longleftrightarrow \Gamma_{\pm}^8$	$E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^7 \longleftrightarrow \Gamma^9$ $\Gamma^8 \longleftrightarrow \Gamma^9$	$\Gamma^7 \longleftrightarrow \Gamma^9$ $\Gamma^8 \longleftrightarrow \Gamma^9$	$\Gamma_{\pm}^7 \longleftrightarrow \Gamma_{\pm}^9$ $\Gamma_{\pm}^8 \longleftrightarrow \Gamma_{\pm}^9$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^9 \longleftrightarrow \Gamma^9$	$\Gamma^9 \longleftrightarrow \Gamma^9$	$\Gamma_{\pm}^9 \longleftrightarrow \Gamma_{\pm}^9$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

T	T_h	
$A \longleftrightarrow A$	$A_{\pm} \longleftrightarrow A_{\pm}$	$(l_1 l_2 + m_1 m_2 + n_1 n_2)^2 = (\hat{\epsilon}_1 \cdot \hat{\epsilon}_2)^2 \equiv A(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \longleftrightarrow E$	$A_{\pm} \longleftrightarrow E_{\pm}$	$(l_1^2 l_2^2 + m_1^2 m_2^2 + n_1^2 n_2^2) - (l_1 l_2 m_1 m_2 + m_1 m_2 n_1 n_2 + n_1 n_2 l_1 l_2) \equiv E(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A \longleftrightarrow T$ $E \longleftrightarrow T$	$A_{\pm} \longleftrightarrow T_{\pm}$ $E_{\pm} \longleftrightarrow T_{\pm}$	$[(m_1 n_2 - m_2 n_1) + \lambda(m_1 n_2 + m_2 n_1)]^2 + [(n_1 l_2 - n_2 l_1) + \lambda(n_1 l_2 + n_2 l_1)]^2 + [(l_1 m_2 - l_2 m_1) + \lambda(l_1 m_2 + l_2 m_1)]^2 \equiv T(\hat{\epsilon}_1 \hat{\epsilon}_2, \lambda)$

Table 3-1 (Contd.)

$E \longleftrightarrow E$	$E_{\pm} \longleftrightarrow E_{\pm}$	$A(\hat{e}_1 \hat{e}_2) + cE(\hat{e}_1 \hat{e}_2)$
$T \longleftrightarrow T$	$T_{\pm} \longleftrightarrow T_{\pm}$	$A(\hat{e}_1 \hat{e}_2) + c_1 E(\hat{e}_1 \hat{e}_2) + c_2 T(\hat{e}_1 \hat{e}_2, \lambda) + c_3 T(\hat{e}_1 \hat{e}_2, \lambda')$
$\Gamma^5 \longleftrightarrow \Gamma^5$	$\Gamma_{\pm}^5 \longleftrightarrow \Gamma_{\pm}^5$	$A(\hat{e}_1 \hat{e}_2) + cT(\hat{e}_1 \hat{e}_2, \lambda)$
$\Gamma^5 \longleftrightarrow (\Gamma^6 \Gamma^7)$	$\Gamma_{\pm}^5 \longleftrightarrow (\Gamma_{\pm}^6 \Gamma_{\pm}^7)$	$E(\hat{e}_1 \hat{e}_2) + cT(\hat{e}_1 \hat{e}_2, \lambda)$
$(\Gamma^6 \Gamma^7) \longleftrightarrow (\Gamma^6 \Gamma^7)$	$(\Gamma_{\pm}^6 \Gamma_{\pm}^7) \longleftrightarrow (\Gamma_{\pm}^6 \Gamma_{\pm}^7)$	$A(\hat{e}_1 \hat{e}_2) + c_1 E(\hat{e}_1 \hat{e}_2) + c_2 T(\hat{e}_1 \hat{e}_2, \lambda)$

O, T_d	O_h	
$A_1 \longleftrightarrow A_1$ $A_2 \longleftrightarrow A_2$	$A_{1\pm} \longleftrightarrow A_{1\pm}$ $A_{2\pm} \longleftrightarrow A_{2\pm}$	$(l_1 l_2 + m_1 m_2 + n_1 n_2)^2 \equiv A_1(\hat{e}_1 \hat{e}_2)$
$A_1 \longleftrightarrow A_2$	$A_{1\pm} \longleftrightarrow A_{2\pm}$	forbidden
$A_1 \longleftrightarrow E$ $A_2 \longleftrightarrow E$	$A_{1\pm} \longleftrightarrow E_{\pm}$ $A_{2\pm} \longleftrightarrow E_{\pm}$	$(l_1^2 l_2^2 + m_1^2 m_2^2 + n_1^2 n_2^2) - (l_1 l_2 m_1 m_2 + m_1 m_2 n_1 n_2 + n_1 n_2 l_1 l_2) \equiv E(\hat{e}_1 \hat{e}_2)$
$A_1 \longleftrightarrow T_1$ $A_2 \longleftrightarrow T_2$	$A_{1\pm} \longleftrightarrow T_{1\pm}$ $A_{2\pm} \longleftrightarrow T_{2\pm}$	$(m_1 n_2 - m_2 n_1)^2 + (l_1 n_2 - l_2 n_1)^2 + (l_1 m_2 - l_2 m_1)^2 = (\hat{e}_1 \times \hat{e}_2)^2 \equiv T_1(\hat{e}_1 \hat{e}_2)$

Table 3-1 (Contd.)

$A_1 \longleftrightarrow T_2$ $A_2 \longleftrightarrow T_1$	$A_{1\pm} \longleftrightarrow T_{2\pm}$ $A_{2\pm} \longleftrightarrow T_{1\pm}$	$(l_1 m_2 + l_2 m_1)^2 + (m_1 n_2 + m_2 n_1)^2$ $+ (l_1 n_2 + l_2 n_1)^2 \equiv T_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$E \longleftrightarrow E$	$E_{\pm} \longleftrightarrow E_{\pm}$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$E \longleftrightarrow T_1$ $E \longleftrightarrow T_2$	$E_{\pm} \longleftrightarrow T_{1\pm}$ $E_{\pm} \longleftrightarrow T_{2\pm}$	$T_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cT_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$T_1 \longleftrightarrow T_1$ $T_2 \longleftrightarrow T_2$	$T_{1\pm} \longleftrightarrow T_{1\pm}$ $T_{2\pm} \longleftrightarrow T_{2\pm}$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 T_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 T_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$T_1 \longleftrightarrow T_2$	$T_{1\pm} \longleftrightarrow T_{2\pm}$	$E(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 T_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 T_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^6 \longleftrightarrow \Gamma^6$ $\Gamma^7 \longleftrightarrow \Gamma^7$	$\Gamma_{\pm}^6 \longleftrightarrow \Gamma_{\pm}^6$ $\Gamma_{\pm}^7 \longleftrightarrow \Gamma_{\pm}^7$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cT_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^6 \longleftrightarrow \Gamma^7$	$\Gamma_{\pm}^6 \longleftrightarrow \Gamma_{\pm}^7$	$T_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^6 \longleftrightarrow \Gamma^8$ $\Gamma^7 \longleftrightarrow \Gamma^8$	$\Gamma_{\pm}^6 \longleftrightarrow \Gamma_{\pm}^8$ $\Gamma_{\pm}^7 \longleftrightarrow \Gamma_{\pm}^8$	$E(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 T_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 T_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma^8 \longleftrightarrow \Gamma^8$	$\Gamma_{\pm}^8 \longleftrightarrow \Gamma_{\pm}^8$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 T_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 T_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Fig.3-1. Definition of axes

Fig.3-2. Definition of axes

Fig.3-3. Definition of axes

T , T_d , and T_h

O and O_h

Fig.3-4. Definition of axes

C. Transitions at Non-central Symmetry Points

It often happens that energy band minima occur at points in the Brillouin zone other than the Γ -point, and these minima are most frequently found at points having higher symmetry than that of a general point in the zone.⁴⁰ It is therefore useful to determine the angular dependence of two-photon absorption for transitions taking place at these symmetry points.

Perhaps the most direct approach to the problem is to note that $|C_i(k_0)\rangle$ and $|V_j(k_0)\rangle$ transform according to irreducible representations, say $D^{\lambda k_0}$ and $D^{\nu k_0}$, of the space group of the crystal.⁴³ Then we could apply Eq.3-3 directly and decompose $D^{\lambda k_0} \times D^{\nu k_0}$ into irreducible representations of the space group. Since $\hat{E}_1 \cdot \vec{T} \cdot \hat{E}_2$ transforms entirely within the set of space group representations for which $\vec{k} = 0$, we would require only the knowledge of which point group representations are contained in $D^{\lambda k_0} \times D^{\nu k_0}$. Unfortunately the Kronecker multiplication properties of space group representations are not accessible. There is an alternative procedure, however, which requires only the knowledge of the representations of the group of the wave vector.

When an element of the space group operates on $|V_j(k_0)\rangle$, it either produces a state having wave vector $\vec{k}_0$ or it generates a state with wave vector in the star⁴⁰ of $\vec{k}_0$. Let us choose from the space group a set of N

elements $\{P(R)\}$ which generates the N-pointed star of $\vec{k}_0$. Thus we can write⁴³

$$P(R) |V_j(k_0)\rangle = |V_j(Rk_0)\rangle,$$

and hence

$$\begin{aligned} & \sum_{k'_0, ij} \left| \langle C_i(k'_0) | \hat{E}_1 \cdot \vec{T} \cdot \hat{E}_2 | V_j(k'_0) \rangle \right|^2 \\ &= \sum_{R, ij} \left| \langle C_i(Rk_0) | \hat{E}_1 \cdot \vec{T} \cdot \hat{E}_2 | V_j(Rk_0) \rangle \right|^2 \\ &= \sum_{R, ij} \left| \langle C_i(k_0) | \hat{E}_1 \cdot [P^{-1}(R) \vec{T} P(R)] \cdot \hat{E}_2 | V_j(k_0) \rangle \right|^2 \\ &= \sum_{R=1}^N \left\{ \sum \left| \langle C_i(k_0) | [P(R) \hat{E}_1] \cdot \vec{T} \cdot [P(R) \hat{E}_2] | V_j(k_0) \rangle \right|^2 \right\} \quad (3-7) \end{aligned}$$

The procedure, then, is to find the angular function for a transition at $\vec{k}_0$ between states belonging to arbitrary irreducible representations of the group of $\vec{k}_0$ and then to add for each $P(R)$ a similar function with $\hat{E}_1$ and $\hat{E}_2$ replaced by $P(R)\hat{E}_1$ and $P(R)\hat{E}_2$.

The angular dependence functions for transitions of the type $d' \rightarrow d^\lambda$, where d^λ is a representation of the group of the wave vector, at non-central symmetry points for simple and face-centered cubic crystals and for zinc blende and diamond structures, have been calculated by Inoue and Toyozawa.¹¹ We can obtain the angular dependence for more general $d'' \rightarrow d^\lambda$ transitions from Inoue and

Toyozawa's functions with the use of Table 3-1. For example, the group of Δ for a face-centered cubic crystal is C_{4v} . The angular function for $\Delta^{\nu} \rightarrow \Delta^{\lambda}$ is that given by $\Gamma^{\nu} \rightarrow \Gamma^{\lambda}$ of C_{4v} in Table 3-1 with the $\gamma^{\mu}(\hat{e}_1, \hat{e}_2)$ replaced by the $\Delta^{\mu}(\hat{e}_1, \hat{e}_2)$ in the table of Inoue and Toyozawa. For reference their table is reproduced in Appendix E, which also contains the Brillouin zones and definitions of the labels of symmetry lines and points for zinc blende, diamond, face-centered cubic, body-centered cubic and simple cubic structures (Fig.E-1).

The angular functions for two more space groups have been calculated and are given below. These are for the hexagonal close-packed structure (space group D_{6h}^4) and the wurtzite structure (C_{6v}^4). Wurtzite differs from HCP in that it does not contain a reflection plane perpendicular to the c axis. Both groups contain point operations associated with fractional lattice translations. Much of the general theory of space group representations has been given by Seitz.⁴⁴ Extensive use of his results was made by Bouckaert, Smoluchowski and Wigner⁴⁰ for some simple crystal structures. Herring⁴⁵ extended the method of space group reduction to more complicated groups, and this was extended further by Elliott⁴⁶ to include the effects of spin-orbit coupling. The character tables for the hexagonal close-packed structure were derived by Herring⁴⁵ and Elliott⁴⁶ and we use their notation. For wurtzite we

use the notation of Glasser⁴⁷ and of Casella.⁴⁸ The Brillouin zone and definition of symmetry lines and points are given in Fig.3-5.

A comment should be made about the calculation of the angular functions. The group of a wave vector other than $\vec{k} = 0$ is usually rather complicated, and it is rarely isomorphic (or homomorphic) to one of the point groups. It is necessary to determine which representations of the group of $\vec{k}$ have basis functions contained in the operator $\vec{T}$; that is, to which representations do the components of $\vec{T}$ belong. This is easily accomplished if one notes that frequently the entire character table is not given for the group of $\vec{k}$. Consider, for example, the character table for the group of A in HCP. The single-valued representations A_1 , A_2 and A_3 reported by Herring have dimensionalities 2, 2 and 4, respectively, as do the double-valued representations A_4 , A_5 and A_6 calculated by Elliott. These, obviously, cannot constitute the entire character table for the double group of A, because they do not contain the identity representation; they are only the representations to which a Bloch function of wave vector $\vec{k}_A$ can belong. The entire group of A is given in Table 3-2. The representations A_μ are those to which the tensor components belong. Just how the tensor components are related to the representations becomes apparent when it is noticed that the representations A_μ are those of the point group

Table 3-2: Complete character table for the double group of A.

	96	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	a_{16}	a_{17}	a_{18}	A_1	A_2	A_3	A_4	A_5	A_6
$(\varepsilon 0)$	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	4	2	2	4
$(\bar{\varepsilon} 0)$	1	1	1	1	1	1	1	1	1	2	2	2	2	-2	-2	-2	-2	-2	-2	2	2	4	-2	-2	-4
(εt_i)	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	-2	-2	-4	-2	-2	-4
$(\bar{\varepsilon} t_i)$	1	1	1	1	1	1	1	1	1	2	2	2	2	-2	-2	-2	-2	-2	-2	-2	-2	-4	2	2	4
$(\delta_6, \delta_6' \tau, \tau+t)$	4	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	$\sqrt{3}$	$\sqrt{3}$	$-\sqrt{3}$	$-\sqrt{3}$	0	0	0	0	0	0	0	0
$(\bar{\delta}_6, \bar{\delta}_6' \tau, \tau+t)$	4	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	$-\sqrt{3}$	$-\sqrt{3}$	$\sqrt{3}$	$\sqrt{3}$	0	0	0	0	0	0	0	0
$(\delta_3, \delta_3' 0)$	2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-2	-2	2	2	-2	-2	-2	2
$(\bar{\delta}_3, \bar{\delta}_3' 0)$	2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	2	2	2	2	-2	-2	-2	-2
$(\delta_3, \delta_3' t_i)$	2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-2	-2	-2	-2	2	2	2	-2
$(\bar{\delta}_3, \bar{\delta}_3' t_i)$	2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	2	2	-2	-2	2	2	-2	-2
$(\delta_2, \delta_2' \tau, \tau+t_i)$	4	1	1	1	1	-1	-1	-1	-1	2	2	-2	-2	0	0	0	0	0	0	0	0	0	0	0	0
$(\delta_{2i}' \tau), (\bar{\delta}_{2i}' \tau+t_i)$	6	1	1	-1	-1	1	1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	2i	-2i	0
$(\bar{\delta}_{2i}' \tau), (\delta_{2i}' \tau+t_i)$	6	1	1	-1	-1	1	1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	-2i	2i	0
$(\delta_{2i}'', \bar{\delta}_{2i}'' \tau, \tau+t_i)$	12	1	1	-1	-1	-1	-1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(\bar{1} \tau, \tau+t_i)$	2	1	-1	-1	-1	1	-1	1	-1	2	-2	2	-2	0	0	0	0	0	0	0	0	0	0	0	0
$(\bar{1} \tau, \tau+t_i)$	2	1	-1	1	-1	1	-1	1	-1	2	-2	2	-2	2	-2	2	-2	2	-2	0	0	0	0	0	0
$(\sigma_3, \sigma_3' 0, t_i)$	4	1	-1	1	-1	-1	1	-1	1	-1	1	-1	-2	2	-2	+2	-2	2	2	0	0	0	0	0	0
$(\bar{\sigma}_3, \bar{\sigma}_3' 0, t_i)$	4	1	-1	1	-1	-1	1	-1	1	-1	1	-1	-2	2	-2	-2	2	2	0	0	0	0	0	0	0
$(\sigma_6, \sigma_6' \tau, \tau+t_i)$	4	1	-1	1	-1	-1	1	-1	1	-1	1	-1	+1	$-\sqrt{3}$	$\sqrt{3}$	$\sqrt{3}$	$-\sqrt{3}$	0	0	0	0	0	0	0	0
$(\bar{\sigma}_6, \bar{\sigma}_6' \tau, \tau+t_i)$	4	1	-1	1	-1	-1	1	-1	1	-1	1	-1	+1	$-\sqrt{3}$	$\sqrt{3}$	$\sqrt{3}$	$-\sqrt{3}$	0	0	0	0	0	0	0	0
$(\varepsilon, \bar{\varepsilon} 0, t_i)$	4	1	-1	1	-1	-1	1	-1	1	2	-2	-2	2	-1	1	-1	1	2	-2	0	0	0	0	0	0
$(\varepsilon_i, \bar{\varepsilon}_i' 0)$	6	1	-1	-1	1	1	-1	-1	1	0	0	0	0	0	0	0	0	0	0	2	-2	0	0	0	0
$(\varepsilon_i, \bar{\varepsilon}_i' t_i)$	6	1	-1	-1	1	1	-1	-1	1	0	0	0	0	0	0	0	0	0	0	-2	2	0	0	0	0
$(\varepsilon_i'', \bar{\varepsilon}_i'' \tau, \tau+t_i)$	12	1	-1	-1	1	1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

C_{6v} , the properties of which are well known. In effect, then, what we must do to calculate the angular functions for $A^\nu \rightarrow A^\lambda$ is to decompose $A^\nu \times A^\lambda$ into irreducible representations A_μ . The angular dependence is given by $\sum_\mu a_\mu(\hat{e}_1, \hat{e}_2)$ where the $a_\mu(\hat{e}_1, \hat{e}_2)$ are the functions defined in Table 3-1 for C_{6v} , and μ runs over the representations contained in $A^\nu \times A^\lambda$. For a point of lower symmetry than A , that is, a point having more than one point in its star, we must sum over R as in Eq.3-7.

The angular functions for all possible transitions at the symmetry points Γ , K , A , H , M and L and on lines Δ , Σ , U , P , T and S are given for HCP in Table 3-3 and for wurtzite in Table 3-4.

Table 3-3

Angular dependence functions for hexagonal close-packed structure. Notation used is that of Herring (Ref. 45) for the single-valued representations and Elliott (Ref. 46) for the double-valued representations.

Γ	K	Δ	
$\Gamma_1^{\pm} \leftrightarrow \Gamma_1^{\pm}$	$K_1 \leftrightarrow K_1$	$\Delta_1 \leftrightarrow \Delta_1$	$[(l_1 l_2 + m_1 m_2) + \lambda_1 n_1 n_2]^2$ $\equiv A_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_2^{\pm} \leftrightarrow \Gamma_2^{\pm}$	$K_2 \leftrightarrow K_2$	$\Delta_2 \leftrightarrow \Delta_2$	
$\Gamma_3^{\pm} \leftrightarrow \Gamma_3^{\pm}$	$K_3 \leftrightarrow K_3$	$\Delta_3 \leftrightarrow \Delta_3$	
$\Gamma_4^{\pm} \leftrightarrow \Gamma_4^{\pm}$	$K_4 \leftrightarrow K_4$	$\Delta_4 \leftrightarrow \Delta_4$	
$\Gamma_1^{\pm} \leftrightarrow \Gamma_2^{\pm}$	$K_1 \leftrightarrow K_3$	$\Delta_1 \leftrightarrow \Delta_3$	$(l_1 m_2 + l_2 m_1)^2 \equiv A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_3^{\pm} \leftrightarrow \Gamma_4^{\pm}$	$K_2 \leftrightarrow K_4$	$\Delta_2 \leftrightarrow \Delta_4$	
$\Gamma_1^{\pm} \leftrightarrow \Gamma_3^{\pm}$	$K_1 \leftrightarrow K_2$	$\Delta_1 \leftrightarrow \Delta_2$	forbidden
$\Gamma_1^{\pm} \leftrightarrow \Gamma_4^{\pm}$	$K_1 \leftrightarrow K_4$	$\Delta_1 \leftrightarrow \Delta_4$	
$\Gamma_2^{\pm} \leftrightarrow \Gamma_3^{\pm}$	$K_3 \leftrightarrow K_2$	$\Delta_3 \leftrightarrow \Delta_2$	
$\Gamma_2^{\pm} \leftrightarrow \Gamma_4^{\pm}$	$K_3 \leftrightarrow K_4$	$\Delta_3 \leftrightarrow \Delta_4$	

Table 3-3 (Contd.)

