# FINE STRUCTURE IN THE OPTICAL ABSORPTION EDGE OF ANISOTROPIC CRYSTALS

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Abstract—The group theory of weakly bound direct excitons is developed without explicit use of effective mass theory. For the usual case in which the direct band gap occurs at a point of high symmetry, direct exciton wave functions can be expanded in one-electron wave functions which have the symmetry of this point. The expansion is the *k*-space analogue to the expansion of a tightly bound exciton envelope wave function in real space. A quasi-cubic model of the valence band structure for hexagonal ZnO, CdS and ZnS is developed. The model, in conjunction with the group theory of weakly bound excitons, explains on a semi-quantitative basis most of the observed exciton fine structure in ZnO and CdS. A theorem which aids in constructing higher order "Kubic Harmonics" (for any point group) is given in an appendix.

# I. INTRODUCTION

It has long been recognized that optical experiments near the fundamental absorption edge can be a useful tool for studying energy band parameters in semiconductors and insulating crystals. Little use has been made of this tool in anisotropic crystals; indeed, very few detailed measurements of the optical properties near the fundamental absorption edge of anisotropic crystals have been made until recently.

DRESSELHAUS<sup>(1)</sup> has pointed out that the shape of the fundamental absorption edge in polarized light can yield information about band symmetries in anisotropic crystals. From an experimental point of view, it has proved difficult to obtain information from the shape of the absorption edges in CdS and ZnO, two anisotropic crystals on which detailed optical measurements have recently been made. In these crystals the shape of the "fundamental absorption edge" is a function of surface treatment.<sup>(2)</sup> Furthermore, the shape of the absorption edge does not always agree with existing theory.<sup>(3)</sup> In CdS and ZnO, however, line structure which can be associated with direct (vertical) transitions is present in the absorption (or reflection) edge spectrum.<sup>(4,5)</sup> The primary purpose of this paper is to lay the groundwork for analysis

of the information available from the exciton spectrum in anisotropic crystals, with particular emphasis on the wurtzite structure. The anisotropic semiconductors of greatest current interest are the II-VI compounds having this structure. We seek to understand as much of the exciton level structure as possible from a symmetry point of view without actually computing exciton binding energies (far too little data is yet available to make detailed mass estimates).

A brief review of direct exciton wave functions is given in Section II. In Section III, the group theory of exciton fine structure is developed. The formal theory of fine structure can be applied to all direct excitons, but has real usefulness only for relatively weakly bound excitons.

The theory of Section III is applied to the wurtzite structure in Section V to determine the exciton fine-structure. It is shown that the observed exciton fine-structure and Zeeman effects are in agreement with the assumed valence and conduction band structure. A quasi-cubic model of the wurtzite energy bands is developed in Section IV to aid in correlating observed exciton oscillator strengths with the observed exciton energies, and by this means to deduce band-structure information from the observed exciton energies.

## II. SELECTION RULES AND EXCITON WAVE FUNCTIONS

Direct excitons (i.e. those excitons having a wave vector near  $\mathbf{k} = 0$ ) can be grouped into two principal classes, according to the behavior of their optical matrix elements. If the matrix element of the operator

$$p_k = \sum_{\substack{n \ \text{electrons}}} \exp(i k \cdot r_n) p_n$$

between the crystal ground state and the exciton state k is finite for  $k \rightarrow 0$ , the excitons will be called "allowed". If the matrix element of  $p_k$ goes to zero for  $\mathbf{k} \to 0$ , the excitons will be called "forbidden". The allowed exciton transitions are the solid-state analogue of atomic dipole transitions; the forbidden exciton transitions are the analogue of atomic quadrupole and higher order transitions. For wavelengths in the optical region, forbidden transitions should have oscillator strengths about 10-4-10-5 times the oscillator strengths of allowed transitions. Forbidden transitions have been observed, but only after the fact. After the exciton level structure is known from the energies and strengths of allowed transitions, it has sometimes been possible to ascribe other weak lines in the spectrum to forbidden transitions. Because these forbidden transitions always occur in conjunction with the much more easily observed allowed excitons and can usually be separated from allowed excitons on the basis of oscillator strength, we will neglect the forbidden transitions and work in the limit  $\boldsymbol{k} \to 0$ .

In order to discuss the details of exciton binding, it is necessary to make an assumption about the most important factors in exciton binding. For one extreme, the tight-binding case, the electron and hole kinetic energy is negligible, and the potential energy of electron-hole interaction is the dominant term in the Hamiltonian. In this case, the Wannier functions are logical basis functions, for they allow maximum localization of the electron and hole, and thus permit fullest utilization of the potential energy for binding. DEXTER, OVERHAUSER and KNOX and INCHAUSPE<sup>(6)</sup> have recently investigated the theory of such models for the alkali halides. It is perhaps simplest to discuss the extension of the transfer model used by OVERHAUSER. OVERHAUSER's treatment is oversimplified in that he forced the electron and hole to be on nearest-neighbor atoms. His treatment could be extended to include the possibility of larger electron-hole separations but would rapidly become unwieldy. The reason for the difficulty is that one would be attempting to characterize a state having a large radius in real space (large compared to a lattice constant) by the symmetries of the  $n^{\text{th}}$  neighbor lattice points in real space. On the other hand, this large radius in real space implies a small radius in k-space. This small radius indicates that in some sense it should be easier to characterize the exciton by the symmetries of the bands from which it is made, rather than the symmetries of the  $n^{\text{th}}$  neighbor Wannier functions.

