THE THEORY OF EXCITONS IN ANISOTROPIC SEMICONDUCTORS

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Abstract. The Effective Mass Theory (EMT) for isotropic crystals is briefly reviewed. Its shortcomings are pointed out. Reference is then made to our earlier work on the extension of this theory : Solving the effective wave equation (EWE) with the effective Hamiltonian expanded to ∇^4 and the static dielectric constant replaced by a dielectric function which depends on the electron-hole separation. A similar approach is now adopted for anisotropic crystals. An Effective Wave Equation (EWE) is developed and solved for a model semiconductor. The model chosen is very simple : a uniaxial semiconductor having an anisotropic band structure such that the anisotropic in the crystal structure and the band structure are small enough to be considered as perturbations on an overall isotropic semiconductor. The theory developed is then applied to the exciton spectrum of CdS. The relative magnitudes of the anisotropy and the dielectric corrections are calculated. The theoretical results are compared with the experimental observations.

Introduction

The electrically neutral nonconducting excited electronic states of an insulating or semiconductor crystal are known as excitons. In the band picture of solids, the process of electronic excitation corresponds to the raising of an electron from the valence band to the conduction band leaving behind a hole in the valence band. When corelations corrections are taken into account, excitons are, then, effectively, the states formed by the electron and the hole interacting with each other in the background of the crystal. The existence of exciton states is revealed by the presence of a complicated structure or a sequence of lines in the fundamental optical absorption edge of many crystals such as Cu_2O,[1] $CuCl$[2] and CdS.[3] The formal theory of the exciton states of crystalline solid has been developed by many investigators.[4,5] In the zero order proximation, the energies of the Wannier[4,6] type exciton states of an insulting crystal of static dielectric constant ϵ_0 are given by the hydrogenic relation :

$$E_n = \text{Constant} - \frac{\mu e^4}{2\epsilon_0^2 \hbar^2 \eta^2}$$

where μ is the effective reduced mass of an electron hole pair. An extension of the conventional theory for Wannier excitons in isotropic crystals is reported in ref. 7 and has been subsequently[8,9] applied to the exciton spectra of Cu_2O and $CuCl$. In the present paper, the extended effective mass theory has been developed for slightly anisotropic crystals such as CdS which has an hexagonal structure with uniaxial symmetry and anisotropic band structure with the two principal components of the effective mass

tensor much greater than the third principal component. The anisotropies are considered as perturbations on effective overall isotropies in the dielectric constant and the band structure of the crystal. Therefore in the first order the procedure adopted for solving the effective wave equation in the anisotropic crystal is the same as for isotropic crystals. For the state $\underline{n} = 1$, the solution is obtained

by the variation method and for higher states by the perturbation method. The extended theory is applied to the exciton spectrum of CdS. The relative magnitudes of the dielectric correction and the anisotropy are calculated. Comparison of the theoretical and the experimental values for the binding energies of excitons in Table I indicates the success of the proposed theory for the type anisotropic crystals considered here.

Review of Effective Mass for Isotropic Semiconductors

The effective Schrödinger equation (ESE) for an exciton formed by raising an electron from a state $\underline{k}_h$ in the valence band $\underline{E}_v(\underline{k})$ to a state $\underline{k}_e$ in the conduction band $\underline{E}_c(\underline{k})$ is known[4] to be

$$\left[\underline{E}_c\left(-i\underline{\nabla} + \frac{\underline{K}}{2}\right) - \underline{E}_{i\gamma}\left(-i\underline{\nabla} + \frac{\underline{K}}{2}\right) - \frac{e^2}{\epsilon\gamma}\right]\underline{U}_{\underline{k}}$$
$$= \underline{E}_{\underline{k}}(\gamma)\,\underline{U}_{\underline{k}}(\gamma) \qquad \ldots(1)$$

$\underline{K} = \underline{k}_e - \underline{k}_h$ is the wave vector of the exciton, γ is the electron-hole separation and ϵ is the dielectric constant of the crystal. For discrete line absorption