Γ	K	Δ	
$\Gamma_1^{\pm} \leftrightarrow \Gamma_6^{\pm}$	$K_1 \leftrightarrow K_6$	$\Delta_1 \leftrightarrow \Delta_6$	$\begin{aligned} & [(m_1 n_2 - m_2 n_1) + \lambda_2 (m_1 n_2 + m_2 n_1)]^2 \\ & [(n_1 l_2 - n_2 l_1) - \lambda_2 (n_1 l_2 + n_2 l_1)]^2 \\ & \equiv E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) \end{aligned}$
$\Gamma_2^{\pm} \leftrightarrow \Gamma_6^{\pm}$	$K_3 \leftrightarrow K_6$	$\Delta_3 \leftrightarrow \Delta_6$	
$\Gamma_3^{\pm} \leftrightarrow \Gamma_5^{\pm}$	$K_2 \leftrightarrow K_5$	$\Delta_2 \leftrightarrow \Delta_5$	
$\Gamma_4^{\pm} \leftrightarrow \Gamma_5^{\pm}$	$K_4 \leftrightarrow K_5$	$\Delta_4 \leftrightarrow \Delta_5$	
$\Gamma_5^{\pm} \leftrightarrow \Gamma_6^{\pm}$	$K_5 \leftrightarrow K_6$	$\Delta_5 \leftrightarrow \Delta_6$	
$\Gamma_1^{\pm} \leftrightarrow \Gamma_5^{\pm}$	$K_1 \leftrightarrow K_5$	$\Delta_1 \leftrightarrow \Delta_5$	$(1 - n_1^2)(1 - n_2^2) \equiv E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_2^{\pm} \leftrightarrow \Gamma_5^{\pm}$	$K_3 \leftrightarrow K_5$	$\Delta_3 \leftrightarrow \Delta_5$	
$\Gamma_3^{\pm} \leftrightarrow \Gamma_6^{\pm}$	$K_2 \leftrightarrow K_6$	$\Delta_2 \leftrightarrow \Delta_6$	
$\Gamma_4^{\pm} \leftrightarrow \Gamma_6^{\pm}$	$K_4 \leftrightarrow K_6$	$\Delta_4 \leftrightarrow \Delta_6$	
$\Gamma_5^{\pm} \leftrightarrow \Gamma_5^{\pm}$	$K_5 \leftrightarrow K_5$	$\Delta_5 \leftrightarrow \Delta_5$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_6^{\pm} \leftrightarrow \Gamma_6^{\pm}$	$K_6 \leftrightarrow K_6$	$\Delta_6 \leftrightarrow \Delta_6$	
$\Gamma_7^{\pm} \leftrightarrow \Gamma_7^{\pm}$	$K_7 \leftrightarrow K_7$	$\Delta_7 \leftrightarrow \Delta_7$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_8^{\pm} \leftrightarrow \Gamma_8^{\pm}$	$K_8 \leftrightarrow K_8$	$\Delta_8 \leftrightarrow \Delta_8$	

Table 3-3 (Contd.)

Γ	K	Δ	
$\Gamma_7^{\pm} \leftrightarrow \Gamma_8^{\pm}$	$K_7 \leftrightarrow K_8$	$\Delta_7 \leftrightarrow \Delta_8$	$E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_7^{\pm} \leftrightarrow \Gamma_9^{\pm}$ $\Gamma_8^{\pm} \leftrightarrow \Gamma_9^{\pm}$	$K_7 \leftrightarrow K_9$ $K_8 \leftrightarrow K_9$	$\Delta_7 \leftrightarrow \Delta_9$ $\Delta_8 \leftrightarrow \Delta_9$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_9^{\pm} \leftrightarrow \Gamma_9^{\pm}$	$K_9 \leftrightarrow K_9$	$\Delta_9 \leftrightarrow \Delta_9$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cA_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

A	H	
$A_1 \leftrightarrow A_1$ $A_2 \leftrightarrow A_2$	$(H_5 H_7) \leftrightarrow (H_5 H_7)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_1 \leftrightarrow A_2$		$A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(A_4 A_5) \leftrightarrow (A_4 A_5)$	$H_1 \leftrightarrow H_1$ $(H_4 H_6) \leftrightarrow (H_4 H_6)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cA_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
	$H_8 \leftrightarrow H_9$ $(H_4 H_6) \leftrightarrow H_8$ $(H_5 H_7) \leftrightarrow H_9$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-3 (Contd.)

A	H	
	$H_2 \leftrightarrow H_3$ $(H_4 H_6) \leftrightarrow H_9$ $(H_5 H_7) \leftrightarrow H_8$	$E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(A_4 A_5) \leftrightarrow A_6$ $A_1 \leftrightarrow A_3$ $A_2 \leftrightarrow A_3$	$H_1 \leftrightarrow H_2$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
	$H_2 \leftrightarrow H_2$ $H_8 \leftrightarrow H_8$ $H_9 \leftrightarrow H_9$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$A_3 \leftrightarrow A_3$ $A_6 \leftrightarrow A_6$		$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
	$(H_4 H_6) \leftrightarrow (H_5 H_7)$	forbidden

Table 3-3 (Contd.)

M	Σ	R	U	T	
$M_1^{\pm} \leftrightarrow M_1^{\pm}$ $M_2^{\pm} \leftrightarrow M_2^{\pm}$ $M_3^{\pm} \leftrightarrow M_3^{\pm}$ $M_4^{\pm} \leftrightarrow M_4^{\pm}$	$\Sigma_1 \leftrightarrow \Sigma_1$ $\Sigma_2 \leftrightarrow \Sigma_2$ $\Sigma_3 \leftrightarrow \Sigma_3$ $\Sigma_4 \leftrightarrow \Sigma_4$	$R_1 \leftrightarrow R_1$ $R_2 \leftrightarrow R_2$ $R_3 \leftrightarrow R_3$ $R_4 \leftrightarrow R_4$	$U_1 \leftrightarrow U_1$ $U_2 \leftrightarrow U_2$ $U_3 \leftrightarrow U_3$ $U_4 \leftrightarrow U_4$	$T_1 \leftrightarrow T_1$ $T_2 \leftrightarrow T_2$ $T_3 \leftrightarrow T_3$ $T_4 \leftrightarrow T_4$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$M_1^{\pm} \leftrightarrow M_2^{\pm}$ $M_1^{\pm} \leftrightarrow M_3^{\pm}$ $M_2^{\pm} \leftrightarrow M_4^{\pm}$ $M_3^{\pm} \leftrightarrow M_4^{\pm}$	$\Sigma_1 \leftrightarrow \Sigma_2$ $\Sigma_1 \leftrightarrow \Sigma_3$ $\Sigma_2 \leftrightarrow \Sigma_4$ $\Sigma_3 \leftrightarrow \Sigma_4$	$R_1 \leftrightarrow R_2$ $R_1 \leftrightarrow R_3$ $R_2 \leftrightarrow R_4$ $R_3 \leftrightarrow R_4$	$U_1 \leftrightarrow U_2$ $U_1 \leftrightarrow U_3$ $U_2 \leftrightarrow U_4$ $U_3 \leftrightarrow U_4$	$T_1 \leftrightarrow T_2$ $T_1 \leftrightarrow T_3$ $T_2 \leftrightarrow T_4$ $T_3 \leftrightarrow T_4$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$M_1^{\pm} \leftrightarrow M_4^{\pm}$ $M_2^{\pm} \leftrightarrow M_3^{\pm}$	$\Sigma_1 \leftrightarrow \Sigma_4$ $\Sigma_2 \leftrightarrow \Sigma_3$	$R_1 \leftrightarrow R_4$ $R_2 \leftrightarrow R_3$	$U_1 \leftrightarrow U_4$ $U_2 \leftrightarrow U_3$	$T_1 \leftrightarrow T_4$ $T_2 \leftrightarrow T_3$	$A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + cE_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$M_5^{\pm} \leftrightarrow M_5^{\pm}$	$\Sigma_5 \leftrightarrow \Sigma_5$	$R_5 \leftrightarrow R_5$	$U_5 \leftrightarrow U_5$	$T_5 \leftrightarrow T_5$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$ $+ c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-3 (Contd.)

L	
$L_1 \leftrightarrow L_1$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$L_1 \leftrightarrow L_2$	$A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(L_3 L_4) \leftrightarrow (L_3 L_4)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_4 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

S	
$S_1 \leftrightarrow S_1$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(S_3 S_4) - (S_3 S_4)$ $(S_2 S_5) - (S_2 S_5)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(S_3 S_4) - (S_2 S_5)$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-3 (Contd.)

P	
$P_1 \leftrightarrow P_1$ $P_2 \leftrightarrow P_2$	$A_1(\hat{\xi}_1 \hat{\xi}_2)$
$P_1 \leftrightarrow P_2$	$A_2(\hat{\xi}_1 \hat{\xi}_2)$
$P_1 \leftrightarrow P_3$ $P_2 \leftrightarrow P_3$ $(P_4 P_5) \leftrightarrow P_6$	$E_1(\hat{\xi}_1 \hat{\xi}_2) + c_1 E_2(\hat{\xi}_1 \hat{\xi}_2)$
$P_3 \leftrightarrow P_3$ $P_6 \leftrightarrow P_6$	$A_1(\hat{\xi}_1 \hat{\xi}_2) + c_1 A_2(\hat{\xi}_1 \hat{\xi}_2) + c_2 E_1(\hat{\xi}_1 \hat{\xi}_2) + c_3 E_2(\hat{\xi}_1 \hat{\xi}_2)$
$(P_4 P_5) \leftrightarrow (P_4 P_5)$	$A_1(\hat{\xi}_1 \hat{\xi}_2) + c_1 A_2(\hat{\xi}_1 \hat{\xi}_2)$

Table 3-4

Angular dependence functions for wurtzite structures. Notations used are those of Glasser (Ref. 47) and of Casella (Ref. 48).

Γ	Δ	A	
$\Gamma_1 \leftrightarrow \Gamma_1$	$\Delta_1 \leftrightarrow \Delta_1$	$(A_1 A_3) \leftrightarrow (A_1 A_3)$	$[(l_1 l_2 + m_1 m_2) + \lambda n_1 n_2]^2 \equiv A_1 (\hat{e}_1 \hat{e}_2)$
$\Gamma_2 \leftrightarrow \Gamma_2$	$\Delta_2 \leftrightarrow \Delta_2$	$(A_2 A_4) \leftrightarrow (A_2 A_4)$	
$\Gamma_3 \leftrightarrow \Gamma_3$	$\Delta_3 \leftrightarrow \Delta_3$		
$\Gamma_4 \leftrightarrow \Gamma_4$	$\Delta_4 \leftrightarrow \Delta_4$		
$\Gamma_1 \leftrightarrow \Gamma_3$	$\Delta_1 \leftrightarrow \Delta_3$		$(l_1 m_2 - l_2 m_1)^2 \equiv A_2 (\hat{e}_1 \hat{e}_2)$
$\Gamma_2 \leftrightarrow \Gamma_4$	$\Delta_2 \leftrightarrow \Delta_4$		
$\Gamma_1 \leftrightarrow \Gamma_2$	$\Delta_1 \leftrightarrow \Delta_2$	$(A_1 A_3) \leftrightarrow (A_2 A_4)$	forbidden
$\Gamma_1 \leftrightarrow \Gamma_4$	$\Delta_1 \leftrightarrow \Delta_4$		
$\Gamma_2 \leftrightarrow \Gamma_3$	$\Delta_2 \leftrightarrow \Delta_3$		
$\Gamma_3 \leftrightarrow \Gamma_4$	$\Delta_3 \leftrightarrow \Delta_4$		

Table 3-4 (Contd.)

Γ	Δ	A	
$\Gamma_1 \leftrightarrow \Gamma_6$	$\Delta_1 \leftrightarrow \Delta_6$		$\left[(m_1 n_2 - m_2 n_1) + \lambda (m_1 n_2 + m_2 n_1) \right]^2$ $+ (n_1 l_2 - n_2 l_1) - \lambda (n_1 l_2 + n_2 l_1)]^2$ $\equiv E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_3 \leftrightarrow \Gamma_6$	$\Delta_3 \leftrightarrow \Delta_6$		
$\Gamma_2 \leftrightarrow \Gamma_5$	$\Delta_2 \leftrightarrow \Delta_5$		
$\Gamma_4 \leftrightarrow \Gamma_5$	$\Delta_4 \leftrightarrow \Delta_5$		
$\Gamma_5 \leftrightarrow \Gamma_6$	$\Delta_5 \leftrightarrow \Delta_6$		
$\Gamma_1 \leftrightarrow \Gamma_5$	$\Delta_1 \leftrightarrow \Delta_5$		$(1 - n^2)(1 - n^2) \equiv E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_3 \leftrightarrow \Gamma_5$	$\Delta_3 \leftrightarrow \Delta_5$		
$\Gamma_2 \leftrightarrow \Gamma_6$	$\Delta_2 \leftrightarrow \Delta_6$		
$\Gamma_4 \leftrightarrow \Gamma_6$	$\Delta_4 \leftrightarrow \Delta_6$		
		$(A_5 A_6) \quad (A_5 A_6)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_5 \leftrightarrow \Gamma_5$	$\Delta_5 \leftrightarrow \Delta_5$		$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_6 \leftrightarrow \Gamma_6$	$\Delta_6 \leftrightarrow \Delta_6$		
$\Gamma_7 \leftrightarrow \Gamma_7$	$\Delta_7 \leftrightarrow \Delta_7$		$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_8 \leftrightarrow \Gamma_8$	$\Delta_8 \leftrightarrow \Delta_8$		
$\Gamma_7 \leftrightarrow \Gamma_8$	$\Delta_7 \leftrightarrow \Delta_8$		$E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-4 (Contd.)

Γ	Δ	A	
$\Gamma_7 \leftrightarrow \Gamma_9$ $\Gamma_8 \leftrightarrow \Gamma_9$	$\Delta_7 \leftrightarrow \Delta_9$ $\Delta_8 \leftrightarrow \Delta_9$	$(A_2 A_4) \leftrightarrow (A_5 A_6)$ $(A_1 A_3) \leftrightarrow (A_5 A_6)$ $(A_7 A_8) \leftrightarrow A_9$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Gamma_9 \leftrightarrow \Gamma_9$	$\Delta_9 \leftrightarrow \Delta_9$	$A_9 \leftrightarrow A_9$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
		$(A_7 A_8) \leftrightarrow (A_7 A_8)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$ $+ c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

H	K	P	
	$K_1 \leftrightarrow K_1$ $K_2 \leftrightarrow K_2$ $K_4 \leftrightarrow K_4$ $K_5 \leftrightarrow K_5$	$P_1 \leftrightarrow P_1$ $P_2 \leftrightarrow P_2$ $P_4 \leftrightarrow P_4$ $P_5 \leftrightarrow P_5$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
	$K_1 \leftrightarrow K_2$ $K_4 \leftrightarrow K_5$	$P_1 \leftrightarrow P_2$ $P_4 \leftrightarrow P_5$	$A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$

Table 3-4 (Contd.)

H	K	P	
$(H_1 H_2) \leftrightarrow H_3$ $(H_4 H_5) \leftrightarrow H_6$	$K_1 \leftrightarrow K_3$ $K_2 \leftrightarrow K_3$ $K_4 \leftrightarrow K_5$ $K_5 \leftrightarrow K_6$	$P_1 \leftrightarrow P_3$ $P_2 \leftrightarrow P_3$ $P_4 \leftrightarrow P_5$ $P_5 \leftrightarrow P_6$	$E_1(\hat{\xi}_1 \hat{\xi}_2) + c_1 E_2(\hat{\xi}_1 \hat{\xi}_2)$
$(H_1 H_2) \leftrightarrow (H_1 H_2)$ $(H_4 H_5) \leftrightarrow (H_4 H_5)$			$A_1(\hat{\xi}_1 \hat{\xi}_2) + cA_2(\hat{\xi}_1 \hat{\xi}_2)$
$H_3 \leftrightarrow H_3$ $H_6 \leftrightarrow H_6$	$K_3 \leftrightarrow K_3$ $K_6 \leftrightarrow K_6$	$P_3 \leftrightarrow P_3$ $P_6 \leftrightarrow P_6$	$A_1(\hat{\xi}_1 \hat{\xi}_2) + c_1 A_2(\hat{\xi}_1 \hat{\xi}_2)$ $+ c_2 E_1(\hat{\xi}_1 \hat{\xi}_2) + c_3 E_2(\hat{\xi}_1 \hat{\xi}_2)$

Table 3-4 (Contd.)

M	U	L
$M_1 \leftrightarrow M_1$	$U_1 \leftrightarrow U_1$	
$M_2 \leftrightarrow M_2$	$U_2 \leftrightarrow U_2$	$A_1(\hat{e}_1 \hat{e}_2) + c_H 2(\hat{e}_1 \hat{e}_2)$
$M_3 \leftrightarrow M_3$	$U_3 \leftrightarrow U_3$	
$M_4 \leftrightarrow M_4$	$U_4 \leftrightarrow U_4$	
$M_1 \leftrightarrow M_2$	$U_1 \leftrightarrow U_2$	$(L_1 L_2) \leftrightarrow (L_1 L_2)$
$M_1 \leftrightarrow M_3$	$U_1 \leftrightarrow U_3$	$(L_1 L_2) \leftrightarrow (L_3 L_4)$
$M_2 \leftrightarrow M_4$	$U_2 \leftrightarrow U_4$	
$M_3 \leftrightarrow M_4$	$U_3 \leftrightarrow U_4$	$H_1(\hat{e}_1 \hat{e}_2)$
$M_1 \leftrightarrow M_4$	$U_1 \leftrightarrow U_4$	
$M_2 \leftrightarrow M_3$	$U_2 \leftrightarrow U_3$	$A_1(\hat{e}_1 \hat{e}_2) + c_H 1 H_1(\hat{e}_1 \hat{e}_2) + c_H 2 H_2(\hat{e}_1 \hat{e}_2)$
$M_1 \leftrightarrow M_4$	$U_1 \leftrightarrow U_4$	
$M_2 \leftrightarrow M_3$	$U_2 \leftrightarrow U_3$	
$M_5 \leftrightarrow M_5$	$U_5 \leftrightarrow U_5$	$L_5 \leftrightarrow L_5$
		$A_1(\hat{e}_1 \hat{e}_2) + c_H 1 A_2(\hat{e}_1 \hat{e}_2) + c_H 2 H_1(\hat{e}_1 \hat{e}_2) + c_H 3 H_2(\hat{e}_1 \hat{e}_2)$

Table 3-4 (Contd.)

Σ	R	T	
$\Sigma_1 \leftrightarrow \Sigma_1$	$R_1 \leftrightarrow R_1$	$T_1 \leftrightarrow T_1$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_2 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Sigma_2 \leftrightarrow \Sigma_2$	$R_2 \leftrightarrow R_2$	$T_2 \leftrightarrow T_2$	
$\Sigma_3 \leftrightarrow \Sigma_3$	$R_3 \leftrightarrow R_3$	$T_3 \leftrightarrow T_3$	
$\Sigma_4 \leftrightarrow \Sigma_4$	$R_4 \leftrightarrow R_4$	$T_4 \leftrightarrow T_4$	
$\Sigma_1 \leftrightarrow \Sigma_2$	$R_1 \leftrightarrow R_2$	$T_1 \leftrightarrow T_2$	$E_1(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$\Sigma_3 \leftrightarrow \Sigma_4$	$R_3 \leftrightarrow R_4$	$T_3 \leftrightarrow T_4$	

S	
$(S_1 S_2) \leftrightarrow (S_1 S_2)$	$A_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_1 A_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$ $+ c_2 E_1(\hat{\epsilon}_1 \hat{\epsilon}_2) + c_3 E_2(\hat{\epsilon}_1 \hat{\epsilon}_2)$
$(S_3 S_4) \leftrightarrow (S_3 S_4)$	

Chapter IV

Forbidden Transitions

In many crystals of interest, such as the alkali halides, in which the point group contains the inversion, the valence band and conduction band at a high symmetry point often have opposite parity. This means that the dependence of the absorption coefficient on the directions of polarization will not be given by the tables in Chapter III for transitions taking place near extrema occurring at these points. In this section we will discuss Mahan's calculations of the angular dependence in a spherical band model with the explicit use of hydrogenic excitons in the initial and final states. A less sophisticated calculation will then be made in which the electron-hole interaction is ignored, and this will be compared with the calculation of Mahan. In this simpler model some refinements can be made more easily. Two of these will be discussed: the special case of valence p-bands near $\vec{k} = 0$ split into a spherical non-degenerate band and a spherical two-fold degenerate band, and ellipsoidal energy surfaces at point X for simple cubic and face-centered cubic crystals.