In the other extreme (weak binding) the exciton binding can be considered to be dominated by the electron and hole "kinetic energies". The logical basis functions are the Bloch functions, which minimize this kinetic energy. In this case, states extending a finite distance in k-space must be used to represent a bound state. If the extent of the wave functions in k-space is not too large, the binding can be treated in the effective mass approximation.<sup>(7)</sup> It seems desirable, however, to treat the group theory of the problem without explicit use of the effective mass formalism in order to more easily investigate selection rules, polarization effects and energy splittings in the presence of complex band structures. (The effective mass approximation often has excess degeneracies not required by group theory.)

In Section III we construct a theory of exciton fine structure for weakly bound excitons. The theory is the analogue of the tight binding theory, with Bloch functions rather than Wannier functions as basis functions.

## III. GROUP THEORY OF EXCITON FINE STRUC-TURE FOR WEAKLY BOUND EXCITONS

The wave function for an exciton can most easily be written in terms of an exciton creation operator  $\psi_{\text{exciton}}$ . Let  $\Psi_{ck}^*$  be the operator which creates an electron in the Bloch state  $|ck\rangle$  (previously unoccupied) and  $\Psi_{vk}$  be the operator which annihilates an electron in the Bloch state  $|vk\rangle$  (previously occupied). The operator

$$\psi_{\text{exciton}} = \sum_{\boldsymbol{k}, v, c} f_{cv}(\boldsymbol{k}) \psi_{c\boldsymbol{k}}^* \psi_{v\boldsymbol{k}} \qquad (1)$$

acting on the crystal ground state  $\psi_G$  creates an

exciton having wave vector zero. The  $f_{cv}(\mathbf{k})$  are expansion coefficients. It is implicitly assumed that the effects of "vacuum polarization" (the virtual excitation of electron-hole pairs by the exciton) can be adequately included as a modification of the electron-hole interaction. In the usual case, only one conduction band and one valence band contribute appreciably to the sum in relation (1).

Equation (1) can be conveniently interpreted as an exciton wave function. If the operators  $\Psi_{ck}^*$ and  $\Psi_{vk}$  are replaced by the Bloch wave functions  $\psi_{ck}(\mathbf{r}_e)$  and  $\psi_{vk}^*(\mathbf{r}_h)$  respectively, equation (1) defines an exciton wave function  $\psi_{exciton}(\mathbf{r}_e, \mathbf{r}_h)$  in ordinary (nonoperator) form. This form of the exciton wave function is useful because it explicitly displays the two particle nature of the wave function. With this definition of the exciton wave function, matrix elements of the total momentum operator P (the matrix elements for optical transitions) between the crystal ground state and a one exciton state are given by

$$\langle \psi_G | \boldsymbol{P} | \psi_{\text{exciton}} \rangle =$$
  
=  $\sum_{c_i v, k} f_{cv}(\boldsymbol{k}) \int \psi_{vk}^*(\boldsymbol{r}) \frac{\hbar}{i} \nabla \psi_{ck}(\boldsymbol{r}) d^3 \boldsymbol{r}.$ 

It would be desirable to be able to characterize weak binding excitons by the symmetry of the electron and hole bands from which the exciton is made and the symmetry of the electron-hole orbit. There are two primary difficulties in attempting this. First, only the total symmetry of the exciton state, not the symmetries of the electron or hole components alone, is a good quantum number. (The analogous difficulty arises in the states of many electron atoms where, for example, the total angular momentum is a good quantum number but the angular momentum of a particular electron is only an approximate quantum number.) Secondly, the important terms in the sum over k in equation (1) come from a region in k-space and the wave function symmetry at a general point in k-space is extremely low.

The first difficulty is inevitable, and will be shown to lead to configuration mixing. The second difficulty can be overcome by choosing expansion functions which have the symmetries of a point in k-space of high symmetry. The direct band gap in most substances lies at a point in k-space of high symmetry, where both conduction and valence bands exhibit extrema. (That the presence of spinorbit coupling can move the extrema a small distance away from the point of high symmetry is unimportant.) In those few crystals in which direct excitons are observed and the band structure is known,\* the symmetry point of interest is the k = 0 symmetry point  $\Gamma$ . We shall therefore assume that the electron and hole valleys are near k = 0. (The treatment we are about to perform could also be done at other symmetry points, but with algebraic complications resulting in the case of several equivalent valleys due to the necessity of performing a multicenter expansion of the wave functions.) Indirect excitons are not considered.

Let the irreducible representations of the group of the wave vector zero be denoted by { $\Gamma_i$ }. The ground state of the entire crystal (if, as in ZnO and CdS, there is no spin degeneracy), is the identity representation denoted by  $\Gamma_1$ . The state of the entire crystal with one  $\mathbf{k} = 0$  exciton present will belong to one of the irreducible representations { $\Gamma_i$ }. The wave functions of single electrons or holes in the crystal belong to representations of the double group; the exciton states representing an electron-hole pair belong to irreducible representations of the single group.