TABLE.   OBSERVED AND CALCULATED BINDING ENERGIES OF THE A SERIES OF EXCITONS IN CdS AT 4.2°K

State	at n, l, m	Σ^{obs} (eV)	Σ^o (eV)	Σ^γ (eV)	Σ^α (eV)	Σ_{nlm} (eV)	$\Sigma^{obs} - \Sigma^o$ (eV)	$\Sigma^{obs} - \Sigma^{(cal)}_{nlm}$ (eV)
1S	1, 0, 0	0.0298	0.0113*	0.0000	0.0185	0.0298	0.0185	0.0000
2S	2, 0, 0	0.0075	0.0067	0.0000	0.0003	0.0070	0.0008	0.0005
2P$_{00}$	2, 1, 0	0.0075	0.0067	0.0004	0.3×10^{-6}	0.0071	0.0008	0.0004
2P$_1$	2, 1, 1	0.0069	0.0067	−0.0002	0.3×10^{-6}	0.0069	0.0008	0.0006
3S	3, 0, 0	—	0.0029	0.0000	0.89×10^{-4}	0.0029	—	—
3P$_0$	3, 1, 0	0.0032	0.0029	0.0001	1.0×10^{-7}	0.0030	0.0003	0.0002
3P$_1$	3, 1, 1	—	0.0029	0.0001	1×10^{-7}	0.0030	—	—
3D$_0$	3, 2, 0	—	0.0029	0.0001	4×10^{-13}	0.0030	—	—
3D$_1$	3, 2, 1	—	0.0029	$< 10^{-4}$	4×10^{-13}	0.0029	—	—
3D$_2$	3, 2, 2	0.0028	0.0029	−0.0001	4×12^{-13}	0.0028	−0.0001	0.0000
4S		0.00168	0.0000	—	—	0.00168	—	—
4P$_0$	4, 1, 0	—	0.00168	$< 10^{-4}$	—	0.00168	—	—
4P$_1$	4, 1, 1	0.0017	0.00168	$< 10^{-4}$	—	0.00168	0.00002	0.00002
4D$_1$	4, 2, 1	0.0017	0.00168	—	—	0.00168	0.00002	0.00002
4D$_2$	4, 2, 2	0.0017	0.00168	—	—	0.00168	0.00002	0.00002

*For $\epsilon = \epsilon_0 = 9.27$; $\Sigma^o = 0.0270$ eV and $\Sigma^o - \Sigma^{obs} = -0.0028$ eV.

by exciton $\underline{K} = 0$. Therefore for the sake of simplicity and without loss of generality of the present article, $\underline{K}$ will be considered zero. Then equation (1) reduces to

$$[E_c(-i\underline{\nabla}) - E_u(-i\underline{\nabla}) - \frac{e^2}{\epsilon r}]\, U(\underline{\gamma}) = E\, U(\underline{\gamma}) \quad \ldots(2)$$

Let ϵ, in equation (2), be taken as the static dielectric constant ϵ_0. Assuming that the valence and conduction bands are nondegenerate, isotropic and have energy extrema at $\underline{k} = 0$, then for small $\underline{k}_e$ and k_h around $\underline{k} = 0$

$$E_c(\underline{k}_e) = E_c(o) + \frac{\hbar^2 \underline{k}_e^2}{2\, m_h^*} \quad \ldots(3)$$

$$E_u(k_h) = E_v(o) - \frac{\hbar^2 k_h^2}{2\, m_h^*} \quad \ldots(4)$$

where m_e^* and m_h^* are respectively the effective masses of electron and hole. Replacing $\underline{k}_e$ and $\underline{k}_h$ in the above equations by $-i\underline{\nabla}$ and substituting in equation (2), we get

$$[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{\epsilon_0 \underline{\gamma}}]\, \underline{U}(\gamma) = (\underline{E} - E_g)\, U_{(\gamma)}, \quad \ldots(5)$$

where

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \quad \ldots(6)$$

is the reciprocal of the reduced mass of the exciton and

$$E_g = E_c(0) - \underline{E}_v(0) \quad \ldots(7)$$

is the energy gap at $\underline{k} = 0$

Equation (5) is exactly like the equation for a hydrogen atom with an effective charge $e/\sqrt{\epsilon_0}$ from which it is concluded that energies of excitons are

$$E_n = E_g - \frac{\mu\, e^4}{2\epsilon_0^2\, \hbar^2\, n^2}; \qquad \ldots(8)$$

and the functions $U(r)$ are given by

$$U_{nlm}(\gamma) = N_{nlm}\, R_{nl}(\gamma)\, Y_{lm}(\theta\,\phi) \qquad \ldots(9)$$

where the hydrogenic $R(\gamma)$ are modified by ϵ_0 to $R_{nl}(\gamma)$.

The frequency ν_n of the absorption lines of the crystal corresponding to the direct or vertical transition ts given by

$$\hbar\,\nu_n = E_g - \frac{\mu\, e^4}{2\epsilon_0^2\, \hbar\, n^2} \qquad \ldots(10)$$

The above simple theory which, from here onwards, will be called the Zero Order Effective Mass Theory (ZEMT) is known to represent the exciton spectra of many crystals[1, 2, 3] but an increasing discrepancy occurs for decreasing order of the quantum number n. This discrepancy between the ZEMT and experiments is a general effect and in view of the existing high optical resolution attained in spectroscopy, it is also substantial for the $n=1$ excitons. For example for Cu_2O, the deviation is 2.4% for the $n=1$ line but is approximately 0.5 per 10^4 for the $n=2$ excitons. For CuCl, the deviation is 0.7% for $n=1$ and is less than 1 part per 10^4 for $n=2$ and $n=3$ lines.