A. Mahan's Model

As was noted after Eq.2-23, for a forbidden two-photon transition the final state exciton envelope must, in the hydrogenic model, be a p-state. Its symmetry is determined by the decomposition of the $\ell = 1$ representation of the full rotation group into representations of the crystal point group. If an envelope function transforms as Γ^α , and if $|C_i(k_o)\rangle$ and $|V_j(k_o)\rangle$ transform as Γ^c and Γ^v , exciton states can be formed^{49,50} which transform as representations contained in the decomposition of $\Gamma^\alpha \times \Gamma^c \times \Gamma^v$. Suppose a p-state in a crystal field decomposes according to $D^1 = \sum_\alpha \Gamma^\alpha$. Then the final state excitons for forbidden transitions will transform according to $\sum_{\lambda\tau_\lambda} \Gamma^{\lambda\tau_\lambda} = \sum_\alpha \Gamma^\alpha \times \Gamma^c \times \Gamma^v$ where, as in Chapter III, τ_λ is an index to account for the fact that Γ^λ might occur more than once in the decomposition. If these states overlap, the angular dependence of the two-photon absorption will be given by

$$\alpha^{(2)} \sim \sum_{\lambda\tau_\lambda} a^{\lambda\tau_\lambda} \gamma^{\lambda\tau_\lambda}(\hat{\epsilon}_1, \hat{\epsilon}_2) \quad (4-1)$$

where $a^{\lambda\tau_\lambda}$ are positive constants and $\gamma^{\lambda\tau_\lambda}$ are the functions of Table 3-1. In a real crystal all paths indicated in Eq.2-23 will contribute to the absorption. The problem now is to see if suitable approximations can be made to simplify Eq.4-1.

Referring to Eq.2-23, for $\vec{M}_{c,n^-}$ of the fourth line

to be non-zero n^- must have the same parity as c_i . As an example of a band structure, consider that of KI⁵¹ shown in Fig.5-9 of Chapter V. As can be seen in this case there are no near conduction bands or valence bands (there will be core bands) with this property at Γ or X. $\vec{M}_{c_i n^-}$ (or $\vec{M}_{n^+ v_j}$ by the same argument) is expected, then, to be small compared with $\vec{M}_{c_i n^+}$ (and $\vec{M}_{n^- v_j}$) due to larger energy denominators and smaller one-electron matrix elements. Also $E_{n^+ v_j}(\nu)$ in the third line of Eq.2-23 will be larger than $E_{n^+ v_j}(\nu)$ in the first line, since in the former case n^+ represents higher conduction bands. Similarly $E_{c_i n^-}(\nu)$ of the fourth line will be larger than $E_{c_i n^-}(\nu)$ of the first line. When the band structure has the stated properties, then, we will neglect the third and fourth lines and their counterparts with subscripts 1 and 2 permuted.

We will now, after Mahan, make the following assumptions: first, that $\vec{M}_{c_i n^+}$ and $\vec{M}_{n^- v_j}$ of Eq.2-23 are sufficiently large when $n^+ = c_i$ and $n^- = v_j$ so that terms due to other bands can be neglected; second, that the Wannier hydrogenic model is a good description of exciton states. The first assumption defines what will be referred to as a two band model, meaning that we can proceed with calculations in which the only bands needed are those contained in the manifolds $\{|c_i(k)\rangle\}$ and $\{|v_j(k)\rangle\}$, both of which are degenerate at the extremum, say at $\vec{k} = 0$. The second

assumption implies that surfaces of constant energy

$E_{c_i}(k) - E_{v_j}(k)$ are spherical near $\vec{k} = 0$. We must here, however, make the additional assumption not stated by Mahan that the bands $\{|c_i(k)\rangle\}$ remain degenerate and the bands $\{|v_j(k)\rangle\}$ remain degenerate near $\vec{k} = 0$. Or, equivalently, the reduced reciprocal effective mass

$$\left(\frac{1}{\mu_{ij}}\right) = \frac{1}{m} [\vec{M}_{c_i c_i} - \vec{M}_{v_j v_j}]$$

is independent of i and j .

Under these conditions only the first term in the sum over intermediate bands of Eq.2-23, and its counterpart with subscripts 1 and 2 interchanged, contribute, with $|n^+\rangle = |c_i\rangle$ and $|n^-\rangle = |v_j\rangle$, giving the result

$$\begin{aligned} P_{fg}^{(2)} = & N^{\frac{1}{2}} \sum_{\nu} \hat{\epsilon}_1 \cdot \left(\frac{\vec{m}}{\mu}\right) \cdot \frac{\langle u_{cv}^{\mu} | \vec{p} | u_{cv}^{\nu} \rangle u_{cv}^{\nu}(0)^*}{E_{cv}(\nu) - \hbar \omega_2} \langle c_i(0) | \hat{\epsilon}_2 \cdot \vec{p} | v_j(0) \rangle \\ & + N^{\frac{1}{2}} \sum_{\nu} \hat{\epsilon}_2 \cdot \left(\frac{\vec{m}}{\mu}\right) \cdot \frac{\langle u_{cv}^{\mu} | \vec{p} | u_{cv}^{\nu} \rangle u_{cv}^{\nu}(0)^*}{E_{cv}(\nu) - \hbar \omega_1} \langle c_i(0) | \hat{\epsilon}_1 \cdot \vec{p} | v_j(0) \rangle \end{aligned} \quad (4-2)$$

where we have dropped the subscripts i and j in the envelope matrix element and in $E_{c_i v_j}(\nu)$, since the equation that $u_{c_i v_j}^{\nu}$ must satisfy (Eq.2-15) is independent of i and j . Since the bands are spherical $(1/\mu)$ is a constant $\frac{1}{\mu}$ times a unit tensor. Referring to Eq.2-24 we write the matrix element

$$\langle u_{cv}^{\mu} | \vec{p} | u^{\nu} \rangle = \int \psi_{nlm}^*(\vec{\beta}) \vec{p} \psi_{n'l'm'}(\vec{\beta}) d^3\beta$$

where we have set $\mu = (n, l, m)$ and $\nu = (n', l', m')$ for hydrogenic excitons, and

$$\sqrt{\frac{N}{V}} \mathcal{U}_{cv}^{\mu}(\vec{\beta}) \equiv \psi_{nlm}(\vec{\beta}).$$

From Eq.2-15 we see that $E_{cv}(\nu) = E_g + E_n$, where

$$E_n = -\mu e^4 / 2\hbar^2 n^2. \quad \text{Eq.4-2 becomes}$$

$$\begin{aligned} P_{fg}^{(2)} = \sqrt{V} \frac{m}{\mu} \left\{ \right. & \left. \psi_{nlm}^*(\beta) \hat{E}_1 \cdot \vec{p} \sum_{n'l'm'} \frac{\psi_{n'l'm'}(\beta) \psi_{n'l'm'}^*(0)}{E_g + E_n - \hbar\omega_2} d^3\beta \langle c_i | \hat{E}_1 \cdot \vec{p} | v_j \rangle \right. \\ & \left. + \psi_{nlm}^*(\beta) \hat{E}_2 \cdot \vec{p} \sum_{n'l'm'} \frac{\psi_{n'l'm'}(\beta) \psi_{n'l'm'}^*(0)}{E_g + E_n - \hbar\omega_1} d^3\beta \langle c_i | \hat{E}_2 \cdot \vec{p} | v_j \rangle \right\} \end{aligned} \quad (4-3)$$

We have already said that since $\psi_{n'l'm'}(0)$ is non-zero only for s-states ψ_{nlm} must be a p-state. Mahan points out in addition that the sum over $n'l'm'$ is the Coulomb Green's function

$$G_{\alpha}(\vec{\beta}, \vec{\beta}') \Big|_{\beta'=0} = \sum_{n'l'm'} \frac{\psi_{n'l'm'}(\vec{\beta}) \psi_{n'l'm'}^*(\vec{\beta}')}{E_{\lambda} - \Omega_{\alpha}} \Big|_{\beta'=0}$$

where $\Omega_{\alpha} \equiv -E_g + \hbar\omega_{\alpha}$, and that this can be expressed in terms of a Whittaker's function,

$$G_{\alpha}(\vec{\beta}, 0) = \frac{\mu}{2\pi\hbar^2\beta} \Gamma(1-\kappa_{\alpha}) W_{\kappa_{\alpha}, \frac{1}{2}}\left(\frac{2\beta}{a\kappa_{\alpha}}\right)$$

where

$$W_{\kappa_{\alpha}, \frac{1}{2}}(z) = \frac{ze^{-z/2}}{\Gamma(1-\kappa_{\alpha})} \int_0^{\infty} e^{-zt} \left(\frac{1+t}{t}\right)^{\kappa_{\alpha}} dt$$

a is the exciton Bohr radius and $\kappa_{\alpha} \equiv [E_B / (E_g - \hbar\omega_{\alpha})]^{\frac{1}{2}}$. E_B is the exciton binding energy. The integrals in Eq.4-3 can then be evaluated numerically to any desired degree of approximation. It is convenient to put these integrals in the form

$$\begin{aligned}
I &= \frac{\hbar}{i} \int \psi_{n p_m}^* (\vec{\beta}) \hat{\epsilon}_r \cdot \hat{\beta} \frac{\partial}{\partial \beta} G_\alpha(\vec{\beta}, 0) d^3 \beta \quad (\gamma, \alpha = 1, 2) \\
&= \frac{\hbar \epsilon_{rm}}{i E_B \sqrt{3\pi a^5}} \sqrt{\frac{n^2 - 1}{n^5}} J_{p,n}(\kappa_\alpha)
\end{aligned} \tag{4-4}$$

for discrete p-states, where the numerically evaluated integral is

$$J_{p,n}(\kappa_\alpha) \equiv \frac{\kappa_\alpha^2}{2} \int_0^\infty (t + \frac{1}{2}) \left(\frac{1+t}{t} \right)^{\kappa_\alpha} \frac{[t + \frac{1}{2} - \frac{\kappa_\alpha}{2n}]^{n-2}}{[t + \frac{1}{2} + \frac{\kappa_\alpha}{2n}]^{n+2}} dt.$$

For continuum states

$$I = \frac{(\hat{\epsilon} \cdot \vec{k}) \hbar}{\sqrt{V} E_B} e^{\eta \frac{\pi}{2}} |\Gamma(2 - i\eta)| J_{p,k}(\kappa_\alpha), \tag{4-5}$$

with

$$J_{p,k}(\kappa_\alpha) \equiv \frac{\kappa_\alpha^2}{2} \int_0^\infty (t + \frac{1}{2}) \left(\frac{1+t}{t} \right)^{\kappa_\alpha} \frac{[t + \frac{1}{2} - i \frac{\kappa_\alpha}{2\eta}]^{-i\eta-2}}{[t + \frac{1}{2} + i \frac{\kappa_\alpha}{2\eta}]^{i\eta-2}} dt$$

where $E_k = -E_B/\eta^2$. Combining Eq.2-7, Eq.4-3 and Eq.4-4 or Eq. 4-5 one obtains the absorption coefficient for discrete or continuum states. The sum over final states in Eq.2-7 is

$$\sum_f = \sum_{ij} \int dE_f \rho(E_f).$$

For a discrete state $\rho(E_f)$ is the normalized line shape function.²²

We assume here that the spectral band widths of the light beams are narrow compared with $\rho(E_f)$. For large n , where the states are close together and

overlap, the density of states is

$$\rho(E_f) = \left(\frac{\partial E_n}{\partial n} \right)^{-1} = \left[\frac{\partial}{\partial n} \left(-\frac{E_B}{n^2} \right) \right]^{-1} = \frac{n^3}{2E_B}.$$

For continuum states

$$\sum_f = \sum_{ij} \frac{V}{(2\pi)^3} \int d^3k.$$

The absorption coefficient becomes

$$\alpha^{(2)} = A \left(1 - \frac{1}{n^2} \right) \frac{2E_B}{n^3} \rho(E_f) \quad (4-6)$$

$$\times \sum_{ijm} \left| \epsilon_{1m} \langle c_i | \hat{E}_2 \cdot \vec{p} | v_j \rangle J_{p,n}(\kappa_1) + \epsilon_{2m} \langle c_i | \hat{E}_1 \cdot \vec{p} | v_j \rangle J_{p,n}(\kappa_2) \right|^2$$

(discrete),

$$\alpha^{(2)} = A \left(1 - \frac{1}{n^2} \right) \times \sum_{ijm} \left| \epsilon_{1m} \langle c_i | \hat{E}_2 \cdot \vec{p} | v_j \rangle J_{p,n}(\kappa_1) + \epsilon_{2m} \langle c_i | \hat{E}_1 \cdot \vec{p} | v_j \rangle J_{p,n}(\kappa_2) \right|^2$$

(overlap),

$$\alpha^{(2)} = A \left(1 - \frac{1}{\eta^2} \right) (1 - e^{-2\pi\eta})^{-1} \times \sum_{ijm} \left| \epsilon_{1m} \langle c_i | \hat{E}_2 \cdot \vec{p} | v_j \rangle J_{p,k}(\kappa_1) + \epsilon_{2m} \langle c_i | \hat{E}_1 \cdot \vec{p} | v_j \rangle J_{p,k}(\kappa_2) \right|^2$$

(continuum),

where $A \equiv \frac{4\pi}{3} \left(\frac{e}{m} \right)^4 \frac{\hbar^3}{E_B^3 a^5 c^2} \frac{F_2}{n_2 \sqrt{n_1} \omega_1 \omega_2}$. We have

changed the notation for the dielectric constants n_1 and n_2 to avoid confusion.

In crystals of symmetry T_h or O_h , i. e., crystals in which p_x , p_y , and p_z transform according to different rows of the same representation, the dependence of the absorption coefficient on $\hat{E}_1$ and $\hat{E}_2$ is independent of the symmetries of $|c_i\rangle$ and $|v_j\rangle$, as long as the matrix

elements are non-zero. To show this, we let $|c_i\rangle$ and $|v_j\rangle$ transform according to rows i and j of representations Γ^c and Γ^v , respectively, let p_m ($m = x, y, z$) transform according to row s of Γ^{ps} of O_h or T_h , and take the absolute square in Eq. 4-6. The first term is proportional to

$$\sum_{ijm} \epsilon_{im}^2 |\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle|^2 = \sum_{ij} |\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle|^2.$$

Now note that $\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle = \langle c_i, v_j | \hat{\epsilon}_2 \cdot \vec{p} | g \rangle$, where $|g\rangle$ transforms under Γ^l . Since

$$|c_i, v_j\rangle = \sum_{\mu \tau_\mu s} [A_{s, ij}^{\mu \tau_\mu, cv}] |\mu \tau_\mu s\rangle$$

we have

$$\begin{aligned} \sum_{ij} |\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle|^2 &= \sum_{ij} \sum_{\mu \tau_\mu s} \sum_{\mu' \tau_{\mu'} s'} [A_{s, ij}^{\mu \tau_\mu, cv}]^* [A_{s', ij}^{\mu' \tau_{\mu'}, cv}] \\ &\quad \times \langle \mu \tau_\mu s | \hat{\epsilon}_2 \cdot \vec{p} | g \rangle \langle g | \hat{\epsilon}_2 \cdot \vec{p} | \mu' \tau_{\mu'} s' \rangle \\ &= \sum_{\tau_4 \tau_4' s s'} \epsilon_{2s} \epsilon_{2s'} \sum_{ij} [A_{s, ij}^{4 \tau_4, cv}]^* [A_{s', ij}^{4 \tau_4', cv}] \\ &\quad \times \langle 4 \tau_4 s | p_s | g \rangle \langle g | p_{s'} | 4 \tau_4' s' \rangle \\ &= \hat{\epsilon}_2 \cdot \hat{\epsilon}_2 |\langle p \rangle_{cv}|^2 = |\langle p \rangle_{cv}|^2, \end{aligned}$$

where

$$|\langle p \rangle_{cv}|^2 \equiv \sum_{\tau_4} \left| \sum_{ij} [A_{x, ij}^{4 \tau_4, cv}] \langle c_i | p_x | v_j \rangle \right|^2. \quad (4-7)$$

Using identical arguments for the other terms, the two-photon absorption coefficient becomes

$$\begin{aligned}
\alpha^{(2)} &= B \left\{ |J_1|^2 + |J_2|^2 + (\hat{E}_1 \cdot \hat{E}_2)^2 [J_1 J_2^* + J_2 J_1^*] \right\} \\
&= B \left\{ (\hat{E}_1 \times \hat{E}_2)^2 [|J_1|^2 + |J_2|^2] + (\hat{E}_1 \cdot \hat{E}_2)^2 |J_1 + J_2|^2 \right\}
\end{aligned}
\tag{4-8}$$

where J_i is $J_{p,n}(\kappa_i)$ or $J_{p,k}(\kappa_i)$, and

$$B = A \times \begin{cases} \left(1 - \frac{1}{n^2}\right) \frac{2E_B}{n^3} \rho(E_f) |\langle p \rangle_{cv}|^2 & \text{(discrete)} \\ \left(1 - \frac{1}{n^2}\right) |\langle p \rangle_{cv}|^2 & \text{(overlap)} \\ \left(1 - \frac{1}{\eta^2}\right) (1 - e^{-2\pi\eta})^{-1} |\langle p \rangle_{cv}|^2 & \text{(continuum)} \end{cases}$$

There are two significant properties of these results. The first is that the angular dependence of the absorption does not depend, in cubic and tetrahedral crystals, on the symmetries of the valence and conduction bands. The second is that it does not depend on the orientations of the polarization vectors with respect to the crystal axes, but only with respect to each other. Absorption for parallel polarizations is larger than for perpendicular polarizations, the ratio of their magnitudes being

$$\frac{\alpha_{||}^{(2)}}{\alpha_{\perp}^{(2)}} = \frac{|J_1 + J_2|^2}{|J_1|^2 + |J_2|^2}
\tag{4-9}$$

This ratio must have a value between 1 and 2.

Probably the largest error in this calculation is

the restriction to the two band model, and it becomes important when, for example, a higher conduction band is close in energy to the conduction band of interest at the extremum. An example of this can be seen in the energy bands of CsI shown in Fig.5-7 of Chapter V, where the $\Gamma_6^+(A_{1g})$ and $\Gamma_8^+(E_g)$ conduction bands are close together. The proximity of another conduction band has two principal effects: it necessitates keeping another term in the sum over intermediate states in Eq.2-23, and it can severely warp the energy bands near the extremum, invalidating the spherical band approximation. These effects immensely complicate calculations for the angular dependence. A second inadequacy of this calculation should be noted; that is, that although calculations have been made for discrete and continuum states, the calculations for the lowest energy discrete states are dubious, since these are the least well described by the Wannier model, especially for s-states, which enter the sum over intermediate states. This is particularly true in large band-gap insulators^{54,55} such as the alkali halides. On the other hand, discrete p-states have not been observed experimentally in two-photon absorption, and, except for some error due to the sum over intermediate s-states, the calculations should be adequate for large n overlapping states and continuum states, insofar as the two spherical band model is adequate.