Unfortunately even this simplest of group theoretic statements is not exactly true. For those excitons for which the dipole matrix element between the crystal ground state and the exciton state vanishes, the above paragraph is correct. For those excitons for which this dipole matrix element is nonzero, long range coulomb effects produce energy differences between longitudinal and transverse excitons.<sup>(8,9)</sup> This energy difference can be calculated from classical dielectric theory if the exciton oscillator strength and the dielectric constant due to all other causes at frequencies near the exciton frequency are known.<sup>(9)</sup> This long range effect can break up "group theoretic degeneracies" even along principal axes of a crystal. For an exciton wave vector  $\boldsymbol{k}$  (infinitesimal) along principal directions there is no mixing of different irreducible representations by this long range coulomb interaction. The relation of the optical effects of excitons and group theory in uniaxial crystals can thus be established in the following order. First, investigate the group theory of the exciton band

<sup>\*</sup> Germanium is perhaps the best example.

structure neglecting the long range coulomb effects. Secondly, insert the coulomb effects and calculate the energy shifts by perturbation theory, noting that the exciton symmetry remains unaltered. Finally, the optical properties for light traveling in a general direction in the crystal can be computed from the optical properties along principal directions. Group theory enters only the first step, where the effects of the long range coulomb interactions are neglected.

We attack the main part of the problem by expanding the Bloch functions in the wave function (1) in terms of the wave functions of effective mass theory.<sup>(10)</sup> If

$$\Psi_{nk} = u_{nk} \exp(i \mathbf{k} \cdot \mathbf{r}),$$

then

$$\Psi_{vk} = \sum_{n} g_{nk} u_{nk} \exp(ik \cdot r). \qquad (2)$$

In an expansion around k = 0,  $g_{vk} = 1 + 0(k)$ , and  $g_{nk}$  for  $v \neq n$  is 0(k). If equation (2) and its equivalent for the valence band are inserted in equation (1), a simple expansion of relation (1) in terms of wave functions at k = 0 results. An individual term referring to two specific bands in the exciton wave function would then have the form

$$h_{nn',k} \exp(i\mathbf{k} \cdot \mathbf{r}_e) \exp(-i\mathbf{k} \cdot \mathbf{r}_h) u_{on,i}(\mathbf{r}_e) u_{on,i'}(\mathbf{r}_h)$$
(3)

The functions  $\{u_{on}\}$  for fixed n (there may be several such functions i if band n is degenerate at k = 0) transform among themselves under the symmetry operations of the crystal. If the exciton state is to belong to irreducible representation  $\Gamma_i$ , each term like expression (3) when summed over k occurring in the expansion must also belong to  $\Gamma_i$ .

So far no use has been made of the restriction to weakly bound excitons formed from bands at k = 0. We shall now proceed to expand around k = 0. The symmetry operations applied to terms such as (3) generate for a given k,  $N_k D_n D_n$ . wave functions which transform among themselves, where  $D_n$  and  $D_{n'}$  are the degeneracies at k = 0 of bands n and n', and  $N_k$  is the number of wave vectors in the "star of k".

"Crystal Harmonics" analogous to "Kubic Harmonics"<sup>(11)</sup> can, of course, be defined for any lattice. Different "Crystal Harmonics" can be characterized physically as having different structures of angular and radial nodes. The weak binding exciton can also be regarded as having angular and radial nodes in its envelope wave function. It seems desirable then to sum certain terms of the form of expression (3) to obtain terms characterized by an angular dependence. The terms of (3) should then be re-expressed as

$$\sum_{\boldsymbol{k},\,m} L_{m,l,\,j^{\prime\prime}}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}_{e}) \times \\ \times \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_{h}) u_{onj}(\boldsymbol{r}_{e}) u_{on^{\prime}j^{\prime}}^{*}(\boldsymbol{r}_{h})$$
(4)

where  $L_{m,l,j''}(\mathbf{k})$  is a "Crystal Harmonic" belonging to irreducible representation m, and i and i' are degeneracy indices. The index l is the order of the harmonic. (There is a problem concerning counting the number of states which is treated in the appendix. The transformation between the functions (3) and (4) is not unitary. The terms in (4) contain the terms (3) in a redundant fashion.)  $L_{m,l,j''}(\mathbf{k})$  belongs to an irreducible representation  $\Gamma_m$  of the single group. The subscript j'' is needed in the event that  $\Gamma_m$  is more than one dimensional. Let  $\Gamma_n$  and  $\Gamma_n$  be the irreducible representations corresponding to bands *n* and *n'* at k = 0. It is now easy to show that the set of  $D_m D_n D_{n'}$  wave functions described by expression (4) belong to the irreducible representations described by the product representation  $\Gamma_m \times \Gamma_n \times \Gamma_{n'}$ .

This relation is the dual of the tight binding case. For the tight binding case,  $\Gamma_n$  and  $\Gamma_n$  for the bands at  $\mathbf{k} = 0$  will be replaced by the irreducible representation of the Wannier functions in bands n and n' (which also belong to  $\Gamma_n$  and  $\Gamma_{n'}$ ), and  $\Gamma_m$  will be replaced by an irreducible representation of the nearest neighbor symmetry.