B. Band Model

We will calculate the absorption coefficient for forbidden two-photon transitions ignoring the electron-hole interaction. We again assume a two band model in which the bands $|c_i(k)\rangle$ and $|v_j(k)\rangle$ are spherical near $\vec{k} = 0$, and in which $|c_i(k)\rangle$ remain degenerate near $\vec{k} = 0$, as do $|v_j(k)\rangle$. Thus in Eq.2-10 we retain only the bands contained in the sets $\{|c_i\rangle\}$ and $\{|v_j\rangle\}$ in the intermediate states n , but we will keep all terms in the sum over l . Noting that $E_c(k) - E_v(k) = \hbar\omega_1 + \hbar\omega_2$, Eq.2-10 becomes

$$\begin{aligned}
 P_{fg}^{(2)} = & \frac{\hbar}{m} \sum_{l \neq c} \sum_{c_i'} \left[\frac{\langle c_i | \vec{k} \cdot \vec{p} | l \rangle \langle l | \hat{E}_1 \cdot \vec{p} | c_i' \rangle}{E_c - E_l} \right. \\
 & \left. + \frac{\langle c_i | \hat{E}_1 \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | c_i' \rangle}{E_c - E_l} \right] \frac{\langle c_i' | \hat{E}_2 \cdot \vec{p} | v_j \rangle}{\hbar\omega_1} \\
 & - \frac{\hbar}{m} \sum_{l \neq v} \sum_{v_j'} \frac{\langle c_i | \hat{E}_1 \cdot \vec{p} | v_j' \rangle}{\hbar\omega_2} \left[\frac{\langle v_j' | \vec{k} \cdot \vec{p} | l \rangle \langle l | \hat{E}_2 \cdot \vec{p} | v_j \rangle}{E_v - E_l} \right. \\
 & \left. + \frac{\langle v_j' | \hat{E}_2 \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | v_j \rangle}{E_v - E_l} \right] \\
 & + \text{terms with subscripts 1 and 2 interchanged} \quad (4-10)
 \end{aligned}$$

Note that under the conditions imposed on the bands (see Appendix A)

$$\frac{1}{m} \sum_{l \neq c} \left[\frac{\langle c_i | \vec{k} \cdot \vec{p} | l \rangle \langle l | \hat{e}_1 \cdot \vec{p} | c_{i'} \rangle}{E_c - E_l} + \frac{\langle c_i | \hat{e}_1 \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | c_{i'} \rangle}{E_c - E_l} \right]$$

$$= \delta_{ii'} \quad \vec{k} \cdot \left[\left(\frac{\vec{m}}{m_c^*} \right) - 1 \right] \cdot \hat{e}_1$$

and

$$\frac{1}{m} \sum_{l \neq v} \left[\frac{\langle v_j | \vec{k} \cdot \vec{p} | l \rangle \langle l | \hat{e}_2 \cdot \vec{p} | v_j \rangle}{E_v - E_l} + \frac{\langle v_j | \hat{e}_2 \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | v_j \rangle}{E_v - E_l} \right]$$

$$= \delta_{jj'} \quad \vec{k} \cdot \left[\left(\frac{\vec{m}}{m_v^*} \right) - 1 \right] \cdot \hat{e}_2$$

where each effective mass tensor is a constant times a unit tensor. Eq.4-10 reduces to

$$P_{fg}^{(2)} =$$

$$\hbar \vec{k} \cdot \left[\frac{\vec{m}}{m_c^*} - 1 \right] \cdot \hat{e}_1 \frac{\langle c_i | \hat{e}_2 \cdot \vec{p} | v_j \rangle}{\hbar \omega_1}$$

$$- \hbar \vec{k} \cdot \left[\frac{\vec{m}}{m_v^*} - 1 \right] \cdot \hat{e}_2 \frac{\langle c_i | \hat{e}_1 \cdot \vec{p} | v_j \rangle}{\hbar \omega_2}$$

$$+ \hbar \vec{k} \cdot \left[\frac{\vec{m}}{m_c^*} - 1 \right] \cdot \hat{e}_2 \frac{\langle c_i | \hat{e}_1 \cdot \vec{p} | v_j \rangle}{\hbar \omega_2}$$

$$- \hbar \vec{k} \cdot \left[\frac{\vec{m}}{m_v^*} - 1 \right] \cdot \hat{e}_1 \frac{\langle c_i | \hat{e}_2 \cdot \vec{p} | v_j \rangle}{\hbar \omega_1}$$

$$\begin{aligned}
&= \hbar \vec{k} \cdot \left(\frac{\vec{m}}{\mu} \right) \cdot \hat{\epsilon}_1 \frac{\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle}{\hbar \omega_1} + \hbar \vec{k} \cdot \left(\frac{\vec{m}}{\mu} \right) \cdot \hat{\epsilon}_2 \frac{\langle c_i | \hat{\epsilon}_1 \cdot \vec{p} | v_j \rangle}{\hbar \omega_2} \\
&= \hbar \frac{m}{\mu} \left[\vec{k} \cdot \hat{\epsilon}_1 \frac{\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle}{\hbar \omega_1} + \vec{k} \cdot \hat{\epsilon}_2 \frac{\langle c_i | \hat{\epsilon}_1 \cdot \vec{p} | v_j \rangle}{\hbar \omega_2} \right].
\end{aligned}$$

Inserting this into Eq.2-7 we find

$$\begin{aligned}
\alpha^{(2)} &= A' \sum_f |P_{fg}^{(2)}|^2 \delta [E_{fg} - \hbar(\omega_1 + \omega_2)] \\
&= A' \hbar^2 \left(\frac{m}{\mu} \right)^2 \sum_{ij} \frac{V}{(2\pi)^3} \int d^3k \delta [E_c(k) - E_v(k) - \hbar(\omega_1 + \omega_2)] \\
&\quad \times \left| \vec{k} \cdot \hat{\epsilon}_1 \frac{\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle}{\hbar \omega_1} + \vec{k} \cdot \hat{\epsilon}_2 \frac{\langle c_i | \hat{\epsilon}_1 \cdot \vec{p} | v_j \rangle}{\hbar \omega_2} \right|^2
\end{aligned} \tag{4-11}$$

where

$$A' \equiv \frac{(2\pi)^3}{V} \frac{\hbar}{c^2} \left(\frac{e}{m} \right)^4 \frac{F_2}{\kappa_2 \sqrt{\kappa_1} \omega_1 \omega_2} . \tag{4-12}$$

As in the last section the form of

$$\sum_{ij} \left| \vec{k} \cdot \hat{\epsilon}_1 \frac{\langle c_i | \hat{\epsilon}_2 \cdot \vec{p} | v_j \rangle}{\hbar \omega_1} + \vec{k} \cdot \hat{\epsilon}_2 \frac{\langle c_i | \hat{\epsilon}_1 \cdot \vec{p} | v_j \rangle}{\hbar \omega_2} \right|^2$$

is independent of the symmetries of c_i and v_j , provided that the matrix elements are non-zero; i. e. provided that $\Gamma^c \times \Gamma^v$ contains Γ^4 , so that we can write the preceding expression as

$$k^2 \sum_s \left[\hat{k} \cdot \hat{\epsilon}_1 \frac{\epsilon_{2s}}{\hbar \omega_1} + \hat{k} \cdot \hat{\epsilon}_2 \frac{\epsilon_{1s}}{\hbar \omega_2} \right]^2 | \langle p \rangle_{cv} |^2,$$

where $| \langle p \rangle_{cv} |^2$ is defined by Eq.4-7. Near $\vec{k} = 0$ let

$E_c(k) - E_v(k) = E_{gap} + \frac{\hbar^2 k^2}{2\mu}$, and $d^3k = k^2 dk d\Omega_k$. The Eq.4-11

becomes

$$\alpha^{(2)} = A' \hbar^2 \left(\frac{m}{\mu}\right)^2 \frac{V}{(2\pi)^3} |\langle p \rangle_{cv}|^2 \int k^4 dk \delta \left[E_{gap} + \frac{\hbar^2 k^2}{2\mu} - \hbar(\omega_1 + \omega_2) \right] \\ \times \sum_s \int d\Omega_k \left[\hat{k} \cdot \hat{\epsilon}_1 \frac{\epsilon_{2s}}{\hbar\omega_1} + \hat{k} \cdot \hat{\epsilon}_2 \frac{\epsilon_{1s}}{\hbar\omega_2} \right]^2 \quad (4-13)$$

Let $z \equiv \frac{\hbar^2 k^2}{2\mu}$. Then

$$\int k^4 dk \delta \left[E_{gap} + \frac{\hbar^2 k^2}{2\mu} - \hbar(\omega_1 + \omega_2) \right] \\ = \frac{1}{2} \left(\frac{2\mu}{\hbar^2} \right)^{5/2} \int z^{3/2} dz \delta \left[E_{gap} + z - \hbar(\omega_1 + \omega_2) \right] \\ = \frac{1}{2} \left(\frac{2\mu}{\hbar^2} \right)^{5/2} \left[\hbar(\omega_1 + \omega_2) - E_{gap} \right]^{3/2} \quad (4-14)$$

This gives the well-known energy dependence for forbidden band-to-band transitions. Let $(\kappa_x, \kappa_y, \kappa_z) \equiv \hat{k}$.

Expanding the square in Eq.4-13 and using the integral

$$\int \kappa_i \kappa_j d\Omega_k = \frac{4\pi}{3} \delta_{ij}$$

the two-photon absorption coefficient reduces to

$$\alpha^{(2)} = \sqrt{\mu} B' \left\{ (\hat{\epsilon}_1 \times \hat{\epsilon}_2)^2 \left| \left(\frac{1}{\hbar\omega_1} \right)^2 + \left(\frac{1}{\hbar\omega_2} \right)^2 \right| + (\hat{\epsilon}_1 \cdot \hat{\epsilon}_2)^2 \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 \right\}, \quad (4-15)$$

where

$$B' \equiv \frac{4\pi}{3} \frac{e^4}{\hbar^2 c^2 m^2} \frac{F_2 2\sqrt{2}}{\kappa_2 \sqrt{\kappa_1} \omega_1 \omega_2} [\hbar(\omega_1 + \omega_2) - E_{gap}]^{3/2} |\langle p \rangle_{cv}|^2 \quad (4-16)$$

The angular dependence of Eq.4-15 is seen to be identical in form with Eq.4-8, with J_i replaced by $1/\hbar\omega_i$. The ratio of parallel polarization absorption to perpendicular polarization absorption is

$$\frac{\alpha_{||}^{(2)}}{\alpha_{\perp}^{(2)}} = \frac{\left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2}\right]^2}{\left(\frac{1}{\hbar\omega_1}\right)^2 + \left(\frac{1}{\hbar\omega_2}\right)^2}, \quad (4-17)$$

similar to Eq.4-9. Eq.4-17 is, of course, much simpler to evaluate than Eq.4-9, in view of the fact that the evaluation of J_i requires a computer.²⁰ The only experimental data available (which will be discussed in Chapter V) with which a comparison of Eq.4-17 and Eq.4-9 can be made, however, indicates that Eq.4-17 more accurately describes the polarization dependence than Eq.4-9. This could be due to uncertain values for the band gap and the exciton binding energy, both of which enter into the expression for J_i in Mahan's model. A possible error also arises in the sum over intermediate s-states, although this is probably small for continuum final states. However with a single comparison the closer agreement of the simpler band model could simply be fortuitous in this case; future experiments should permit further comparison.

C. p-like Valence Bands

An assumption in the two previous calculations was that the valence bands $\{|c_i(\vec{k})\rangle\}$ were degenerate near $\vec{k} = 0$. This, of course, is never really the case; in general, if there is degeneracy at $\vec{k} = 0$, then a short distance away in a general direction at least some of the degeneracy will be lifted.⁵⁶ In this section we will examine the splitting of p-like states near $k = 0$ in a crystal with O_h symmetry and determine what effect this has on the two-photon absorption coefficient for forbidden transitions.

Let the p-like valence band states at $\vec{k} = 0$ be labeled $|x\rangle$, $|y\rangle$ and $|z\rangle$. In order to find the energies of the bands at a nearby $\vec{k}$ we must diagonalize the matrix (see Appendix A)

$$\left[\sum_{\ell \neq x, y, z} \frac{\langle i | \vec{k} \cdot \vec{p} | \ell \rangle \langle \ell | \vec{k} \cdot \vec{p} | j \rangle}{E_i - E_\ell} \right],$$

where i and j are x , y or z , and where all states and energies are at $\vec{k} = 0$. This really requires knowledge of matrix elements involving all intermediate states, but substantial information can be obtained from symmetry considerations. Let us consider the intermediate states of the five possible symmetries $\Gamma^H(A_{1g}, A_{2g}, E_g, T_{1g}$ and $T_{2g})$ one at a time. (The odd parity (ungerade) intermediate states do not contribute, since p and $|i\rangle$ are both odd.) Thus we relabel the intermediate states:

$$\begin{aligned}
\sum_{\ell} \frac{|l\rangle\langle l|}{E_i - E_{\ell}} &= \sum_{\alpha} \frac{|A_{1g};\alpha\rangle\langle A_{1g};\alpha|}{E_i - E_{\alpha}} + \sum_{\alpha} \frac{|A_{2g};\alpha\rangle\langle A_{2g};\alpha|}{E_i - E_{\alpha}} \\
&\quad + \sum_{\alpha,m} \frac{|E_g m;\alpha\rangle\langle E_g m;\alpha|}{E_i - E_{\alpha}} + \sum_{\alpha,m} \frac{|T_{1g} m;\alpha\rangle\langle T_{1g} m;\alpha|}{E_i - E_{\alpha}} \\
&\quad + \sum_{\alpha,m} \frac{|T_{2g} m;\alpha\rangle\langle T_{2g} m;\alpha|}{E_i - E_{\alpha}},
\end{aligned}$$

where m labels the row of the representation and α represents all other quantum numbers. The procedure for finding the form of the matrix is as follows: a) determine the matrices $[\langle i|\vec{k}\cdot\vec{p}|\Gamma^{\mu}m;\alpha\rangle]$ for each representation Γ^{μ} , b) multiply from the right by its adjoint, c) divide by $E_i - E_{\alpha}$ and sum over α , and d) sum over representations Γ^{μ} .

a) First write $[\langle i|\vec{k}\cdot\vec{p}|\Gamma^{\mu}m;\alpha\rangle] = \sum_s k_s [\langle i|p_s|\Gamma^{\mu}m;\alpha\rangle]$

Each matrix $[\langle i|p_s|\Gamma^{\mu}m;\alpha\rangle]$ is given in terms of an unknown constant C_{α}^{μ} in the book by Koster et al.⁴² We have

$$[\langle i|\vec{k}\cdot\vec{p}|A_{1g};\alpha\rangle] = \frac{1}{\sqrt{3}} C_{\alpha}^I \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix}$$

$$[\langle i|\vec{k}\cdot\vec{p}|A_{2g};\alpha\rangle] = 0$$

$$[i|\vec{k} \cdot \vec{p}|E_g m; \alpha\rangle] = C_\alpha^3 \begin{bmatrix} -\frac{1}{\sqrt{6}}k_x & \frac{1}{\sqrt{2}}k_x \\ -\frac{1}{\sqrt{6}}k_y & -\frac{1}{\sqrt{2}}k_y \\ \frac{1}{\sqrt{3}}k_z & 0 \end{bmatrix}$$

$$[i|\vec{k} \cdot \vec{p}|T_{1g} m; \alpha\rangle] = C_\alpha^4 \begin{bmatrix} 0 & -\frac{1}{\sqrt{2}}k_z & \frac{1}{\sqrt{2}}k_y \\ \frac{1}{\sqrt{2}}k_z & 0 & -\frac{1}{\sqrt{2}}k_x \\ -\frac{1}{\sqrt{2}}k_y & \frac{1}{\sqrt{2}}k_x & 0 \end{bmatrix}$$

$$[i|\vec{k} \cdot \vec{p}|T_{2g} m; \alpha\rangle] = C_\alpha^5 \begin{bmatrix} 0 & \frac{1}{\sqrt{2}}k_z & \frac{1}{\sqrt{2}}k_y \\ \frac{1}{\sqrt{2}}k_z & 0 & \frac{1}{\sqrt{2}}k_x \\ \frac{1}{\sqrt{2}}k_y & \frac{1}{\sqrt{2}}k_x & 0 \end{bmatrix}$$

where the C_α^u are complex matrix elements. For example,
 $C_\alpha^1 = \langle x | p_x | A_{1g}; \alpha \rangle.$

b)

$$[i|\vec{k} \cdot \vec{p}|A_{1g}; \alpha\rangle \langle A_{1g}; \alpha | \vec{k} \cdot \vec{p} | j\rangle] = \frac{|C_\alpha^1|^2}{3} \begin{bmatrix} k_x^2 & k_x k_y & k_x k_z \\ k_x k_y & k_y^2 & k_y k_z \\ k_x k_z & k_y k_z & k_z^2 \end{bmatrix}$$

$$\left[\sum_m \langle i | \vec{k} \cdot \vec{p} | E_g m; \alpha \rangle \times \langle E_g m; \alpha | \vec{k} \cdot \vec{p} | j \rangle \right] = |C_\alpha^3|^2 \begin{bmatrix} \frac{2}{3}k_x^2 & -\frac{1}{3}k_x k_y & -\frac{1}{3}k_x k_z \\ -\frac{1}{3}k_x k_y & \frac{2}{3}k_y^2 & -\frac{1}{3}k_y k_z \\ -\frac{1}{3}k_x k_z & -\frac{1}{3}k_y k_z & \frac{2}{3}k_z^2 \end{bmatrix}$$

$$\left[\sum_m \langle i | \vec{k} \cdot \vec{p} | T_{1g} m; \alpha \rangle \right. \\ \left. \times \langle T_{1g} m; \alpha | \vec{k} \cdot \vec{p} | j \rangle \right] = \frac{|C_\alpha^4|^2}{2} \begin{bmatrix} (k_y^2 + k_z^2) & -k_x k_y & -k_x k_z \\ -k_x k_y & (k_x^2 + k_z^2) & -k_y k_z \\ -k_x k_z & -k_y k_z & (k_x^2 + k_y^2) \end{bmatrix}$$

$$\left[\sum_m \langle i | \vec{k} \cdot \vec{p} | T_{2g} m; \alpha \rangle \right. \\ \left. \times \langle T_{2g} m; \alpha | \vec{k} \cdot \vec{p} | j \rangle \right] = \frac{|C_\alpha^5|^2}{2} \begin{bmatrix} (k_y^2 + k_z^2) & k_x k_y & k_x k_z \\ k_x k_y & (k_x^2 + k_z^2) & k_y k_z \\ k_x k_z & k_y k_z & (k_x^2 + k_y^2) \end{bmatrix}$$

c) For the sum over all sets α having symmetry Γ^μ we make the definition

$$\sigma^\mu \equiv \sum_\alpha \frac{|C_\alpha^\mu|^2}{E_i - E_\alpha} \quad (4-18)$$

where σ^μ is a real constant.

d) Summing over μ , and keeping in mind that $k^2 = k_x^2 + k_y^2 + k_z^2$, we obtain

$$\left[\sum_{l \neq x, y, z} \frac{\langle i | \vec{k} \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | j \rangle}{E_i - E_l} \right] \\ = \frac{1}{2} (\sigma^4 + \sigma^5) k^2 \mathbb{1} + \begin{bmatrix} \xi k_x^2 & \eta k_x k_y & \eta k_x k_z \\ \eta k_x k_y & \xi k_y^2 & \eta k_y k_z \\ \eta k_x k_z & \eta k_y k_z & \xi k_z^2 \end{bmatrix} \quad (4-19)$$

where

$$\xi \equiv \frac{1}{3} \sigma^1 + \frac{2}{3} \sigma^3 - \frac{1}{2} \sigma^4 - \frac{1}{2} \sigma^5 \\ \eta \equiv \frac{1}{3} \sigma^1 - \frac{1}{3} \sigma^3 - \frac{1}{2} \sigma^4 + \frac{1}{2} \sigma^5. \quad (4-20)$$

Eq.4-19 is identical to that given by Shockley⁵⁷ for a p-like valence band, except that, in addition, we have obtained the dependence of the coefficients ξ and η on the intermediate state symmetries, by Eq.4-20 and Eq.4-18. The diagonalization of Eq.4-19 involves the solution of a cubic secular equation, and the energies of the bands, given by

$$E_s(\vec{k}) = E_s(0) + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{\ell \neq \{s\}} \frac{\langle s | \vec{k} \cdot \vec{p} | \ell \rangle \langle \ell | \vec{k} \cdot \vec{p} | s \rangle}{E_s - E_\ell}$$

$$= E_s(0) + \frac{\hbar^2}{2} \sum_{\beta} k_{\beta}^2 \left[\frac{1}{m_s^*(\vec{k})} \right]_{\beta\beta},$$

depend, for a given magnitude k , on the direction $\hat{k}$. The states $|s\rangle \equiv |1\rangle, |2\rangle, |3\rangle$ are

$$|s\rangle = \sum_{j=x,y,z} u_{js} |j\rangle,$$

where u (a function of $\hat{k}$) is the unitary matrix which diagonalizes Eq.4-19.

Let us suppose that $\xi = \eta$. As will be shown in a moment this leads to spherical energy bands. Our supposition implies, by Eq.4-20, that $\sigma^3 = \sigma^5$, or that, in the sum over intermediate states, those of symmetry E_g give the same contribution as those of symmetry T_{2g} . Usually the states with these symmetries of most consequence are those that derive from atomic d-states. We can therefore say, approximately, that p-like valence bands at

$\vec{k} = 0$ are spherical if the E_g and T_{2g} states derived from atomic d-states are negligibly crystal-field split. (This is also true of Γ^6 and Γ^8 bands derived from spin-orbit split T_{1g} bands (which will not be shown here) as can be seen by inspecting the valence bands of KI and CsI of Fig.5-9 and Fig.5-7.)

Returning to Eq.4-19, with $\xi = \eta$, let us focus our attention on the second matrix on the right, since the first is invariant under any unitary transformation. We will factor out the magnitude k and, as in the last section, let $\hat{k} = (K_x, K_y, K_z)$. The determinantal equation

$$\det \begin{vmatrix} K_x^2 - \lambda & K_x K_y & K_x K_z \\ K_x K_y & K_y^2 - \lambda & K_y K_z \\ K_x K_z & K_y K_z & K_z^2 - \lambda \end{vmatrix} = 0$$

has solutions $\lambda = 1$ and $\lambda = 0$ (twice). The unitary transformation which gives the states $|s\rangle$ in terms of $|x\rangle$, $|y\rangle$ and $|z\rangle$ is obtained from

$$(K_x^2 - \lambda_s) u_{xs} + K_x K_y u_{ys} + K_x K_z u_{zs} = 0$$

$$K_x K_y u_{xs} + (K_y^2 - \lambda_s) u_{ys} + K_y K_z u_{zs} = 0$$

$$K_x K_z u_{xs} + K_y K_z u_{ys} + (K_z^2 - \lambda_s) u_{zs} = 0$$

For $\lambda_s = 1 \equiv \lambda_1$, $(u_{x1}, u_{y1}, u_{z1}) = (K_x, K_y, K_z)$.

Since $\lambda_2 = \lambda_3 = 0$ we can choose any two vectors orthogonal to (K_x, K_y, K_z) . We will choose these

to be $(\theta_x, \theta_y, \theta_z)$ and (ϕ_x, ϕ_y, ϕ_z) which are the usual unit vectors denoted by $\hat{\theta}$ and $\hat{\phi}$:

$$\hat{k} = \hat{i} \sin \theta \cos \phi + \hat{j} \sin \theta \sin \phi + \hat{k} \cos \theta$$

$$\hat{\theta} = \hat{i} \cos \theta \cos \phi + \hat{j} \cos \theta \sin \phi - \hat{k} \sin \theta$$

$$\hat{\phi} = -\hat{i} \sin \phi + \hat{j} \cos \phi$$

In summation we have

$$\left[\sum_l' \frac{\langle s | \vec{k} \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | s' \rangle}{E_s - E_l} \right]$$

$$= \frac{1}{2} [\sigma^4 + \sigma^5] k^2 \mathbb{1} + \xi k^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

with (see Appendix A)

$$[\sigma^4 + \sigma^5] + 2\xi = \left[\frac{m^2}{m_1^*} - m \right]$$

$$[\sigma^4 + \sigma^5] = \left[\frac{m^2}{m_2^*} - m \right] \quad (4-21)$$

$$\xi = \frac{1}{2} \left[\frac{m^2}{m_1^*} - \frac{m^2}{m_2^*} \right] = \frac{m^2}{2} \left[\frac{1}{\mu_2} - \frac{1}{\mu_1} \right] \equiv \frac{m^2}{2} \left(\Delta \frac{1}{\mu} \right)$$

where m_1^* and m_2^* are the effective masses of the non-degenerate and the two-fold degenerate bands, respectively, and $\mu_s^{-1} \equiv (m_c^*)^{-1} - (m_s^*)^{-1}$ is the reduced reciprocal effective mass.

$$|s\rangle = \sum_j u_{js} |j\rangle, \quad (4-22)$$

where

$$U = \begin{bmatrix} K_x & \theta_x & \phi_x \\ K_y & \theta_y & \phi_y \\ K_z & \theta_z & \phi_z \end{bmatrix} \quad (4-23)$$

The problem now is to determine the angular dependence of absorption for transitions to a conduction band (which we will assume to be totally symmetric) from two spherical valence bands. The situation is depicted in Fig. 4-1. The degeneracies of the bands are indicated in parentheses (the ordering of the valence bands is arbitrary). In calculating the absorption coefficient we will need to know the expression

$$\sum_l' \left\{ \frac{\langle s | \vec{k} \cdot \vec{p} | l \rangle \langle l | \hat{E} \cdot \vec{p} | s' \rangle}{E_s - E_l} + \frac{\langle s | \hat{E} \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | s' \rangle}{E_s - E_l} \right\}.$$

In a manner identical to that of finding Eq. 4-19 we obtain (with $\hat{E} \equiv (\ell, m, n)$)

$$\begin{aligned} & \sum_l' \left\{ \frac{\langle i | \vec{k} \cdot \vec{p} | l \rangle \langle l | \hat{E} \cdot \vec{p} | j \rangle}{E_i - E_l} + \frac{\langle i | \hat{E} \cdot \vec{p} | l \rangle \langle l | \vec{k} \cdot \vec{p} | j \rangle}{E_i - E_l} \right\} \\ &= [\sigma^4 + \sigma^5] (\hat{E} \cdot \vec{k}) \mathbb{1} + \begin{bmatrix} 2\ell k_x & \ell k_y + m k_x & \ell k_z + n k_x \\ \ell k_y + m k_x & 2m k_y & m k_z + n k_y \\ \ell k_z + n k_x & m k_z + n k_y & 2n k_z \end{bmatrix} \end{aligned}$$

Multiplication from the left by $U^\dagger$ and from the right by

Fig.4-1. Two-photon absorption for spherical p-like bands

$\mathcal{U}$ yields

$$\left[\sum_{\ell}' \left\{ \frac{\langle s | \vec{k} \cdot \vec{p} | \ell \rangle \langle \ell | \hat{\vec{E}} \cdot \vec{p} | s' \rangle}{E_s - E_{\ell}} + \frac{\langle s | \hat{\vec{E}} \cdot \vec{p} | \ell \rangle \langle \ell | \vec{k} \cdot \vec{p} | s' \rangle}{E_s - E_{\ell}} \right\} \right]$$

$$= [\sigma^4 + \sigma^5] (\hat{\vec{E}} \cdot \hat{\vec{k}}) k_1 + \xi k \begin{bmatrix} 2\hat{\vec{E}} \cdot \hat{\vec{k}} & \hat{\vec{E}} \cdot \hat{\vec{\theta}} & \hat{\vec{E}} \cdot \hat{\vec{\phi}} \\ \hat{\vec{E}} \cdot \hat{\vec{\theta}} & 0 & 0 \\ \hat{\vec{E}} \cdot \hat{\vec{\phi}} & 0 & 0 \end{bmatrix}$$

(4-24)

The second-order matrix element of Eq.2-10 is

$$P_{fg}^{(2)} = \frac{\hbar k}{m} \sum_{\ell \neq c} \left[\frac{\langle c | \hat{\vec{k}} \cdot \vec{p} | \ell \rangle \langle \ell | \hat{\vec{E}}_1 \cdot \vec{p} | c \rangle}{E_c - E_{\ell}} + \frac{\langle c | \hat{\vec{E}}_1 \cdot \vec{p} | \ell \rangle \langle \ell | \hat{\vec{k}} \cdot \vec{p} | c \rangle}{E_c - E_{\ell}} \right] \frac{\langle c | \hat{\vec{E}}_1 \cdot \vec{p} | s' \rangle}{\hbar \omega_1}$$

$$- \frac{\hbar k}{m} \sum_{\ell \neq v} \sum_s \frac{\langle c | \hat{\vec{E}}_1 \cdot \vec{p} | s \rangle}{\hbar \omega_2} \left[\frac{\langle s | \hat{\vec{k}} \cdot \vec{p} | \ell \rangle \langle \ell | \hat{\vec{E}}_2 \cdot \vec{p} | s' \rangle}{E_{s'} - E_{\ell}} + \frac{\langle s | \hat{\vec{E}}_2 \cdot \vec{p} | \ell \rangle \langle \ell | \hat{\vec{k}} \cdot \vec{p} | s' \rangle}{E_{s'} - E_{\ell}} \right]$$

$$+ (1 \leftrightarrow 2)$$

$$\equiv \frac{\hbar k}{m} P_{cs'}^{(2)},$$

where the symbol $(1 \leftrightarrow 2)$ means similar terms with the subscripts 1 and 2 on $\hat{\vec{E}}$ and ω interchanged. Substitution into Eq.2-7 yields

$$\alpha^{(2)} = A' \sum_f |P_{fg}|^2 \delta [E_{fg} - \hbar(\omega_1 + \omega_2)]$$

$$\begin{aligned}
&= A' \frac{\hbar^2}{m^2} \frac{V}{(2\pi)^3} \sum_{s'} \int d^3k \, k^2 |P_{cs'}^{(2)}|^2 \delta \left[E_{gap} + \frac{\hbar k^2}{2\mu_{s'}} - \hbar(\omega_1 + \omega_2) \right] \\
&= A' \frac{\hbar^2}{m^2} \frac{V}{(2\pi)^3} \int k^4 dk \sum_{s'} \int d\Omega_k |P_{cs'}^{(2)}|^2 \delta \left[E_{gap} + \frac{\hbar k^2}{2\mu_{s'}} - \hbar(\omega_1 + \omega_2) \right]
\end{aligned}$$

where A' is defined in Eq.4-12. We perform the integral over k , using Eq.4-14:

$$\alpha^{(2)} = A' \frac{\hbar^2}{m^2} \frac{V}{(2\pi)^3} \frac{1}{2} \left(\frac{2}{\hbar^2} \right)^{5/2} [\hbar(\omega_1 + \omega_2) - E_{gap}]^{3/2} \sum_{s'} \int d\Omega_k \mu_{s'}^{5/2} |P_{cs'}^{(2)}|^2$$

Using Eq.4-24 and the fact that $\langle c | \hat{\mathbf{E}} \cdot \hat{\mathbf{p}} | s \rangle = \hat{\mathbf{E}} \cdot \hat{\mathbf{r}}_s \langle c | p_x | x \rangle$
 $\equiv \hat{\mathbf{E}} \cdot \hat{\mathbf{r}}_s \langle p \rangle_{cv}$, where $\hat{\mathbf{r}}_s$, by Eq.4-22 and Eq.4-23,
 is $\hat{\mathbf{k}}, \hat{\boldsymbol{\theta}}$ or $\hat{\boldsymbol{\phi}}$, we obtain

$$\begin{aligned}
\alpha^{(2)} &= A' \frac{V}{(2\pi)^3} \frac{\hbar^2}{m^2} \frac{1}{2} \left(\frac{2}{\hbar^2} \right)^{5/2} [\hbar(\omega_1 + \omega_2) - E_{gap}]^{3/2} |\langle p \rangle_{cv}|^2 \int d\Omega_k \\
&\times \left\{ \mu_1^{5/2} \left| \frac{(\hat{\mathbf{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathbf{E}}_2 \cdot \hat{\mathbf{k}})}{\hbar \omega_1} \left[\frac{m^2}{m_c^*} - m \right] - \frac{(\hat{\mathbf{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathbf{E}}_2 \cdot \hat{\mathbf{k}})}{\hbar \omega_2} \left[\frac{m^2}{m_1^*} - m \right] \right. \right. \\
&\quad \left. \left. - \left[\frac{(\hat{\mathbf{E}}_1 \cdot \hat{\boldsymbol{\theta}})(\hat{\mathbf{E}}_2 \cdot \hat{\boldsymbol{\theta}})}{\hbar \omega_2} + \frac{(\hat{\mathbf{E}}_1 \cdot \hat{\boldsymbol{\phi}})(\hat{\mathbf{E}}_2 \cdot \hat{\boldsymbol{\phi}})}{\hbar \omega_2} \right] \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) + (1 \leftrightarrow 2) \right| \right|^2 \\
&+ \mu_2^{5/2} \left| \frac{(\hat{\mathbf{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathbf{E}}_2 \cdot \hat{\boldsymbol{\theta}})}{\hbar \omega_1} \left[\frac{m^2}{m_c^*} - m \right] - \frac{(\hat{\mathbf{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathbf{E}}_2 \cdot \hat{\boldsymbol{\theta}})}{\hbar \omega_2} \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right. \\
&\quad \left. - \frac{(\hat{\mathbf{E}}_1 \cdot \hat{\boldsymbol{\theta}})(\hat{\mathbf{E}}_2 \cdot \hat{\mathbf{k}})}{\hbar \omega_2} \left[\frac{m^2}{m_2^*} - m \right] + (1 \leftrightarrow 2) \right| \right|^2
\end{aligned}$$

$$+ \mu_2^{5/2} \left\{ \frac{(\hat{\mathcal{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathcal{E}}_2 \cdot \hat{\boldsymbol{\phi}})}{\hbar \omega_1} \left[\frac{m^2}{m_e^*} - m \right] - \frac{(\hat{\mathcal{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathcal{E}}_2 \cdot \hat{\mathbf{k}})}{\hbar \omega_2} \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right. \\ \left. - \frac{(\hat{\mathcal{E}}_1 \cdot \hat{\boldsymbol{\phi}})(\hat{\mathcal{E}}_2 \cdot \hat{\mathbf{k}})}{\hbar \omega_2} \left[\frac{m^2}{m_e^*} - m \right] + (1 \leftrightarrow 2) \right\}^2$$

The integrand can be rewritten

$$m^4 \mu_1^{5/2} \left| (\hat{\mathcal{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathcal{E}}_2 \cdot \hat{\mathbf{k}}) \left[\frac{1}{\hbar \omega_1} + \frac{1}{\hbar \omega_2} \right] \frac{1}{\mu_1} \right. \\ \left. - [(\hat{\mathcal{E}}_1 \cdot \hat{\boldsymbol{\theta}})(\hat{\mathcal{E}}_2 \cdot \hat{\boldsymbol{\theta}}) + (\hat{\mathcal{E}}_1 \cdot \hat{\boldsymbol{\phi}})(\hat{\mathcal{E}}_2 \cdot \hat{\boldsymbol{\phi}})] \left[\frac{1}{\hbar \omega_1} + \frac{1}{\hbar \omega_2} \right] \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right|^2 \\ + m^4 \mu_2^{5/2} \left| (\hat{\mathcal{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathcal{E}}_2 \cdot \hat{\boldsymbol{\theta}}) \left[\frac{1}{\hbar \omega_1} \frac{1}{\mu_2} - \frac{1}{\hbar \omega_2} \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right] \right. \\ \left. + (\hat{\mathcal{E}}_1 \cdot \hat{\boldsymbol{\theta}})(\hat{\mathcal{E}}_2 \cdot \hat{\mathbf{k}}) \left[\frac{1}{\hbar \omega_2} \frac{1}{\mu_2} - \frac{1}{\hbar \omega_1} \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right] \right|^2 \\ + m^4 \mu_2^{5/2} \left| (\hat{\mathcal{E}}_1 \cdot \hat{\mathbf{k}})(\hat{\mathcal{E}}_2 \cdot \hat{\boldsymbol{\phi}}) \left[\frac{1}{\hbar \omega_1} \frac{1}{\mu_2} - \frac{1}{\hbar \omega_2} \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right] \right. \\ \left. + (\hat{\mathcal{E}}_1 \cdot \hat{\boldsymbol{\phi}})(\hat{\mathcal{E}}_2 \cdot \hat{\mathbf{k}}) \left[\frac{1}{\hbar \omega_2} \frac{1}{\mu_2} - \frac{1}{\hbar \omega_1} \frac{1}{2} \left(\Delta \frac{1}{\mu} \right) \right] \right|^2.$$

Taking the absolute squares and integrating over the angles we obtain, after considerable algebra,

$$\begin{aligned}
\alpha^{(2)} &= \frac{1}{5} B' \\
&\times \left[(\hat{\mathcal{E}}_1 \cdot \hat{\mathcal{E}}_2)^2 \left\{ \sqrt{\mu_1} \left[3 - 2 \left(\frac{\mu_1}{\mu_2} - 1 \right) + 2 \left(\frac{\mu_1}{\mu_2} - 1 \right)^2 \right] \right. \right. \\
&\quad \left. \left. + \frac{1}{2} \sqrt{\mu_2} \left[1 + \frac{\mu_2}{\mu_1} \right]^2 \right\} \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 \right. \\
&\quad \left. + (\hat{\mathcal{E}}_1 \times \hat{\mathcal{E}}_2)^2 \left\{ \frac{1}{4} \sqrt{\mu_1} \left[1 + \frac{\mu_1}{\mu_2} \right]^2 \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 \right. \right. \\
&\quad \left. \left. + 2 \sqrt{\mu_2} [2a^2 + 2b^2 - ab] \right\} \right]
\end{aligned}$$

(4-25)

where

$$\begin{aligned}
a &\equiv \frac{1}{\hbar\omega_1} - \frac{1}{\hbar\omega_2} \frac{1}{2} \left(1 - \frac{\mu_2}{\mu_1} \right), \\
b &\equiv \frac{1}{\hbar\omega_2} - \frac{1}{\hbar\omega_1} \frac{1}{2} \left(1 - \frac{\mu_2}{\mu_1} \right),
\end{aligned}$$

and B' is defined by Eq.4-16.

Thus we have the result, when the conduction band is totally symmetric, that a spherical splitting of a p-like valence band does not alter the absorption's independence of the orientation of the polarizations with respect to the crystal axes. The splitting, however, changes the expression for the ratio of parallel polarization absorption to perpendicular polarization absorption. This ratio is seen to be a rather complicated function of the photon energies and the ratio of reduced effective masses. To determine how severe the splitting effect is on this

ratio, the maximum and minimum of $\alpha_{\parallel}^{(2)} / \alpha_{\perp}^{(2)}$ has been plotted, and the curves are given in Fig.4-2 and Fig.4-3. Fig.4-2 applies when $\mu_1 \geq \mu_2$ and Fig.4-3 is for

$\mu_2 \geq \mu_1$. The upper curve in each figure represents the maximum ratio, which occurs when $\hbar\omega_1 = \hbar\omega_2$; the lower curves give the minimum ratio, which is the limit as $\hbar\omega_1$ becomes large compared with $\hbar\omega_2$, or vice-versa. Thus, for a given reduced mass ratio, the ratio of $\alpha_{\parallel}^{(2)}$ to $\alpha_{\perp}^{(2)}$ lies within the shaded portion, its precise value determined by the photon energies. The range of $\alpha_{\parallel}^{(2)} / \alpha_{\perp}^{(2)}$ does not differ too drastically from the range $1 \rightarrow 2$ when $\mu_2 = \mu_1$ except when μ_1 is much larger than μ_2 . The curves in Fig.4-2 approach the limit 8 with no photon energy dependence for large μ_1 / μ_2 .

For crystals in which two-photon forbidden transitions at the Γ -point have been observed, mostly heavy halides, the spin-orbit coupling is appreciable. Although it is a simple matter to determine the energy dependence of spin-orbit split p-like bands near $\vec{k} = 0$, finding an equation analogous to Eq.4-24 is not, nor would be the evaluation of the required integrals over k-space. For this reason the inclusion of spin-orbit coupling has been omitted. In itself our calculation is of limited usefulness until experiments are performed on crystals having negligibly spin-orbit split p-like spherical valence bands, such as, perhaps, some chlorides. However, this calculation serves

to show that $\vec{k} \cdot \vec{p}$ splitting does affect the polarization dependence, at the very least to the extent of altering the ratio of maximum to minimum absorption.

Fig.4-2. Ratio of parallel to perpendicular polarization absorption for $\mu_1 > \mu_2$

Fig.4-3. Ratio of parallel to perpendicular polarization absorption for $\mu_2 > \mu_1$

D. X-point Transitions

The preceding sections in this chapter have dealt with transitions at the Γ -point in cubic and tetrahedral crystals. If an extremum occurs at some other point where the conduction band and valence band have opposite parity, the polarization dependence will generally be different, because of the non-spherical nature of the energy surfaces. In this section we will consider transitions at the X-point in simple cubic and face-centered cubic crystals (see Fig.E-1 in Appendix E.)

The group of the wave vector at X is D_{4h} , so that symmetry dictates that the surfaces of constant energy near X be ellipsoids of revolution for non-degenerate bands and for bands degenerate at X which remain degenerate near X. The energy surfaces are described by

$$\begin{aligned} E_n(\vec{k}) &= E_n(\vec{k}_0 + \vec{k}') \\ &= E_n(\vec{k}_0) + \frac{\hbar^2}{2} [a(k'_{r_1})^2 + a(k'_{r_2})^2 + b(k'_{r_3})^2] \end{aligned}$$

where (r_1, r_2, r_3) is any permutation of (x, y, z) ; k_0 is one of the X-points, and

$$\begin{aligned} a &= \left(\frac{1}{m_n^*} \right)_{r_1 r_1} = \left(\frac{1}{m_n^*} \right)_{r_2 r_2} \\ b &= \left(\frac{1}{m_n^*} \right)_{r_3 r_3} \end{aligned}$$

Fig.4-4 is a sketch of the surfaces when they are prolate spheroids, when $a > b$. The surfaces can also be oblate

Fig.4-4. Constant energy surfaces near X-point extremum

spheroids, for which $a < b$. The dotted lines indicate the intersections of zone surfaces $\vec{k} = \frac{1}{2}\vec{K}_{r_i}$, where $\vec{K}_{r_i}$ is a reciprocal lattice vector. The states corresponding to the values $\vec{k}$ on the surface of each ellipsoid are equivalent to the states having value $\vec{k} - \vec{K}_{r_i}$. We have therefore indicated by heavy lines the $\vec{k}$ values which we will use.