There are essentially two different kinds of mixing which can go on to destroy m as a good quantum number. First, even within the effective mass theory, it is necessary to include mixing with other bands in order to obtain the effective mass.<sup>(10)</sup> This perturbation gives rise to a mixing in of other bands in an amount which is of the order of the effective mass "kinetic energy" of the electron and hole divided by a typical interband energy (e.g. the direct band gap). This mixing is small, and of primary importance in selection rules only when the  $k = 0 \rightarrow k = 0$  optical matrix element is small or zero for the bands from which the exciton is chiefly made.\* The second kind of mixing which destroys m as a quantum number is due to degenerate energy bands. This kind of behavior also occurs in acceptor-state wave functions in germanium, where the "orbital" part of the acceptor wave function contains both S and D terms even in the effective mass approximation.<sup>(12)</sup>

We are not going to make use of the full formalism for ZnO. Too little is known about the band parameters to enable one to make energy level calculations. It will be shown, however, that rather simple symmetry arguments based on the general ideas of this section will be sufficient to make rather Denote the orbitals for the six degenerate valence bands by  $(P_x, P_y, P_z) \times (\alpha, \beta)$  where  $\alpha$  and  $\beta$  are the spin-wave functions for spin parallel to z and spin antiparallel to z. The zero of energy for the system is taken as the valence band at k = 0. The band gap will be denoted by  $E_g$ .

If a small amount of spin-orbit coupling is now turned on (such that the spin-orbit energy  $\delta$  is small compared to  $E_g$ ), the only matrix elements of importance will be those which mix the *P*-bands. The *S*-states will still be doubly degenerate ( $S\alpha$  and  $S\beta$ ); the *P*-states will now have a Hamiltonian matrix which can be written

	$\frac{\delta}{3}$	$i\frac{\delta}{3}$	$-\frac{\delta}{3}$	0	0	0	$P_{x}\alpha$	
	$-i\frac{\delta}{3}$	$\frac{\delta}{3}$	$-i\frac{\delta}{3}$	0	0	0	Pya	
Н	$V = \left  -\frac{\delta}{3} \right $	$i\frac{\delta}{3}$	$\frac{\delta}{3} + \Delta$	0	0	0	$P_z\beta$	
	0	0	0	$\frac{\delta}{3}$	$-irac{\delta}{3}$	$\frac{\delta}{3}$	$P_x \beta$	
	0	0	0	$i\frac{\delta}{3}$	$\frac{\delta}{3}$	$i\frac{\delta}{3}$	$P_y \beta$	
	0	0	0	$\frac{\delta}{3}$	$-i\frac{\delta}{3}$	$\frac{\delta}{3} + \Delta$	Pza	(5)

detailed predictions about degeneracies and splittings in the ZnO exciton level structure.

### IV. A QUASI-CUBIC MODEL OF THE k = 0 BAND STRUCTURE FOR THE WURTZITE LATTICE

Consider a cubic crystal having *P*-like valence bands and an *S*-like conduction band at k = 0. For the present,  $\Delta$  should be set equal to zero. This form can be obtained by transforming from the  $P_{3/2}$ ,  $P_{1/2}$  representation where  $H_{\text{spin-orbit}}$  is diagonal and the eigenvalues are respectively 0 and  $\delta$ . If a small strain is applied to the crystal (the strain energy  $\Delta \ll E_g$ ) in the z-direction, all states are unaffected in lowest order. In second order, however,

addition exciton-states for which ELLIOTT's equations (3.6) (optical matrix element for "allowed" processes) and (3.14) (optical matrix element for "forbidden" excitons) contribute comparable amounts to the oscillator strength of a single exciton. Such an exciton cannot really be considered either "allowed" or "forbidden" in ELLIOTT's notation. For these reasons we have abandoned his use of these terms. The qualitative distinction made by ELLIOTT (caused from the present point of view by band mixing) is nevertheless of use in estimating the strengths of many exciton lines.

<sup>\*</sup> ELLIOTT<sup>(3)</sup> has classified the direct excitons as "allowed" if this matrix element exists and "forbidden" if the matrix element vanishes. We have defined the terms somewhat differently, reserving the term "forbidden" for those excitons (not considered by ELLIOTT) which do not interact with light of infinite wavelength. In ZnO, the weak spin-orbit coupling results in excitons which are so weakly "allowed" (in the Elliott notation) that they are considerably weaker than "forbidden" lines would be in the same material. There are in [continued in next column

the state  $P_z$  suffers an energy shift different from that undergone by the equivalent states  $P_x$  and  $P_{y}$ . Let this difference in energy shifts be denoted by  $\Delta$ . If  $\Delta$  is much less than  $E_g$ , we may neglect the wave function admixtures between the *P*-bands and other bands (percentage admixtures of order  $(\Delta/E_g)^2$  and simply add the term  $\Delta$  to the energies of the  $P_z$  states. The total Hamiltonian matrix then becomes that of equation (5). The basis functions are still, to lowest order, the P-basis functions. It is important to note that there will be errors only of order  $\Delta/E_g$  and  $\delta/E_g$  in the optical matrix elements between the P-band and the S-like conduction band, and that the crystal Hamiltonian has the symmetry of a uniaxial crystal. The eigenstates of equation (5) are:

 $\Delta$  is of course zero.) In cubic crystals, it can be shown that the error in the model is only of order  $(\delta/E_g)$ . In the wurtzite structure, each atom retains in a general way the tetrahedral nearest neighbor environment present in the cubic crystal. If, as it seems reasonable to assume, the holes are concentrated chiefly on the sulfur atoms, the fact that the third neighbors are in a hexagonal configuration should not influence appreciably the spin-orbit interaction; i.e., the spin-orbit interaction should remain roughly isotropic. The error in the quasi-cubic model spin-orbit interaction is then probably of order  $(\Delta/E_g)$ . (There are also errors of order  $(\delta/E_g)$  which occur in cubic crystals.)

The effect of the deviation of the c/a ratio from

States	Energy E
$[2]^{-1/2} \begin{vmatrix} (P_x + iP_y)\alpha \\ (P_x - iP_y)\beta \end{vmatrix}$	$E_1 = 0$
$\left[2 + \left(2 - \frac{3E}{\delta}\right)^2\right]^{-1/2} \begin{vmatrix} (P_x - iP_y)\alpha + \left(2 - \frac{3E}{\delta}\right)P_z\beta \\ (P_x + iP_y)\beta - \left(2 - \frac{3E}{\delta}\right)P_z\alpha \end{vmatrix}$	$E_{2} = \frac{\delta + \Delta}{2} + \sqrt{\left[\left(\frac{\delta + \Delta}{2}\right)^{2} - \frac{2}{3}\delta\Delta\right]}$
Same form of states as on line above.	$E_{3} = \frac{\delta + \Delta}{2} - \sqrt{\left[\left(\frac{\delta + \Delta}{2}\right)^{2} - \frac{2}{3}\delta\Delta\right]}$

If the crystal has been squashed far enough along the z-axis, it is possible that the optical matrix elements between  $P_x$  and S will not be quite the same as the optical matrix elements between  $P_z$  and S.

Let the optical matrix element (for light polarized in the x-direction) between the conduction band and the  $P_x$  state be H. The matrix element (for light polarized parallel to the x-direction) between the conduction band  $P_z$  state will be written  $(1 + \epsilon)H$ . (From previous arguments,  $\epsilon$  is small.) This then provides a model of a slightly uniaxial crystal.

This model may represent a reasonable approximation to the actual band-structure in hexagonal (or cubic) ZnO, CdS and ZnS. (In cubic crystals, ideal (the distortion of the nearest neighbor tetrahedra) is taken into effect in a general way by the parameters  $\Delta$  and  $\epsilon$ . The error which is most difficult to estimate arises from the fact that this zincblende structure has only one molecule per unit cell, while the wurtzite structure has two. Because the molecules in this wurtzite structure are crystallographically equivalent (but not translationally equivalent), it is possible to calculate wave functions for only one molecule to obtain band wave functions, if appropriate nonperiodic boundary conditions are used. The error made in the energies by distorting the boundary shape and boundary conditions on this cell to those appropriate to the zincblende is the chief error in the model. Clearly if the tight binding approximation were a reasonable starting point for energy band calculations in ZnO, CdS or ZnS, the quasi-cubic model should also be a reasonable approximation.

It may be hoped that all errors do not add, and that the model represents a valid approximation to ZnO, CdS and ZnS. In the last analysis, the model stands or falls on the basis of its agreement with experiment.

In CdS, where the energy bands are separated by reasonable distances compared to the exciton binding energies (and thus optical matrix elements could be determined unambiguously), excellent agreement was found between the predictions of the model and experimental fact.<sup>(5)</sup> In brief review of Ref. (5),  $\epsilon$  (poorly determined experimentally) was found to be about 1/7, a bit larger than expected but small compared to 1. The matrix element H was, of course, determined from experiment. The *three* parameters  $\epsilon$ , H and  $(\delta/\Delta)$ give correctly-by using the optical matrix elements determined from the band wave functions (6)—all five optical matrix elements within experimental error. The determination of  $(\delta/\Delta)$  (which does not depend on the value of  $\epsilon$ ) could be made within about 10 per cent. The ratio  $E_2/E_3$  can be computed directly from  $(\delta/\Delta)$  and was found to agree within experimental error with the measured value. One prediction that would be of interest to check is the valence band splitting in cubic CdS. This valence band splitting should be  $\delta$  rather than  $E_2$  or  $E_3$ .

The work of THOMAS<sup>(2)</sup> has shown that the quasi-cubic model succeeds only qualitatively in predicting the properties of ZnO. The parameter  $\epsilon$ is zero within experimental accuracy. The chief failing is that the model predicts the existence of weak lines in the "wrong" mode of polarization having strengths about 1/50 of the strong lines, whereas the observed ratio is about 1/5000. There exists some difficulty in experimentally identifying the optical matrix elements referring to a given band (rather than to a given exciton) since the two highest valence bands are only split by about 1/10of the exciton binding energy, and exciton and configuration mixing is inevitable. The interpretation given to the experimental results may therefore be in error. Alternatively, the model may simply not be accurate enough in powers of  $(\delta/E_a)$ and  $\Delta/E_g$  to expect to be able to calculate such

small matrix elements with any degree of precision.