The second order matrix element is

$$\begin{aligned}
 P_{fg}^{(2)} &\equiv \frac{\hbar k'}{m} P_{cv}^{(2)}(k_0) = \\
 &\frac{\hbar k'}{m} \sum_{\ell}' \left[\frac{\langle c_i(k_0) | \hat{k}' \cdot \vec{p} | \ell(k_0) \rangle \langle \ell(k_0) | \hat{E}_1 \cdot \vec{p} | c_i(k_0) \rangle \langle c_i(k_0) | \hat{E}_2 \cdot \vec{p} | v_j(k_0) \rangle}{(E_c - E_{\ell}) \hbar \omega_1} \right. \\
 &\quad + \frac{\langle c_i(k_0) | \hat{E}_1 \cdot \vec{p} | \ell(k_0) \rangle \langle \ell(k_0) | \hat{k}' \cdot \vec{p} | c_i(k_0) \rangle \langle c_i(k_0) | \hat{E}_2 \cdot \vec{p} | v_j(k_0) \rangle}{(E_c - E_{\ell}) \hbar \omega_1} \\
 &\quad - \frac{\langle c_i(k_0) | \hat{E}_1 \cdot \vec{p} | v_j(k_0) \rangle \langle v_j(k_0) | \hat{k}' \cdot \vec{p} | \ell(k_0) \rangle \langle \ell(k_0) | \hat{E}_2 \cdot \vec{p} | v_j(k_0) \rangle}{(E_v - E_{\ell}) \hbar \omega_2} \\
 &\quad - \frac{\langle c_i(k_0) | \hat{E}_1 \cdot \vec{p} | v_j(k_0) \rangle \langle v_j(k_0) | \hat{E}_2 \cdot \vec{p} | \ell(k_0) \rangle \langle \ell(k_0) | \hat{k}' \cdot \vec{p} | v_j(k_0) \rangle}{(E_v - E_{\ell}) \hbar \omega_2} \\
 &\quad \left. + (1 \leftrightarrow 2) \right]
 \end{aligned}$$

Recalling that

$$\begin{aligned}
 \sum_{\ell}' &\left[\frac{\langle n(k_0) | \hat{k} \cdot \vec{p} | \ell(k_0) \rangle \langle \ell(k_0) | \hat{E} \cdot \vec{p} | n(k_0) \rangle}{E_n - E_{\ell}} \right. \\
 &\quad \left. + \frac{\langle n(k_0) | \hat{E} \cdot \vec{p} | \ell(k_0) \rangle \langle \ell(k_0) | \hat{k} \cdot \vec{p} | n(k_0) \rangle}{E_n - E_{\ell}} \right]
 \end{aligned}$$

$$= \hat{k} \cdot \left[\left(\frac{\vec{m}^2}{m_n^*} \right) - m \mathbb{1} \right] \cdot \hat{\epsilon}$$

we have

$$P_{cv}^{(2)}(k_0) = m^2 \left[\hat{k}' \cdot \left(\frac{\vec{1}}{\mu_{k_0}} \right) \cdot \hat{\epsilon}_1 \frac{\langle C_i(k_0) | \hat{\epsilon}_2 \cdot \vec{p} | V_j(k_0) \rangle}{\hbar \omega_1} + \hat{k}' \cdot \left(\frac{\vec{1}}{\mu_{k_0}} \right) \cdot \hat{\epsilon}_2 \frac{\langle C_i(k_0) | \hat{\epsilon}_1 \cdot \vec{p} | V_j(k_0) \rangle}{\hbar \omega_2} \right] \quad (4-26)$$

From Eq.2-7

$$\begin{aligned} \alpha^{(2)} &= A' \frac{\hbar^2}{m^2} \frac{V}{(2\pi)^3} \sum_{i,j,k_0} \int d^3 k' (k')^2 |P_{cv}^{(2)}(k_0)|^2 \delta \left[E_{gap} + \frac{\hbar^2}{2} \hat{k}' \cdot \left(\frac{\vec{1}}{\mu_{k_0}} \right) \cdot \hat{k}' - \hbar(\omega_1 + \omega_2) \right] \\ &= A' \frac{\hbar^2}{m^2} \frac{V}{(2\pi)^3} \frac{1}{2} \left(\frac{2}{\hbar^2} \right)^{5/2} [\hbar(\omega_1 + \omega_2) - E_{gap}]^{3/2} \sum_{i,j,k_0} \int d\Omega_{k'} \frac{|P_{cv}^{(2)}(k_0)|^2}{\left[\hat{k}' \cdot \left(\frac{\vec{1}}{\mu_{k_0}} \right) \cdot \hat{k}' \right]^{5/2}} \end{aligned} \quad (4-27)$$

Consider the X-point on the k_z axis. The matrix element

$$\langle C_i(k_{0z}) | \hat{\epsilon} \cdot \vec{p} | V_j(k_{0z}) \rangle \quad \text{is non-zero only if } X^c \times X^v$$

contains X_2 or X_5 . Let us suppose that $|V_j(k_{0z})\rangle =$

$|X_1(k_{0z})\rangle$ and $|C_i(k_{0z})\rangle = |X_2(k_{0z})\rangle$. Then (for $\hat{\epsilon} = (1, m, n)$)

$$\begin{aligned} \langle X_2(k_{0z}) | \hat{\epsilon} \cdot \vec{p} | X_1(k_{0z}) \rangle &= n \langle X_2 | p_z | X_1 \rangle \\ &= n \langle p \rangle_{cv} \end{aligned} \quad (4-28)$$

If $|C_i(k_{0z})\rangle = |X_{5i}(k_{0z})\rangle,$

$$\begin{aligned}
\langle X_{51}(k_{0z}) | \hat{\mathbf{E}} \cdot \vec{p} | X_1(k_{0z}) \rangle &= \ell \langle X_{51} | p_x | X_1 \rangle \\
&= \ell \langle p \rangle_{cv}, \\
\langle X_{52}(k_{0z}) | \hat{\mathbf{E}} \cdot \vec{p} | X_1(k_{0z}) \rangle &= m \langle p \rangle_{cv}. \quad (4-29)
\end{aligned}$$

Expanding the absolute square in Eq.4-27, the integral over the angles of the first term is

$$\begin{aligned}
&m^4 \sum_i \frac{|\langle c_i | \hat{\mathbf{E}}_2 \cdot \vec{p} | v \rangle|^2}{(\hbar \omega_1)^2} \int d\Omega_{\vec{k}'} \frac{\left[\vec{k}' \cdot \left(\frac{1}{\mu_{k_{0z}}} \right) \cdot \hat{\mathbf{E}}_1 \right]^2}{\left[\vec{k}' \cdot \left(\frac{1}{\mu_{k_{0z}}} \right) \cdot \vec{k}' \right]^{5/2}} \\
&= m^4 \sum_i \frac{|\langle c_i | \hat{\mathbf{E}}_2 \cdot \vec{p} | v \rangle|^2}{(\hbar \omega_1)^2} \int d\Omega_{\vec{k}'} \frac{(a\ell k_x + am k_y + bn k_z)^2}{[a k_x^2 + a k_y^2 + b k_z^2]^{5/2}} \\
&= m^4 \sum_i \frac{|\langle c_i | \hat{\mathbf{E}}_2 \cdot \vec{p} | v \rangle|^2}{(\hbar \omega_1)^2} \frac{4\pi}{3} \frac{1}{\sqrt{b}} \left[\ell^2 + m^2 + \frac{b}{a} n^2 \right]
\end{aligned}$$

The cross terms in the absolute square give

$$\begin{aligned}
&\frac{m^4}{(\hbar \omega_1)(\hbar \omega_2)} \sum_i \left\{ \langle c_i | \hat{\mathbf{E}}_1 \cdot \vec{p} | v \rangle \langle c_i | \hat{\mathbf{E}}_2 \cdot \vec{p} | v \rangle^* + \text{c.c.} \right\} \\
&\quad \times \int d\Omega_{\vec{k}'} \frac{\left[\vec{k}' \cdot \left(\frac{1}{\mu_{k_{0z}}} \right) \cdot \hat{\mathbf{E}}_1 \right] \left[\vec{k}' \cdot \left(\frac{1}{\mu_{k_{0z}}} \right) \cdot \hat{\mathbf{E}}_2 \right]}{\left[\vec{k}' \cdot \left(\frac{1}{\mu_{k_{0z}}} \right) \cdot \vec{k}' \right]^{5/2}} \\
&= \frac{m^4}{(\hbar \omega_1)(\hbar \omega_2)} \sum_i \left\{ \langle c_i | \hat{\mathbf{E}}_1 \cdot \vec{p} | v \rangle \langle v | \hat{\mathbf{E}}_2 \cdot \vec{p} | c_i \rangle + \text{c.c.} \right\} \\
&\quad \times \frac{4\pi}{3} \frac{1}{\sqrt{b}} \left[\ell_1 \ell_2 + m_1 m_2 + \frac{b}{a} n_1 n_2 \right]
\end{aligned}$$

Similar expressions result for the two other X-points, with l and n permuted and m and n permuted. Using these expressions and Eq.4-28 and Eq.4-29 we obtain

$$\underline{X_1^{\pm} \longleftrightarrow X_2^{\mp}}$$

$$\alpha^{(2)} = B' \frac{1}{\sqrt{b}} \left\{ (\hat{\epsilon}_1 \cdot \hat{\epsilon}_2)^2 \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 + (\hat{\epsilon}_1 \times \hat{\epsilon}_2)^2 \left[\left(\frac{1}{\hbar\omega_1} \right)^2 + \left(\frac{1}{\hbar\omega_2} \right)^2 \right] \right. \\ \left. + [\ell_1^2 \ell_2^2 + m_1^2 m_2^2 + n_1^2 n_2^2] \left[\frac{b}{a} - 1 \right] \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 \right\}$$

(4-30)

$$\underline{X_1^{\pm} \longleftrightarrow X_5^{\mp}}$$

$$\alpha^{(2)} = B' \frac{1}{\sqrt{b}} \left\{ (\hat{\epsilon}_1 \cdot \hat{\epsilon}_2)^2 \left[\frac{b}{a} + 1 \right] \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 \right. \\ \left. + (\hat{\epsilon}_1 \times \hat{\epsilon}_2)^2 \left[\frac{b}{a} + 1 \right] \left[\left(\frac{1}{\hbar\omega_1} \right)^2 + \left(\frac{1}{\hbar\omega_2} \right)^2 \right] \right. \\ \left. - [\ell_1^2 \ell_2^2 + m_1^2 m_2^2 + n_1^2 n_2^2] \left[\frac{b}{a} - 1 \right] \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2} \right]^2 \right\}$$

(4-31)

where B' is defined in Eq.4-16.

When a forbidden transition occurs at the X-point the absorption coefficient is seen to have two important features. It depends on the symmetries of the valence and conduction bands, and it depends on the orientation of the polarization vectors with respect to the crystal axes. In the limit $b = a$, i. e., spherical energy surfaces, the absorption coefficient reduces to the form given in Eq.4-15 for Γ -point transitions.

Chapter V

Application to Experiment

The optical spectra of solids generally show complicated structures over wide ranges of energy, and the interpretation of the various peaks and steps in an absorption spectrum aids in understanding the electronic structure of a material. Studies of the polarization dependence of two-photon absorption are aimed at examining the symmetry properties of the electronic states responsible for the absorption. This chapter contains a brief review of some two-photon absorption experiments in which polarization studies have been made and includes an examination of the experimental data in terms of the theory discussed in Chapters III and IV. The first two materials (CuCl and ZnS) crystallize in structures without inversion symmetry, and so one expects to discuss the polarization dependences in terms of allowed transitions. The last four (RbI, CsI, KI, and TlCl) have inversion invariant structures in which the valence band and conduction band states at the band minima are of opposite parity, indicating forbidden transitions near the absorption edge.

A. CuCl

Two-photon measurements on CuCl were made by Fröhlich, Staginnus and Schönherr,¹³ who for the first time reported sharp exciton lines in a two-photon spectrum. CuCl has T_d point group symmetry (which does not contain the inversion) and therefore there are no parity-forbidden transitions. The band gap, according to the energy band calculations of Song⁵⁸ (see Fig.5-1), is 3.43 eV, neglecting spin-orbit coupling, and occurs at the Γ -point. Spin-orbit coupling splits the valence band at Γ by 0.072 eV.⁵⁸ The two-photon spectrum of Fröhlich, Staginnus and Schönherr is shown in Fig.5-2. Cardona⁵⁹ observed relatively weak one-photon absorption in the region above the exciton lines, in contrast to the strong two-photon absorption in this region. The polarization dependence of the two-photon absorption was studied by Fröhlich et al. at the energy of the second exciton (3.29 eV) and in the continuum region (3.5 eV). Their results for the exciton line are shown in Fig.5-3; they did not report their results for 3.5 eV, but stated that they were different. In Fig.5-3 θ is the angle in a (100) plane between the probe polarization and a [100] axis. Parts (a) and (b) give the absorption coefficient as a function of θ with the laser polarized at 0° and 135° , respectively. The data points in (a) are seen to be described by $\sin^2\theta$, and in (b) by $\frac{1}{2}(1-\sin\theta)$. The only angular function which has this behavior is $T_2(\hat{e}_1, \hat{e}_2)$,

which is the angular dependence expected for a T_2 valence band and A_1 conduction band. Actually the valence band is spin-orbit split into a Γ^7 band and a Γ^8 band, indicating an angular dependence $E(\hat{e}_1, \hat{e}_2) + cT_1(\hat{e}_1, \hat{e}_2) + c'T_2(\hat{e}_1, \hat{e}_2)$ for the s exciton derived from Γ^8 and $\Gamma^6(\Gamma')$ states (see Table 3-1). However, the spin-orbit coupling is small, so that the T_2 contribution is expected to dominate.

In the one-photon measurements of Cardona⁵⁹, the region above 3.35 eV is smooth and relatively flat, indicating small absorption at the X-point. Song⁵⁸ has calculated the electric dipole moments for transitions $T_2 \rightarrow A_1$ (3.43 eV) and $X_1, X_5 \rightarrow X_3$ ⁶⁰ (3.77 eV and 3.84 eV). He finds

$$\frac{|\langle \vec{r} \rangle_r|^2}{|\langle \vec{r} \rangle_x|^2} \approx 30 ,$$

which he suggests to be the reason for the lack of structure in the continuum of Cardona's data. For two-photon absorption one needs the matrix elements

$$\sum_l \frac{\langle A_1 | \vec{p} | l \rangle \langle l | \vec{p} | T_2 \rangle}{E_l - E_{T_2} - \hbar\omega} \quad \text{and} \quad \sum_l \frac{\langle X_1 | \vec{p} | l \rangle \langle l | \vec{p} | X_3 \rangle}{E_l - E_{X_3} - \hbar\omega} .$$

The nearest intermediate states at $\vec{k} = 0$ which connect T_2 and A_1 are the lower valence band states of symmetry T_2 and the upper conduction band states of symmetry T_2 . On the other hand, the state at X_5 immediately below X_1

connects X_1 and X_3 . Thus one might find that X-point transitions give a larger contribution to the absorption in the two-photon spectrum than in the one-photon spectrum. If the strong absorption observed by Fröhlich, Stagninus and Schönherr above 3.35 eV is due in part to X-point excitons and continuum transitions, one would expect a polarization dependence different than that observed for the exciton at 3.29 eV. However, the absence of nearby connecting intermediate states at Γ indicates that "forbidden" transitions (i. e. taking place away from the Γ -point, in the band-to-band picture) might give a larger contribution to the absorption than "allowed" transitions. Mahan²⁰ has previously suggested (in the more correct exciton picture) that p-state absorption would be stronger than s-state absorption in the continuum. If this forbidden absorption is larger than the X-point allowed absorption, the polarization dependence would be given by Eq.4-8 or Eq.4-15, again quite different from that of the 3.29eV exciton.

Fig.5-1. Band structure of CuCl (after Song, Ref. 58)

Fig.5-2. Two-photon absorption spectrum of CuCl (after Frohlich, Stagninus and Schonherr, Ref. 13)

Fig.5-3. Polarization dependence of two-photon absorption in CuCl (after Frohlich, Staginnus and Schonherr, Ref. 13)

B. ZnS

ZnS crystallizes in the zinc blende (T_d) and wurtzite (C_{6v}) structures, of which the wurtzite form has been the subject of two-photon absorption measurements.^{61,17}

Energy bands for wurtzite ZnS have been calculated by Bergstresser and Cohen⁶² and are shown in part in Fig.5-4. These energy bands were calculated ignoring spin-orbit interactions. With the inclusion of spin the lowest conduction band at Γ is Γ^7 , while the upper valence bands are Γ^9 , Γ^7 , and Γ^7 , in order of decreasing energy, resulting primarily from combined crystal field and spin-orbit splitting of the 3p states of the sulfur ions. In Fig.5-4 the energy separation between valence bands Γ^7 and Γ^6 (E_1 in the notation of Table 2-1) is 0.05 eV, while the spin-orbit splitting of these states in the absence of the crystal field interaction is 0.09 eV.^{62,63} The relative magnitudes of these energies indicate that the spin-orbit coupling can not be ignored, as it could be for CuCl, in favor of crystal field splitting alone. This conclusion was drawn by Thomas and Hopfield⁶⁴ regarding the valence bands in CdS, which has a band structure closely resembling that of ZnS.⁶² This is important in discussing selection rules for optical absorption.

The two-photon spectrum of wurtzite ZnS has been investigated by Park and Waff⁶¹ and by Reilly.¹⁷ Park and Waff measured the absorption coefficient up to about

4 eV at liquid helium temperature, but they reported no measurements of polarization dependence. Reilly measured the absorption coefficient from 4 eV to 4.4 eV, and the polarization dependence, given in Fig.5-5, at (a) 4.05 eV and (b) 4.15 eV. From Table 3-1 we find that the $\Gamma^9 \rightarrow \Gamma^7$ transition is a constant with respect to θ , the laser polarization, in both case A (probe polarized in xy plane) and case B (probe polarized along the z axis). The $\Gamma^7 \rightarrow \Gamma^7$ transitions, however, behave in case A as $c_1 \sin^2 \theta + c_2 \cos \theta$ where c_1 and c_2 are positive constants, and in case B as a constant. The transitions at both 4.05 eV and 4.15 eV include $\Gamma^9 \rightarrow \Gamma^7$ and $\Gamma^7 \rightarrow \Gamma^7$ transitions. Since the Γ^9 valence band is the highest, the $\Gamma^7 \rightarrow \Gamma^7$ transitions would be expected to give a larger contribution to the absorption at 4.15 eV than at 4.05 eV. This is confirmed in the more pronounced sinusoidal behavior at 4.15 eV in the A case. The possibility that forbidden transitions (wave vector dependent) are responsible for the two-photon absorption can be disregarded, in spite of the fact that the polarization dependence would be qualitatively the same, because forbidden transitions predict a slightly lower ratio of maximum to minimum at the higher energy, in contrast to the increase observed in this ratio.

Fig.5-4. Band structure of ZnS (after Bergstresser and Cohen, Ref. 62)

Fig.5-5. Polarization Dependence of two-photon absorption in ZnS at a) 4.05 eV b) 4.15 eV (after Reilly, Ref. 17)

C. RbI

Fröhlich and Stagninus¹² measured the two-photon absorption spectrum of RbI and several alkali bromides, which have point group O_h . Since O_h contains the inversion, the energy bands have well-defined parity at some points in the Brillouin zone. Generally in alkali halides the uppermost valence bands are derived chiefly from the p-states of the halide ion, becoming Γ_-^8 and Γ_-^6 at $\vec{k} = 0$. The lowest conduction band is composed mostly of alkali s-states, which become Γ_+^6 at $\vec{k} = 0$.⁶⁵ Since the minimum vertical energy gap is usually assumed to be at the center of the zone, the two-photon absorption near the edge can be discussed in terms of the forbidden transitions of Chapter IV, assuming, of course, that the two band model is valid and that the highest valence band (Γ_-^8) has the well-behaved properties required.

The two-photon spectrum of Fröhlich and Stagninus for RbI is given in Fig.5-6 with the one-photon absorption measurements of Teegarden and Baldini.⁶⁶ Also in Fig.5-6 is the polarization dependence of the two-photon absorption for RbI at 6.8 eV. Fröhlich and Stagninus used a ruby laser (1.78 eV) for one of their sources, and a conventional flash lamp for the other (6.8 eV - 1.78 eV = 5.02 eV). The polarization dependence of Fig.5-6 is seen to have the predicted behavior; that is, $(\hat{\epsilon}_1 \cdot \hat{\epsilon}_2)^2$ and a smaller amount of $(\hat{\epsilon}_1 \times \hat{\epsilon}_2)^2$, with the ratio of minimum to maximum

between $\frac{1}{2}$ and 1. More precisely this ratio is estimated from the data to be about 0.625. Mahan¹⁹ has calculated the theoretical value from Eq.4-9 to be

$$\frac{|J_1|^2 + |J_2|^2}{|J_1 + J_2|^2} = 0.69$$

In the simple band model using the above energies of the photons we obtain from Eq.4-17

$$\frac{\left(\frac{1}{\hbar\omega_1}\right)^2 + \left(\frac{1}{\hbar\omega_2}\right)^2}{\left(\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2}\right)^2} = 0.613$$

As we have said in Chapter IV, the closer agreement of the simple band model could be due to errors in the values of the exciton binding energy and the band gap and a possible error due to the sum over intermediate Wannier s-states in the evaluation of J, or in this single instance to accident.

Fig.5-6. Polarization dependence of two-photon absorption and two-photon spectrum of RbI (after Frohlich and Stagninus, Ref. 12). One-photon spectrum is from Teegarden and Baldini, Ref. 66.

D. CsI

CsI has the simple cubic CsCl structure and therefore has point group symmetry O_h . Fröhlich and Stagin¹⁵ measured the two-photon absorption spectrum of CsI shown in the lower diagram of Fig.5-7, superimposed on the one-photon spectrum measured by Teegarden and Baldini.⁶⁶ The upper diagram shows the ratio of $\alpha_{\parallel}^{(2)}$ to $\alpha_{\perp}^{(2)}$ measured by Fröhlich and Stagin¹⁵. Note that this ratio is larger than two over most of the spectrum. This disagreement with the theoretical ratio of Mahan²⁰, as pointed out by Fröhlich and Stagin¹⁵, and of the simpler band model is probably due to the proximity of the $\Gamma_+^8(E_g)$ and $\Gamma_+^6(A_{1g})$ conduction bands (see the CsI band structure, calculated by Onodera,⁶⁷ in Fig.5-8). As we said in Chapter IV, a second conduction band would have to be kept in the intermediate states, and the fact that one is of E_g symmetry invalidates the assumption of a spherical valence band.

The two two-photon peaks at 6.25 eV and 6.42 eV superimposed on the band absorption have been assigned by Fröhlich and Stagin¹⁵ to s excitons associated with X_7^- and $X_7^- (X_3)$, since the only states of the same parity in the correct energy range occur at X.