Perhaps the most important single piece of evidence relating to the inadequacy of the model is the fact that  $\delta$  has the wrong sign (opposite to the usual free ion sign) in ZnO. This sign is a direct consequence of the experimental interpretation which paces the  $\Gamma_9$  valence band below the  $\Gamma_7$ valence band from which it is split only by spinorbit coupling. There are many possible reasons for the "observation" of an inverted multiplet in the bands of ZnO. If the valence band actually represents an inverted multiplet (which in the atomic case, can arise only from configuration interactions between different spatial one-electron wave functions) it is likely that the model (which allows for no configuration interactions between wave functions of different one-electron bands) is not adequate.

The model could be made to agree with experiment by the *ad hoc* introduction of a nonisotropic spin-orbit interaction (and one additional parameter to characterize this additional interaction). This elaboration has not been added, for the model in its present crude form seems to fulfill its purpose of providing a semiquantitative basis for correlating the observed properties of the valence band.

# V. APPLICATION TO ZnO

The point group of ZnO is  $C_{6v}^4$ . The symmetry operations, irreducible representations, and character table have recently been discussed by BIRMAN<sup>(13)</sup> and CASELLA<sup>(14)</sup>. A copy of BIRMAN's character table is included for reference in Table 1. There are believed to be three *P*-like valence bands at  $\mathbf{k} = 0$ , two belonging to  $\Gamma_7$  and one belonging to  $\Gamma_9$ .<sup>(15)</sup> The existence of the three valence bands and the general character of the wave functions can be understood on the basis of the quasi-cubic model. The conduction band at  $\mathbf{k} = 0$  is believed to be *S*-like, and also belongs to  $\Gamma_7$ .

For light traveling in a principal direction in the crystal, excitons belonging to  $\Gamma_5$  are observable for light polarized perpendicular to the *c*-axis, and excitons belonging to  $\Gamma_1$  are observable in light polarized parallel to the *c*-axis. All other exciton transitions are forbidden.

Experimental evidence<sup>(2)</sup> supports the assumption that the electron is lighter than the hole and

	E	$\overline{E}$	$2C_2$	2C3	$2\overline{C}_3$	2 <i>C</i> 6	$2\overline{C}_6$	6 <i>0a</i>	6 <i>o</i> v
$\Gamma_1$	1	1	1	1	1	1	1	1	1
$\Gamma_2$	1	1	1	1	1	1	1	-1	-1
$\Gamma_3$	1	1	-1	1	1	-1	-1	1	-1
Γ4	1	1	-1	1	1	-1	-1	-1	1
$\Gamma_5$	2	2	-2	-1	-1	1	1	0	0
$\Gamma_6$	2	2	2	-1	-1	-1	-1	0	0
$\Gamma_7$	2	-2	0	1	-1	√(3)	$-\sqrt{(3)}$	0	0
$\Gamma_8$	2	-2	0	1	-1	√(3)	√(3)	0	0
Г9	2	-2	0	-2	2	0	0	0	0

Table 1. Character table for the double groups of the wave vector 0 in the wurtzite structure (after BIRMAN).

dominates the reduced mass. The off diagonal components of the effective mass tensor in this case arise only from spin-orbit interaction and can be regarded as small. The most likely estimate for the ground-state wave function would be that it is roughly hydrogenic, so that the spatial part of the wave function belongs to  $\Gamma_1$  and is analogous to a 1 S-state in hydrogen. In the lowest approximation, applying the rules of Section III, there are three sets of four ground state excitons derived from the bands as shown in Table 2. Corresponding

Table 2. The ground-state excitons in ZnO. The rows represent the different valence bands

Valence band	States analogous to the hydrogenic S-state	Oscillator strength		
$\Gamma_7$	$ \begin{array}{c} \Gamma_1 \text{ (weak)} \\ \Gamma_2 \\ \Gamma_5 \text{ (strong)} \end{array} $	$\begin{array}{c}f_1\\0\\f_2\end{array}$		
Г9	$\Gamma_5$ (strong)	$f_3$		
	$\Gamma_6$	0		
$\Gamma_{7} \qquad \begin{array}{c} \Gamma_{1} (strong) \\ \Gamma_{2} \\ \Gamma_{5} (weak) \end{array}$		f4 0 f5		

to these twelve states should be five optically observable lines, three observable for  $E \perp c$  and two for  $E \parallel c$ . To lowest order, the strengths of these lines are proportional to the  $\mathbf{k} = 0$  matrix elements for band-to-band transitions, and have been estimated by THOMAS<sup>(2)</sup> on the basis of the band model of Section IV. The lines listed as weak have oscillator strengths which vanish if the spin-orbit interaction is zero.

In the absence of electron-hole spin interactions (which arise chiefly from the exclusion principle) and long range coulomb effects, all the exciton states would be four-fold (accidentally) degenerate, corresponding to the four orientations of electron and hole spin. We have found by a rather general argument three sets of four states, each set of which is expected to have approximately the same energy. This must continue to be true (neglecting the above two interactions) in spite of the various configuration interactions which can occur.

For hydrogenic excitons, the spin-spin interaction is expected to be very small because of the relatively large exciton radius. Experimentally, the  $\Gamma_1$  exciton belonging to the highest lying valence band has little oscillator strength, and should be little affected by the long-range Coulomb effects. The same statement should be true for the  $\Gamma_5$ exciton belonging to the lowest valence band. The two lowest energy  $\Gamma_5$  excitons are separated in energy rather little compared to their experimental energy of binding, and have large oscillator strengths. The long-range coulomb interactions are then expected to mix and shift these two excitons.

The optical matrix elements are much more sensitive to band mixing, and therefore more difficult to estimate. On the basis of the model of Section IV, and neglecting configuration mixing, it is expected that  $f_2 \approx f_3 \approx \frac{1}{2}f_4$ . The mixing of excitons 2 and 3 can easily upset  $f_2 \approx f_3$ , but  $f_2 +$  $f_3 = f_4$  is still expected to be valid (and is true spatial symmetries for the envelope functions will be respectively  $\Gamma_5$ ,  $\Gamma_1$  and  $\Gamma_1$ . The optically observable excitons which should arise from these configurations are given in Table 3. The lines classified as weak involve either the spin-orbit interaction (which is very small) or band mixing (as in Section III) or both to produce their oscillator strength, and will be unobservable in reflection. The lines for which the intensity is given by a question mark are weak for the same reasons, but can be easily mixed with the corresponding 2 S (strong) states by deviations from the effective mass approximation and the nondiagonal part of the

Table 3. The low lying optically observable excited states of excitons in ZnO. The column heading gives the analogous hydrogenic state; the rows represent the different valence bands

Valence band	$2P_{\pm 1}$	2.5	2 P <sub>0</sub>	
$\Gamma_7$	2Γ5(accidentally degenerate)(?) Γ1(weak)	Γ5(strong) Γ1(weak)	Γ <sub>δ</sub> (?) Γ <sub>1</sub> (weak)	
Г9	$\Gamma_5(?)$ $\Gamma_1(\text{weak})$	$\Gamma_5(\text{strong})$	Γ <sub>5</sub> (?)	
Γ7	$2\Gamma_5(\text{accidentally})$ degenerate) (weak) $\Gamma_1(?)$	Γ5(weak) Γ1(strong)	Γ5(weak) Γ1(?)	

within experimental error). The difficulty in estimating  $f_1$  was briefly considered in Section IV.

It is experimentally observed<sup>(2)</sup> that the lowest energy (weak)  $\Gamma_1$  (nondegenerate from the point of view of group theory) line exhibits what appears to be a *linear* Zeeman effect for a magnetic field applied along the hexagonal axis. Such a magnetic field has symmetry  $\Gamma_2$ , and mixes  $\Gamma_1$  only with  $\Gamma_2$  (or other  $\Gamma_1$  states) to all orders. The linear Zeeman effect is expected from the previous theoretical argument, for we have shown that the energy difference between the lowest  $\Gamma_1$  and  $\Gamma_2$ states arises only from the very weak spin-spin forces between electrons and holes.

The excited states observed in reflection are much more complicated. On the basis of a hydrogenic model the possible low lying excited states should be  $2 P_{\pm 1}$ , 2 S and  $2 P_0$ . The (approximate) tensor mass. This mixing will certainly take place if the 2  $P_{\pm 1}$  and 2 S (or 2  $P_0$  and 2 S) states lie close together.

The observation of one strong line and one or two weak lines for each band is then easily understood on the basis of Section III. Since the effective mass approximation should be a fair approximation for these excited states, the experimental observations by THOMAS<sup>(2)</sup> of multiplet n = 2levels indicates the presence of a small reduced mass anisotropy (the dielectric constant is very nearly isotropic) in ZnO at k = 0. This anisotropy must be small, for the accidental 2S-2P degeneracy of the hydrogen atom is very nearly present in the excitons in ZnO.

#### VI. CONCLUSION

The group theory of weakly bound excitons was

developed in terms of the symmetries of electron and hole bands. Direct excitons belong to irreducible representations of the single group of the point  $\Gamma$  (whether or not the optical band gap occurs at  $\Gamma$ ). The symmetries of weakly bound excitons can be found in two steps. On the basis of the effective mass approximation, the orbital symmetry which should correspond to a given energy level can be estimated. This orbital symmetry is not an exact quantum number. The exact exciton symmetries of excitons having approximately the effective mass energy can then be found by taking products of electron and hole symmetries with the orbital symmetry estimated in the effective mass approximation.

If sufficient further experiments can be performed on ZnO, it should be possible to completely determine the  $\mathbf{k} = 0$  bands parameters from the optical absorption spectrum. The present work was performed because of the observed complexity of the exciton spectrum. Allowed excitons, forbidden excitons, longitudinal excitons and excited states of excitons have all been observed in ZnO. Both group theory and a band model seemed necessary to interpret the observed data. The combination of a simple band model with a knowledge of the symmetry properties and accidental degeneracies of weakly bound exciton states has produced a qualitative (and in some respects quantitative) understanding of the exciton level structure in ZnO and CdS. This understanding is necessary in order to make use of the exciton states as a tool for the energy band structure in ZnO and CdS.