Fig.5-7. One- and two-photon absorption in CsI

E. KI

KI is face centered cubic (point group O_h). Energy bands have been calculated by Onodera, Okazaki and Inui⁵¹ and are shown in Fig.5-9. The first two-photon spectroscopic experiments on KI were performed by Hopfield, Worlock and Park⁶⁸ and Hopfield and Worlock,⁴ who measured the two-photon absorption up to about 6.4 eV. Park and Stafford¹⁶ have extended the measurements to 7.5 eV. Their data is shown in Fig.5-10 along with the one-photon measurements of Teegarden and Baldini.⁶⁶ Park and Stafford report two peaks in the spectrum, one at 7.21 eV, the other at 7.375 eV. Their attention is focused on the lower energy peak (the second peak will wait until a later date due to difficulties in measurement at 7.375 eV). Park and Stafford believe that the absorption peak at 7.21 results from the same states which produce the one-photon peak at 7.24 eV, due to their similarity in shapes and their proximity in energy. Under the assumption that the two peaks (7.21 eV and 7.24 eV) have the same origin, they argue that the absorption can not be due to an s exciton associated with Γ^- and Γ_+^+ bands, as suggested by Onodera et al.⁵¹ and Teegarden et al.,⁶⁶ since parity would not allow two-photon absorption to this state. On the same basis they discard the possibility of transitions at X . Σ , K , S and Λ lines are disregarded because of unsuitable energy differences and densities of states (see the

energy band calculations of Onodera et al. in Fig.5-9), and hence they conclude that the transitions producing the peak at 7.21 eV occur on Δ . In order to obtain more information about the absorption Park and Stafford measured the polarization dependence at 7.1 eV, which is reproduced in the upper diagram of Fig.5-11. The absorption appears to have a $\cos^2 \alpha$ dependence, where α is the angle between laser and probe polarization vectors. Since all the angular functions of O_h except $A_{1g}(\hat{e}_1, \hat{e}_2)$ have dips when $\hat{e}_1 \cdot \hat{e}_2 = 1$, they conclude that $\Delta_6 \rightarrow \Delta_6$ is the correct choice, this being the only Δ transition which contains an A_{1g} dependence. Park and Stafford seem to be in error here; $\Delta_7 \rightarrow \Delta_7$ also contains an $A_{1g}(\hat{e}_1, \hat{e}_2)$ function, as can be seen in Table E-1 and Table 3-1 for C_{4v} .

There appears, however, to be another possibility. Suppose the transition takes place between the ellipsoidal surfaces about X_7^- and X_7^+ . In Chapter IV we calculated the angular dependence functions for $X_1^\pm \rightarrow X_2^\mp$ and $X_1^\pm \rightarrow X_5^\mp$ transitions. The transition $X_7^- \rightarrow X_7^+$ would have as an angular dependence a linear combination of those functions, since $X_7^- \times X_7^+$ contains X_2 and X_5 (see, for example, Koster et al.⁴²). In Fig.5-9 it can be seen that the effective mass of X_7^+ is larger along Δ than along Σ , so that in Eq.4-30 and Eq.4-31, $a > b$. The precise values of a and b are not known, but for $a = 2b$ we have plotted the angular functions for $X_1 \rightarrow X_5$ and $X_1 \rightarrow X_2$ in the

lower diagram in Fig.5-11, with the conditions of Park and Stafford: $\hbar\omega_1 = 1.78$ eV, $\hbar\omega_2 = 5.43$ eV, and the laser polarized 32° from the (100) axis in a [100] plane. The vertical arrows indicate the angles at which $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ are parallel and perpendicular. We see that the functions have the correct shape, with the maximum for $X_1 \rightarrow X_5$ shifted to the left of 32° and the $X_1 \rightarrow X_2$ maximum shifted to the right. The data of Park and Stafford in the upper diagram appears to have its maximum slightly to the right of 32° . Thus if the matrix element for $X_1 \rightarrow X_2$ is larger than that for $X_1 \rightarrow X_5$, the polarization dependence would be sinusoidal with the maximum shifted in the same way as that measured by Park and Stafford.

The ratios of maximum to minimum, however, are different, with the experimental value of about 1.5 and the calculated value for $X_1 \rightarrow X_2$ of 1.82. This could be due to the fact that a forbidden X-point transition can not be the only transition occurring at 7.21 eV, and small contributions of other transitions could alter this ratio. It should be noted that a sole addition of $X_1 \rightarrow X_5$ dependence can not sufficiently improve the calculated ratio; the minimum ratio for any linear combination of $X_1 \rightarrow X_2$ and $X_1 \rightarrow X_5$ functions is 1.59.

The possibility of the peak at 7.21 eV occurring near X is given some support by the fact that the energy difference (~ 0.15) between the peaks at 7.21 eV and 7.375

is close to the energy difference of points X_7^- and X_6^- of 0.21 eV calculated by Onodera et al., and it is close to the energy difference between the one-photon peaks at 6.7 eV and 6.9 eV which have been interpreted⁵¹ as due to s excitons for X_7^+ , X_7^- and X_6^- , X_7^+ . The question now remains of why a peak did not appear in the one-photon spectrum which would correspond to the $X_6^- \rightarrow X_7^+$ transition. This could result if the one-photon 7.24 peak occurred with $\Gamma_-^8 \rightarrow \Gamma_+^6$ interband absorption which falls off rapidly at slightly higher energy. A more likely possibility, however, is that the 7.24 eV peak does not have its origin in the $X_7^- \rightarrow X_7^+$ transition, but is indeed due to a Γ_-^6 , Γ_+^6 s exciton, as suggested by Onodera et al.⁵¹ and Teegarden et al.⁶⁶

As mentioned earlier, Park and Stafford could not measure the polarization dependence of the peak at 7.375 eV, but they indicated that they would attempt this after new equipment is prepared. Since $X_6^- \times X_7^+$ contains X_5 but not X_2 , we can predict that if in fact the peak at 7.375 eV is due to an $X_6^- \rightarrow X_7^+$ forbidden transition, the polarization dependence will have the behavior indicated in Fig. 5-10 for $X_1 \rightarrow X_5$, with the maximum shifted to the left of 32° .

Fig.5-9. Band structure of KI (after Onodera, Okazaki and Inui, Ref. 51)

Fig.5-10. Two-photon absorption spectrum of KI (after Park and Stafford, Ref. 16). One-photon spectrum is from Teegarden and Baldini, Ref. 66.

Fig.5-11. (a) Polarization dependence of two-photon absorption in KI (after Park and Stafford, Ref. 16). (b) Theoretical dependence for forbidden X-point transitions.

F. TlCl

Matsuoka¹⁴ has measured the two-photon absorption spectrum of TlCl near the absorption edge, from about 3.4 eV to about 3.7 eV, and has obtained polarization dependence data at energies ranging from 3.55 eV to 4.33 eV. At each of these energies the absorption coefficient was measured as a function of the angle θ_1 , of the probe light polarization in a (100) plane with respect to a [100] axis for two angles θ_2 of the laser polarization: $\theta_2 = 0$ and $\theta_2 = \frac{\pi}{4}$. Any final state of the crystal must transform according to a representation of O_h . Therefore the angular dependence for transitions to any possible combination of final states must have the form

$$\alpha^{(2)} = a_1 A_{1g}(\hat{E}_1, \hat{E}_2) + a_2 E_g(\hat{E}_1, \hat{E}_2) \\ + a_3 T_{1g}(\hat{E}_1, \hat{E}_2) + a_4 T_{2g}(\hat{E}_1, \hat{E}_2)$$

where a_i is a positive constant and $A_{1g}(\hat{E}_1, \hat{E}_2)$, etc., are defined in Table 3-1. For Matsuoka's configurations we find

$$\alpha_{\max}^{(2)}(0) = a_1 + a_2$$

$$\alpha_{\min}^{(2)}(0) = a_3 + a_4$$

and

$$\alpha_{\max}^{(2)}\left(\frac{\pi}{4}\right) = a_1 + \frac{1}{4}a_2 + a_4$$

$$\alpha_{\min}^{(2)}\left(\frac{\pi}{4}\right) = \frac{3}{4}a_2 + a_3$$

(The labels indicating maximum and minimum might be interchanged, but this is unimportant here.) Therefore we must have

$$\alpha_{\max}^{(2)}(0) + \alpha_{\min}^{(2)}(0) = \alpha_{\max}^{(2)}\left(\frac{\pi}{4}\right) + \alpha_{\min}^{(2)}\left(\frac{\pi}{4}\right)$$

for any possible combination of final states. Matsuoka's data do not conform to this restriction, and hence his polarization measurements can not be explained in terms of any electronic states of the crystal.

Chapter VI

Conclusion

Angular dependence functions for allowed two-photon absorption have been found for transitions between one-electron states of arbitrary symmetries for Γ -point transitions in all crystal point groups. Those obtained for $\Gamma' \longrightarrow \Gamma''$ transitions agree in most cases with those obtained earlier by Inoue and Toyozawa.¹¹ For non-central symmetry points it was shown how to obtain the angular dependence for transitions between states of arbitrary symmetries using the tables of Inoue and Toyozawa for these symmetry points and the tables for the Γ -point transitions. Angular functions were calculated and tabulated for transitions occurring at symmetry points in hexagonal close-packed and wurtzite structures. The angular functions for allowed transitions are supplementary to those obtained by the earlier workers, and they are intended to aid the experimentalist in determining one-electron state symmetries responsible for observed two-photon absorption.

The angular dependence for forbidden transitions has been calculated in a simple two band model neglecting exciton effects. In this model the ratio of maximum to

minimum absorption was found to be a simple function of the energies of the photons participating in the absorption. The earlier calculation of Mahan²⁰ which included exciton effects gave similar results with, however, a more complicated expression for the ratio of maximum to minimum absorption. The neglect of exciton effects is expected to be a good approximation in the continuum region of the absorption due to the small electron-hole pairs. Since band gap energies and exciton binding energies upon which Mahan's maximum to minimum ratio depends are often not known very accurately, the simpler model is expected to give more accurate results for the polarization dependence in the continuum. This contention has been given experimental support in the measurements on RbI.¹²

The effect of $\vec{k} \cdot \vec{p}$ splitting in the case of p-like valence bands has been shown to alter the ratio of maximum to minimum; when substantial splitting occurs in the valence bands this ratio is no longer confined to values between 1 and 2, as predicted when $\vec{k} \cdot \vec{p}$ splitting is neglected, and this should be kept in mind when interpreting the polarization dependence.

Since the group of the wave vector at the X-point in simple cubic and face-centered cubic structures contains the inversion, forbidden transitions can occur near this point. The energy surfaces about X, however, are not in general spherical, so that the previous calculations are not

applicable. The polarization dependence was calculated for these transitions, and it was found to depend both on the symmetries of the initial and final states and on the orientations of the polarization vectors with respect to the crystal axes. The results were used to suggest that two absorption peaks in KI¹⁶ could be due to transitions near X. The peak upon which polarization dependence measurements were made showed the correct polarization behavior; the polarization dependence of the second peak, which is separated from the first approximately by the energy difference of two valence bands near X, has been predicted on the basis of the symmetries of the valence and conduction bands at this point.

Polarization studies of two-photon absorption in solids very quickly followed the initial theoretical work by Inoue and Toyozawa, and Mahan's extension of the theory to forbidden transitions has given added impetus to the experimental work. The increasing interest in this work reflected in the rising frequency of experimental reports has indicated that further theoretical work has been warranted. It is hoped that the investigations contained herein will be of assistance in the interpretation of two-photon absorption spectra.

Appendix A

$\vec{k} \cdot \vec{p}$ Perturbation Theory

Bloch functions are solutions to an equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_{nk}(\vec{r}) = E_n(k) \psi_{nk}(\vec{r}) \quad (\text{A-1})$$

where $V(\vec{r})$ is a potential which has the periodicity of the crystal lattice. Bloch's theorem states that one can write

$$\psi_{nk}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{nk}(\vec{r}),$$

where $u_{nk}(\vec{r})$ has the periodicity of the lattice. If this expression is substituted into Eq. A-1, one obtains

$$\begin{aligned} \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] u_{nk}(\vec{r}) + \left[\frac{\hbar}{m} \vec{k} \cdot \vec{p} + \frac{\hbar^2 k^2}{2m} \right] u_{nk}(\vec{r}) \\ = E_n(k) u_{nk}(\vec{r}). \end{aligned}$$

If we know the solution of this equation at some point, say $\vec{k} = 0$ for simplicity, an approximate solution at a nearby point can be obtained by treating the second term on the left as a perturbation. Assume that $u_{n0}(\vec{r})$ is non-degenerate. To second order²¹ we have

$$\begin{aligned} E_n(\vec{k}) &= E_{n(0)} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{l \neq n} \frac{\langle n(0) | \vec{k} \cdot \vec{p} | l(0) \rangle \langle l(0) | \vec{k} \cdot \vec{p} | n(0) \rangle}{E_{n(0)} - E_{l(0)}} \\ &= E_{n(0)} + \frac{\hbar^2}{2} \vec{k} \cdot \left(\frac{1}{m^*} \right) \cdot \vec{k} \end{aligned} \quad (\text{A-2})$$

where the effective mass

$$\left(\frac{1}{m^*}\right)_{\alpha\beta} \equiv \frac{1}{m} + \frac{1}{m^2} \sum_{\ell \neq n} \left[\frac{\langle n(o) | p_\alpha | \ell(o) \rangle \langle \ell(o) | p_\beta | n(o) \rangle}{E_n(o) - E_\ell(o)} + \frac{\langle n(o) | p_\beta | \ell(o) \rangle \langle \ell(o) | p_\alpha | n(o) \rangle}{E_n(o) - E_\ell(o)} \right]$$

The perturbed function is

$$u_{nk}(\vec{r}) \cong u_{n0}(\vec{r}) + \frac{\hbar}{m} \sum_{\ell \neq n} \frac{\langle \ell(o) | \vec{k} \cdot \vec{p} | n(o) \rangle}{E_n(o) - E_\ell(o)} u_{\ell 0}(\vec{r}) \quad (A-3)$$

When $u_{nk}(\vec{r})$ is degenerate at $\vec{k} = 0$ one must diagonalize the matrix

$$\sum_{\ell \in \{n_i\}} \frac{\langle n_i(o) | \vec{k} \cdot \vec{p} | \ell(o) \rangle \langle \ell(o) | \vec{k} \cdot \vec{p} | n_j(o) \rangle}{E_n(o) - E_\ell(o)}$$

The solution of the associated secular equation enables one to find the correct linear combinations $u_{s0}(\vec{r})$ of $u_{n_i0}(\vec{r})$ such that the energy of band s is given by

$$E_s(k) = E_s(o) + \frac{\hbar^2}{2} \vec{k} \cdot \left(\frac{1}{m_s^*} \right) \cdot \vec{k}$$

and the perturbed functions by

$$u_{sk}(\vec{r}) \cong u_{s0}(\vec{r}) + \frac{\hbar}{m} \sum_{\ell \neq \{s\}} \frac{\langle \ell(o) | \vec{k} \cdot \vec{p} | s(o) \rangle}{E_s(o) - E_\ell(o)} u_{\ell 0}(\vec{r}) .$$

In general $(1/m_s^*)$ is a function of $\hat{k}$ for bands which are degenerate at $\vec{k} = 0$. For bands which remain degenerate near $\vec{k} = 0$, the matrix diagonalization is not necessary and the effective masses for these bands are all equal.

Appendix B
Symmetry of $\Lambda(\omega)$

Let us first consider the sum over intermediate states ignoring exciton effects. Let $|n(k_0)\rangle = |\nu m, a\rangle$, where m is the row of representation ν , and a labels all other quantum numbers.

$$\Lambda(\omega) = \sum_{a \nu m} \frac{|\nu m, a\rangle \langle \nu m, a|}{E(\nu, a) - \hbar\omega}$$

Operate on this by an element P_R of the group of $\vec{k}_0$:

$$\begin{aligned} P_R \Lambda(\omega) P_R^{-1} &= \sum_{a \nu m} \frac{P_R |\nu m, a\rangle \langle \nu m, a| P_R^{-1}}{E(\nu, a) - \hbar\omega} \\ &= \sum_{a \nu m} \sum_{ns} \Gamma_{nm}^\nu(R) \Gamma_{ms}^\nu(R) \frac{|\nu n, a\rangle \langle \nu s, a|}{E(\nu, a) - \hbar\omega} \\ &= \sum_{a \nu ns} \Gamma_{ns}^\nu(RR^{-1}) \frac{|\nu n, a\rangle \langle \nu s, a|}{E(\nu, a) - \hbar\omega} \\ &= \sum_{a \nu ns} \delta_{ns} \frac{|\nu n, a\rangle \langle \nu s, a|}{E(\nu, a) - \hbar\omega} \\ &= \sum_{a \nu n} \frac{|\nu n, a\rangle \langle \nu n, a|}{E(\nu, a) - \hbar\omega} \end{aligned}$$

When excitons are included in the intermediate states the proof is exactly the same because of our neglect of the dependence of

$$N^{\frac{1}{2}} \sum_{\nu\beta} \frac{\mathcal{U}_{c_i\nu_j}^{\mu}(\vec{\beta})^* \mathcal{U}_{n_i^+\nu_j}^{\nu}(\vec{\beta}) \mathcal{U}_{n_i^+\nu_j}^{\nu}(0)^*}{E_{n_i^+\nu_j}(\nu) - \hbar\omega}$$

and the similar expression with n_l^- , on the index 1.

Appendix C

Derivation of the Clebsch-Gordan Symmetry Relation

Since* the Clebsch-Gordan coefficients are elements of a unitary matrix they obey the orthogonality relations

$$\sum_{jl} [A^{\lambda\tau_\lambda, \mu\nu}_{s, lj}]^* [A^{\lambda'\tau'_{\lambda'}, \mu\nu}_{s', lj}] = \delta(\lambda, \lambda') \delta(\tau_\lambda, \tau'_{\lambda'}) \delta(s, s')$$

and

$$\sum_{\lambda\tau_\lambda s} [A^{\lambda\tau_\lambda, \mu\nu}_{s, lj}]^* [A^{\lambda\tau_\lambda, \mu\nu}_{s, l'j'}] = \delta(l, l') \delta(j, j').$$

From the definition of the Clebsch-Gordan coefficients we can write

$$\Gamma^{\lambda}_{s'i}(R) \Gamma^{\nu}_{kj}(R) = \sum_{\rho\tau_\rho} \sum_{pl} [A^{\rho\tau_\rho, \lambda\nu}_{l, ij}]^* \Gamma^{\rho\tau_\rho}_{pj}(R) [A^{\rho\tau_\rho, \lambda\nu}_{p, s'k}] \quad (C-1)$$

and

$$\Gamma^{\mu}_{ml}(R) \Gamma^{\nu}_{kj}(R) = \sum_{\gamma\tau_\gamma} \sum_{ss'} [A^{\gamma\tau_\gamma, \mu\nu}_{s, lj'}]^* \Gamma^{\gamma\tau_\gamma}_{s's}(R) [A^{\gamma\tau_\gamma, \mu\nu}_{s', mk}]. \quad (C-2)$$

Multiply Eq.C-2 by $\Gamma^{\nu}_{kj}(R)^*$ and sum over k to obtain

$$\Gamma^{\mu}_{ml}(R) \delta(j, j') = \sum_{\gamma\tau_\gamma} \sum_{ss'k} [A^{\gamma\tau_\gamma, \mu\nu}_{s, lj'}]^* \Gamma^{\gamma\tau_\gamma}_{s's}(R) \Gamma^{\nu}_{kj}(R)^* [A^{\gamma\tau_\gamma, \mu\nu}_{s', mk}],$$

where it has been observed that $\Gamma^{\gamma\tau_\gamma}_{s's}(R) = \Gamma^{\gamma}_{s's}(R)$.