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#### APPENDIX

Let  $Y_{lm}(\theta, \phi)$  be a spherical harmonic, and S a proper rotation of three-dimensional space. Then the function

$$f_{lm} = \sum_{S} Y_{lm}(S^{-1}\theta, \phi) \exp(i\mathbf{k}S\mathbf{r})$$

transforms under rotations like  $Y_{lm}$ . The sum is performed over all proper rotations S. The function  $f_{lm}$  is orthogonal to  $f_{l'm}$  for either  $m \neq m'$  or  $l \neq l'$ . Let  $L_{m,l,i}(k)$  be a crystal harmonic, and S be a symmetry operation of the point group. The analogous theorem would be that the functions

$$f_{m,l,i} = \sum_{S} L_{m,l} i(S^{-1}k) \psi_k(Sr)$$
(A1)

were also orthogonal as in the case of the continuous group. (If they were orthogonal, the transformation from the terms in equation (3) to those in equation (4) would be unitary.) This, however, can clearly not be true, since there are but a finite number of operations S and thus a finite number of equivalent functions  $\psi_k$ , whereas there are an infinite number of functions  $f_{m,l,i}$ . For a general k there are exactly N possible independent functions  $f_{m,l,i}$ , where N is the order of the group. The symmetry of the possible functions  $f_{m,l,i}$  can be deduced by noting that the set  $\{\psi_k(Sr)\}$  is a basis for the regular representation. Thus if  $\Gamma_i$  is an  $M_i$  dimensional representation of the point group exactly  $M_i$  sets (of  $M_i$  functions each) of functions of equation (A.1) will belong to  $M_i$ . This is the basis of the counting difficulty in equation (4). Writing the sum over all crystal harmonics is redundant.

The following theorem can then be proved. Let  $\Gamma_i$  be an  $M_i$  dimensional representation of a point group. Let  $\Gamma_1$  be the identity representation. For  $i \neq 1$ , there are exactly  $M_i$  sets (of  $M_i$  functions) of crystal harmonics belonging to  $\Gamma_i$  can be written as linear combinations of these  $M_i$  sets times crystal harmonic belonging to  $\Gamma_1$ .

As an example, the crystal harmonics for the wurtzite structure are given below. The simplest co-ordinate system to use is cylindrical co-ordinates r, z,  $\phi$ . The normalization factors have been omitted.

$$\begin{split} &\Gamma_{1}f(r,z) \times \left[1, \ e^{6i\phi} + e^{-6i\phi}, \ e^{12i\phi} + e^{-12i\phi}, \ \dots\right] \\ &\Gamma_{2} & \times \left[e^{6i\phi} - e^{-6i\phi}, \ e^{12i\phi} - e^{-12i\phi}, \ \dots\right] \\ &\Gamma_{3} & \times \left[e^{3i\phi} + e^{-3i\phi}, \ e^{9i\phi} + e^{-9i\phi}, \ \dots\right] \\ &\Gamma_{4} & \times \left[e^{3i\phi} - e^{-3i\phi}, \ e^{9i\phi} - e^{-9i\phi}, \ \dots\right] \\ &\Gamma_{5} & \times \left[\frac{e^{i\phi}, \ e^{-5i\phi}, \ e^{7i\phi}, \ e^{-11i\phi}, \ e^{13i\phi}, \ \dots\right] \\ &\Gamma_{6} & \times \left[\frac{e^{2i\phi}, \ e^{-4i\phi}, \ e^{8i\phi}, \ e^{-10i\phi}, \ e^{14i\phi}, \ \dots \right] \\ &\Gamma_{6} & \times \left[\frac{e^{2i\phi}, \ e^{-4i\phi}, \ e^{8i\phi}, \ e^{-10i\phi}, \ e^{14i\phi}, \ \dots \right] \end{aligned}$$

For illustration of the theorem, we see that  $e^{5i\phi}$  and  $e^{-5i\phi}$  cannot be made up of linear combinations of harmonics belonging to  $\Gamma_1$  and  $e^{i\phi}$  and  $e^{-i\phi}$ . On the other hand

$$e^{7i\phi} = e^{i\phi}[e^{6i\phi} + e^{-6i\phi}] - e^{-5i\phi}$$

The theorem can be used as an aid in constructing higher order crystal harmonics. Similarly, VON DER LAGE and BETHE'S Kubic Harmonics<sup>(11)</sup> ( $\gamma_{6}$ )<sub>1</sub> and ( $\gamma_{6}$ )<sub>2</sub> can be written as linear combinations of  $[(\gamma_4)_1 \text{ and } (\gamma_2)_1]$  and  $[(\gamma_4)_2 \text{ and } (\gamma_2)_2]$ , respectively.

Perhaps the simplest way to understand the redundancy of expression (4) is in analogy with the full rotation group. For the full rotation group, a general function can be expanded

$$f(\mathbf{r}) = \sum_{l, m} g_{lm}(|\mathbf{r}|) Y_{lm}(\theta, \phi)$$

where  $g_{lm}(|\mathbf{r}|)$  is a rotationally invariant function. The sum goes over all l and all m. For a finite group, one may write

$$f(\mathbf{r}) = \sum_{m \ l, \ i} g_{m,l,i}(\mathbf{r}) L_{m,l \ i}(\mathbf{r})$$

where  $g_{m,l,i}(r)$  is a function which is invariant under the symmetry operations of the finite group, and  $L_{m,l,i}(r)$  are crystal harmonics. If the group has order N, it is necessary to keep only N terms in the sum. If these N terms are properly chosen, all other possible terms will be redundant.

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