Multiplying this by $A^{\lambda\tau_\lambda, \mu\nu}_{i, lj'}$ and summing over l and j' yields

$$\sum_l [A^{\lambda\tau_\lambda, \mu\nu}_{i, l_j}] \Gamma_{ml}^\mu(R) = \sum_{s'k} \Gamma_{s'i}^\lambda(R) \Gamma_{kj}^\nu(R)^* [A^{\lambda\tau_\lambda, \mu\nu}_{s', mk}] \quad (C-3)$$

Change ν to $\bar{\nu}$ in Eq.C-1 and substitute into Eq.C-3 to obtain

$$\begin{aligned} \sum_l [A^{\lambda\tau_\lambda, \mu\nu}_{i, l_j}] \Gamma_{ml}^\mu(R) \\ = \sum_{\rho\tau_\rho p} \sum_{ls'k} [A^{\rho\tau_\rho, \lambda\bar{\nu}}_{l, ij}]^* \Gamma_{pl}^\rho(R) [A^{\rho\tau_\rho, \lambda\bar{\nu}}_{p, s'k}] [A^{\lambda\tau_\lambda, \mu\nu}_{s', mk}] \end{aligned}$$

Multiply by $A^{\sigma\tau_\sigma, \lambda\bar{\nu}}_{n, ij}$ and sum over i and j :

$$\begin{aligned} \sum_{lij} \Gamma_{ml}^\mu(R) [A^{\lambda\tau_\lambda, \mu\nu}_{i, l_j}] [A^{\sigma\tau_\sigma, \lambda\bar{\nu}}_{n, ij}] \\ = \sum_{ps'k} [A^{\sigma\tau_\sigma, \lambda\bar{\nu}}_{p, s'k}] [A^{\lambda\tau_\lambda, \mu\nu}_{s', mk}] \Gamma_{pn}^\sigma(R). \end{aligned}$$

This can be written

$$\sum_l \Gamma_{ml}^\mu(R) M_{ln} = \sum_p M_{mp} \Gamma_{pn}^\sigma(R),$$

where

$$M_{ln} = \sum_{ij} [A^{\lambda\tau_\lambda, \mu\nu}_{i, l_j}] [A^{\sigma\tau_\sigma, \lambda\bar{\nu}}_{n, ij}],$$

or, in matrix form,

$$\Gamma^\mu(R) M = M \Gamma^\sigma(R).$$

If Γ^μ and Γ^σ are inequivalent then Schur's lemma says that M is the null matrix. If Γ^μ is equivalent to Γ^σ , then M is a constant multiple of the unit matrix:

$$\sum_{ij} |A^{\lambda\tau_\lambda, \mu\nu}_{i, l_j}| |A^{\sigma\tau_\sigma, \lambda\bar{\nu}}_{n, ij}| = C[(\lambda\mu)\bar{\nu}; \tau_\lambda \tau_\mu] \delta(\sigma, \mu) \delta(n, l),$$

where the parentheses in the constant C indicate the pairs of indices which are interchanged on the Clebsch-Gordan coefficients. Bringing the second factor on the left side to the right we have the result

$$[A^{\lambda\tau_\lambda, \mu\nu}_{i, n_j}] = \sum_{\tau_\mu} C[(\lambda\mu)\bar{\nu}; \tau_\lambda \tau_\mu] [A^{\mu\tau_\mu, \lambda\nu}_{n, ij}]^*.$$

*This follows the treatment given by M. Hamermesh Group Theory (Addison-Wesley Publishing Co., Reading, Mass., 1962), p. 260 for real representations in his discussion of the symmetric group.

Appendix D

Table D-1: Correspondence of present notation with that of Koster et al. (Ref. 42) for the single-valued representations.

Group	C_1	S_2	C_2		C_{1h}		C_{2h}		D_2			
Present Notation	A	$A_{\pm}$	A	B	A'	A''	$A_{\pm}$	$B_{\pm}$	A	B_1	B_2	B_3
Notation of Ref.	Γ_1	$\Gamma_1^{\pm}$	Γ_1	Γ_2	Γ_1	Γ_2	$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	Γ_1	Γ_3	Γ_2	Γ_4

C_{2v}				D_{2h}				C_4			S_4		
A_1	A_2	B_1	B_2	$A_{\pm}$	$B_{1\pm}$	$B_{2\pm}$	$B_{3\pm}$	A	B	E	A	B	E
Γ_1	Γ_3	Γ_2	Γ_4	$\Gamma_1^{\pm}$	$\Gamma_3^{\pm}$	$\Gamma_2^{\pm}$	$\Gamma_4^{\pm}$	Γ_1	Γ_2	$(\Gamma_3 \Gamma_4)$	Γ_1	Γ_2	$(\Gamma_3 \Gamma_4)$

C_{4h}			D_4					C_{4v}					D_{2d}				
$A_{\pm}$	$B_{\pm}$	$E_{\pm}$	A_1	A_2	B_1	B_2	E	A_1	A_2	B_1	B_2	E	A_1	A_2	B_1	B_2	E
$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	$(\Gamma_3^{\pm} \Gamma_4^{\pm})$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5

D_{4h}					C_3		S_6		D_3		
$A_{1\pm}$	$A_{2\pm}$	$B_{1\pm}$	$B_{2\pm}$	$E_{\pm}$	A	E	$A_{\pm}$	$E_{\pm}$	A_1	A_2	E
$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	$\Gamma_3^{\pm}$	$\Gamma_4^{\pm}$	$\Gamma_5^{\pm}$	Γ_1	$(\Gamma_2 \Gamma_3)$	$\Gamma_1^{\pm}$	$(\Gamma_2^{\pm} \Gamma_3^{\pm})$	Γ_1	Γ_2	Γ_3

Table D-1, continued:

C_{3v}			D_{3d}			C_6				C_{3h}			
A_1	A_2	E	$A_{1\pm}$	$A_{2\pm}$	$E_{\pm}$	A	B	E'	E''	A'	A''	E'	E''
Γ_1	Γ_2	Γ_3	$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	$\Gamma_3^{\pm}$	Γ_1	Γ_4	$(\Gamma_5 \Gamma_6)$	$(\Gamma_2 \Gamma_3)$	Γ_1	Γ_4	$(\Gamma_2 \Gamma_3)$	$(\Gamma_5 \Gamma_6)$

C_{6h}				D_6						C_{6v}					
$A_{\pm}$	$B_{\pm}$	$E'_{\pm}$	$E''_{\pm}$	A_1	A_2	B_1	B_2	E_1	E_2	A_1	A_2	B_1	B_2	E_1	E_2
$\Gamma_1^{\pm}$	$\Gamma_4^{\pm}$	$(\Gamma_5^{\pm} \Gamma_6^{\pm})$	$(\Gamma_2^{\pm} \Gamma_3^{\pm})$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_1	Γ_2	Γ_4	Γ_3	Γ_5	Γ_6

D_{3h}						D_{6h}						T		
A_1	A'_2	A''_1	A''_2	E'	E''	$A_{1\pm}$	$A_{2\pm}$	$B_{1\pm}$	$B_{2\pm}$	$E_{1\pm}$	$E_{2\pm}$	A	E	T
Γ_1	Γ_2	Γ_3	Γ_4	Γ_6	Γ_5	$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	$\Gamma_3^{\pm}$	$\Gamma_4^{\pm}$	$\Gamma_5^{\pm}$	$\Gamma_6^{\pm}$	Γ_1	$(\Gamma_2 \Gamma_3)$	Γ_4

T			T_h			O					T_d				
A	E	T	$A_{\pm}$	$E_{\pm}$	$T_{\pm}$	A_1	A_2	E	T_1	T_2	A_1	A_2	E	T_1	T_2
Γ_1	$(\Gamma_2 \Gamma_3)$	Γ_4	$\Gamma_1^{\pm}$	$(\Gamma_2^{\pm} \Gamma_3^{\pm})$	$\Gamma_4^{\pm}$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5

O_h				
$A_{1\pm}$	$A_{2\pm}$	$E_{\pm}$	$T_{1\pm}$	$T_{2\pm}$
$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	$\Gamma_3^{\pm}$	$\Gamma_4^{\pm}$	$\Gamma_5^{\pm}$

Appendix E

Table E-1: Angular dependence functions for face-centered cubic (fcc), diamond, zinc blende and simple cubic (sc) structures (after Inoue and Toyozawa, Ref. 11). A , E , T , and T are the angular functions defined in Table 3-1 for O , T_d and O_h .

fcc diamond	zinc blende	sc	fcc diamond	zinc blende	sc
Δ					
A_1	A_1	A_1	$ \lambda_1+2 ^2 A_1 + 2 \lambda_1-1 ^2 E$	$[1+\lambda_1+\lambda_2]^2 A_1 + \{[1-\lambda_1]^2 + [1-\lambda_2]^2 + \lambda_1-\lambda_2 ^2\} E$	$ \lambda_1+2 ^2 A + 2 \lambda_1-1 ^2 E$
A_2	A_2	A_2	T_1	$ \lambda_3 ^2 T_1 + T_2$	T_1
B_1	B_1	B_1	E	$ \lambda_4 ^2 T_1 + T_2$	E
B_2	B_2	B_2	T_2	$ \lambda_5 ^2 T_1 + T_2$	T_2
E		E	$ \lambda_2 ^2 T_1 + T_2$		$ \lambda_2 ^2 T_1 + T_2$
X					
A_{1g}	A_1	A_{1g}	$ \lambda_1+2 ^2 A_1 + 2 \lambda_1-1 ^2 E$	$ \lambda_1+2 ^2 A_1 + 2 \lambda_1-1 ^2 E$	$ \lambda_1+2 ^2 A_1 + 2 \lambda_1-1 ^2 E$
A_{2g}	A_2	A_{2g}	T_1	T_1	T_1
B_{1g}	B_1	B_{1g}	E	E	E_2
B_{2g}	B_2	B_{2g}	T_2	T_2	T_2
E_g	E	E_g	$ \lambda_2 ^2 T_1 + T_2$	$ \lambda_2 ^2 T_1 + T_2$	$ \lambda_2 ^2 T_1 + T_2$

Table E-1 (Contd.)

Λ						
A_1			$4 1-\lambda_1 ^2 T_2 + 2+\lambda_1 ^2 A_1$	$4 1-\lambda_1 ^2 T_2 + 2+\lambda_1 ^2 A_1$	$4 1-\lambda_1 ^2 T_2 + 2+\lambda_1 ^2 A_1$	
A_2			T_1	T_1	T_1	
E			$\frac{2}{3} \sqrt{2}+\lambda_3 ^2 E$ $+\frac{1}{3} \sqrt{2}\lambda_3-1 ^2 T_2 + \lambda_4 ^2 T_1$	$\frac{2}{3} \sqrt{2}+\lambda_3 ^2 E$ $+\frac{1}{3} \sqrt{2}\lambda_3-1 ^2 T_2 + \lambda_4 ^2 T_1$	$\frac{2}{3} \sqrt{2}+\lambda_3 ^2 E$ $+\frac{1}{3} \sqrt{2}\lambda_3-1 ^2 T_2 + \lambda_4 ^2 T_1$	
L		R				
A_{1g}	A_1	A_{1g}	$4 1-\lambda_1 ^2 T_2 + 2+\lambda_1 ^2 A_1$	$4 1-\lambda_1 ^2 T_2 + 2+\lambda_1 ^2 A_1$	A_1	
A_{2g}	A_2	E_g	T_1	T_1	E	
E_g	E	T_{1g}	$\frac{2}{3} \sqrt{2}+\lambda_3 ^2 E$ $+\frac{1}{3} \sqrt{2}\lambda_3-1 ^2 T_2 + \lambda_4 ^2 T_1$	$\frac{2}{3} \sqrt{2}+\lambda_3 ^2 E$ $+\frac{1}{3} \sqrt{2}\lambda_3-1 ^2 T_2 + \lambda_4 ^2 T_1$	T_1	
		T_{2g}			T_2	

Table E-1 (Contd.)

Σ					
A_1	A	A_1	$\frac{2}{3} 1+\lambda_1+\lambda_2 ^2 A_1$ $+\frac{1}{3} 2-\lambda_1-\lambda_2 ^2 E$ $+\frac{1}{2} \lambda_1-\lambda_2 ^2 T_2$	$\frac{2}{3} 1+\lambda_1+\lambda_2 ^2 A_1$ $+\frac{1}{3} 2-\lambda_1-\lambda_2 ^2 E$ $+\left\{\frac{1}{2} \lambda_1-\lambda_2 ^2 + 2 \lambda_3 ^2\right\} T_2$ $+2 \lambda_4 ^2 T_1$	$\frac{2}{3} 1+\lambda_1+\lambda_2 ^2 A_1$ $+\frac{1}{3} 2-\lambda_1-\lambda_2 ^2 E$ $+\frac{1}{2} \lambda_1-\lambda_2 ^2 T_2$
A_2	B	A_2	$ \lambda_3 ^2 T_1 + T_2$	$2T_2 + \{2 \lambda_5 ^2 + \lambda_7 ^2\} T_1$ $+2 \lambda_6 ^2 E$	$ \lambda_3 ^2 T_1 + T_2$
B_1		B_1	$ \lambda_4 ^2 T_1 + T_2$		$ \lambda_4 ^2 T_1 + T_2$
B_2		B_2	$ \lambda_5 ^2 T_1 + 2E$		$ \lambda_5 ^2 T_1 + 2E$

Table E-1 (Contd.)

K		M			
A ₁	A	A _{1g}	$\frac{2}{3} 1+\lambda_1+\lambda_2 ^2 A_1$	$\frac{2}{3} 1+\lambda_1+\lambda_2 ^2 A_1$	$\frac{1}{3} 1+\lambda_1+\lambda_2 ^2 A_1$
			$+\frac{1}{3} 2-\lambda_1-\lambda_2 ^2 E$	$+\frac{1}{3} 2-\lambda_1-\lambda_2 ^2 E$	$+\frac{1}{3} 2-\lambda_1-\lambda_2 ^2 E$
			$+\frac{1}{2} \lambda_1-\lambda_2 ^2 T_2$	$+\left\{\frac{1}{2} \lambda_1-\lambda_2 ^2 + 2 \lambda_3 ^2\right\} T_2$	$+\frac{1}{2} \lambda_1-\lambda_2 ^2 T_2$
				$+2 \lambda_4 ^2 T_1$	
A ₂	B	A _{2g}	$ \lambda_3 ^2 T_1 + T_2$	$2T_2 + \{2 \lambda_3 ^2 + \lambda_7 ^2\} T_1$	T ₁
				$+2 \lambda_6 ^2 E$	
B ₁		B _{1g}	$ \lambda_4 ^2 T_1 + T_2$		6E + T ₂
B ₂		B _{2g}	$ \lambda_3 ^2 T_1 + 2E$		T ₂
		E _g			$3 \lambda_2 ^2 T_1 + 2T_2 + 2E$

Fig.E-1. Brillouin zones of a) simple cubic structure, c) body-centered cubic structure and b) face-centered cubic, diamond and zinc blende structures

References

1. J. C. Phillips, Solid State Physics, vol. 18, p. 55 (Academic Press, 1966).
2. P. A. Franken and J. F. Ward, Revs. of Mod. Phys. 35, 23 (1963).
3. M. Goeppert-Mayer, Ann. Physik 9, 273 (1931).
4. J. J. Hopfield and J. M. Worlock, Phys. Rev. 137, A1455 (1965).
5. H. R. Philipp and E. A. Taft, Phys. Rev. 113, 1002 (1959).
6. J. E. Eby, K. J. Teegarden and D. B. Dutton, Phys. Rev. 116 1099 (1959).
7. D. L. Dexter, Photoconductivity Conference, R. G. Breckenridge et al., Eds. pp. 135-183 (Wiley, New York, 1956).
8. J. Tauc, Progress in Semiconductors, vol. 9, pp. 87-133 (Temple Press Books, London, 1965).
9. T. P. McLean, Progress in Semiconductors, vol. 5, p. 55 (John Wiley and Sons, Inc., New York, 1960).
10. G. Dresselhaus, Phys. Rev. 105, 135 (1956).
11. M. Inoue and Y. Toyozawa, J. Phys. Soc. Japan 20, 363 (1965).
12. D. Frohlich and B. Stagginnus, Phys. Rev. Letters 19, 469 (1967).
13. D. Frohlich and B. Stagginnus and E. Schonherr, Phys. Rev. Letters 19, 1032 (1967).
14. M. Matsuoka, J. Phys. Soc. Japan 23, 1028 (1967).
15. D. Frohlich and B. Stagginnus, to be published.
16. K. Park and R. G. Stafford, to be published.

17. T. H. Reilly, thesis (Institute of Optics, University of Rochester), unpublished.
18. M. D. Galanin and Z. A. Chizhikova, *Opt. Spektrosk*, 113 (1967).
19. G. D. Mahan, *Phys. Rev. Letters* 20, 332 (1968).
20. G. D. Mahan, *Phys. Rev.* 170, 825 (1968).
21. L. I. Schiff, Quantum Mechanics, (McGraw-Hill Book Co., New York, 1949).
22. For a review of two-photon absorption see A. Gold, "Two Photon Spectroscopy", to be published in the Proceedings of the 1967 Varenna Summer School on Quantum Optics, R. J. Glauber, Ed.
23. P. A. M. Dirac, *Proc. Roy. Soc. (London) Ser. A* 114, 243 (1927).
24. A thorough discussion of the quantized electromagnetic field is given in W. Heitler, The Quantum Theory of Radiation, (Oxford: Clarendon Press, 1954).
25. It should be noted here that coherence effects will be ignored. This is justified when one works with two beams of different frequency as long as the two-photon absorption is weak, which is generally the case. In the single beam case the absorption is smaller when the source is coherent than when it is chaotic. For a discussion of coherence effects see Y. R. Shen, *Phys. Rev.* 155, 921 (1967).
26. R. J. Elliott, *Phys. Rev.* 108, 1384 (1957).
27. R. S. Knox, Theory of Excitons (Academic Press, New York, 1963).
28. J. Callaway, Energy Band Theory (Academic Press, New York, 1964).
29. J. C. Slater, *Phys. Rev.* 76, 1592 (1949); 87, 807 (1952).
30. G. F. Koster, *Phys. Rev.* 89, 67 (1953).
31. W. Kohn, *Phys. Rev.* 115, 809 (1959).
32. G. Wannier, *Phys. Rev.* 52, 191 (1937).

33. G. Dresselhaus, J. Phys. Chem. Solids 1, 14 (1956).
34. G. Dresselhaus, Phys. Rev. 106, 76 (1956).
35. R. J. Elliott, T. P. McLean and G. G. Macfarlane, Proc. Phys. Soc. 72, 553 (1958).
36. R. J. Elliott, Phys. Rev. 124, 340 (1961).
37. R. Braunstein, Phys. Rev. 125, 475 (1962).
38. R. Braunstein and N. Ockman, Phys. Rev. 134, A 499, (1964).
39. R. Loudon, Proc. Phys. Soc. 80, 952 (1962).
40. L. P. Bouckaert, R. Smoluchowski and E. Wigner, Phys. Rev. 50, 100 (1936).
41. For a discussion of group theory and its application to solids see, for example, R. S. Knox and A. Gold, Symmetry in the Solid State, (W. A. Benjamin, Inc., New York, 1964).
42. G. F. Koster, J. O. Dimmock, R. G. Wheeler and H. Statz, Properties of the Thirty-Two Point Groups (M.I.T. Press, Cambridge, Mass., 1963).
43. G. F. Koster, in Solid State Physics (F. Seitz and D. Turnbull, Eds.) vol. 5, p. 173 (Academic Press, New York, 1957).
44. F. Seitz, Annals of Math 37, 17 (1936); Zeits. f. Kristallographie (A) 88, 433 (1934); 90, 289 (1935); 91, 336 (1935); 94, 100 (1936).
45. C. Herring, Journal of the Franklin Institute 233, 525 (1942).
46. R. J. Elliott, Phys. Rev. 96, 280 (1954).
47. M. L. Glasser, J. Phys. Chem. Solids 10, 229 (1959).
48. R. C. Casella, Phys. Rev. 114, 1514 (1959).
49. J. J. Hopfield, J. Phys. Chem. Solids 15, 97 (1960).
50. M. Balkanski and J. des Cloizeaux, J. Phys. Rad. 22, 41 (1961).
51. Y. Onodera, M. Okazaki and T. Inui, J. Phys. Soc.

- Japan 21, 2229 (1966).
52. L. Hostler, J. Math. Phys. 5, 591 (1964).
 53. Handbook of Mathematical Functions, M. Abramowitz and I. A. Stegun, Eds. (U. S. Dept. of Commerce, N. B. S., Washington, D. C., 1964) Appl. Math. Ser. 55.
 54. A. W. Overhauser, Phys. Rev. 101, 1702 (1956).
 55. D. L. Dexter, Phys. Rev. 108, 707 (1957).
 56. When a crystal has inversion symmetry there will be $2n$ degenerate states at $k = 0$, including spin, which will split into n 2-fold degenerate states. In crystals without inversion symmetry the $2n$ states will split into $2n$ non-degenerate states when spin-orbit coupling is present. For a discussion of these splittings see V. Heine, Group Theory in Quantum Mechanics (Pergamon Press, 1960) Chapter VI, section 26.
 57. W. Shockley, Phys. Rev. 50, 754 (1936).
 58. M. K. Song, J. Physique 28, 195 (1967).
 59. M. Cardona, Phys. Rev. 129, 69 (1963).
 60. The group of the wave vector at X is D_{2d} . The representation labels used here are those of R. H. Parmenter, Phys. Rev. 100, 573 (1955), and are not numbered in order of those given in Table 3-1. Parmenter's X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , and X_7 correspond respectively to A_1 , B_1 , B_2 , A_2 , E , Γ^6 and Γ^7 of Table 3-1.
 61. K. Park and H. S. Waff, Phys. Letters 28A, 305 (1968).
 62. T. K. Bergstresser and M. L. Cohen, Phys. Rev. 164, 1067 (1967).
 63. W. W. Piper, P. D. Johnson and D. T. F. Marple, J. Phys. Chem. Solids 8, 457 (1959).
 64. D. G. Thomas and J. J. Hopfield, Phys. Rev. 116, 573 (1959).
 65. See, for example, R. S. Knox and K. Teegarden, "Electronic Excitations of Perfect Alkali Halide Crystals," in Physics of Color Centers (Academic Press, Inc., New York, 1968).

66. K. Teegarden and G. Baldini, Phys. Rev. 155, 896 (1967).
67. Y. Onodera, J. Phys. Soc. Japan 25, 469 (1968).
68. J. J. Hopfield, J. M. Worlock and K. Park, Phys. Rev. Letters 11, 414 (1963).