Khattak and Goodman accounted[7] for these deviations by introducing two corrections to the ZEMT : (i) the expansion of the kinetic energy operators of the effective Hamiltonian up to ∇^4 terms and representation of the screening of the electron and hole charges in the crystal by an γ-dependent dielectric function which has the feature of interpolating between the static dielectric constant ϵ_0 corresponding to the maximum screening and the value unity corresponding to bare coulomb interaction. As for the qualitative justification of the γ-dependent dielectric function $\epsilon_{(\gamma)}$, it is obvious that, when the two particles are very close, the frequency of their internal motion will be so high that neither the ion-cores nor the extra-core valence electrons can follow this rapid motion. Polarization effects will thus be absent and the dielectric constants will then be unity. On the other hand, when the particles are far apart, the lattice of the crystal as a whole can respond to the relatively slow motion of the particles. Screening of the interaction will thus be essentially

complete and ϵ will be the static dielectric constant. A definite mathematical expression for the dielectric function possessing the desirable feature of interpolating between the two limits ($\epsilon_{(\gamma)} \to 1$ as $\gamma \to 0$ while $\epsilon_{(\gamma)} \to \epsilon_0$ as $\gamma \to \infty$) is given in ref. 7. The result is given here

$$\frac{1}{\epsilon_{(\gamma)}} = \frac{1}{\epsilon_0} + \frac{\epsilon_0 - 1}{\epsilon_0}\left[\frac{\bar{e}\, e^{-K_e\gamma} + \bar{e}^{-K_h\gamma}}{2}\right] \qquad \ldots(11)$$

where K_e^{-1} and K_h^{-1} are characteristic screening distances of the crystal for electron and hole respectively. Replacing ϵ in equation 2 by $\epsilon_{(\gamma)}$ in the equation 11 the ESE for excitons in crystalline dielectrics becomes

$$\left[E_c(-i\nabla) - E_v(-i\nabla) - \frac{e^2}{\epsilon_{(\gamma)}\gamma}\right]U_{(\gamma)} = E\,U_{(\gamma)} \qquad \ldots(12)$$

This equation, expanded upto ∇^4 has been solved[7] for crystals with isotropic band-structure and isotropic dielectric constant. The extended EMT is then applied to the calculations of the relative magnitudes of the ∇^4 and dielectric corrections to the exciton energies in Cu_2O[1] and $CuCl$.[2] These calculations are in very good agreement with experiments and also show that the ∇^4 correction is small compared with the dielectric correction. A similar theory is now developed for anisotropic crystals. In this case, the expansion of kinetic energies will be carried only upto ∇^2 terms but in the potential energy $\epsilon_{(\gamma)}$ will not be taken as a constant.

Development of Effective Wave Equation for Excitons in Anisotropic Crystals

Fnr anisotropic crystals and for crystals having anisotropic band structure near $k=0$, the effective Hamiltonian takes a form different than equation 5. The anisotropy considered here will be that of uniaxial crystals exhibiting an anisotropy so small that it can be considered as a first-order perturbation on the isotropic case and having a band structure such that one of the two important bands participating in exciton formation is isotropic and the other has an assymetry in only one direction. CdS is a good example of this model of anisotropic semiconductor.

Let us define the Z-direction as the direction of asymmetry. Let the condition band be isotropic and the valence band be anisotropic in the k_z-direction Let p and s stand respectively for components of tensor quantities parallel and perpendicular to the principal z-axis. The isotropic potential energy

operator $-e^2/\epsilon_0^\gamma$ corresponding to the static dielectric constant is then[10, 11]

$$V_{(\gamma)}^0 = -\frac{e^2}{[\epsilon_s\epsilon_p(x_e-x_h)^2+\epsilon_s\epsilon_p(y_e-y_h)^2+\epsilon_s^2(z_e-z_h)^2]^{\frac{1}{2}}} \qquad \ldots(13)$$

The kinetic energy operator is $E_c(i\,\nabla_e)-E_v(i\,\nabla_h)$.

Expanding this and retaining terms upto ∇^2, the zero order Schrödinger equation for excitons of this model of anisotropic semiconducting crystal is

$$\left[-\frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_{hs}^*}\left(\frac{\partial^2}{\partial x_h^2}+\frac{\partial^2}{\partial y_h^2}\right) - \frac{\hbar^2}{2m_{hp}^*}\frac{\partial^2}{\partial z^2} \right.$$
$$\left. -\frac{e^2}{\epsilon_s\epsilon_p(x_e-x_h)^2+\epsilon_s\epsilon_p(y_e-y_h)^2+\epsilon_s^2(z_e-z_h)^2} \right\} U_{(\gamma)} = \mathcal{E}U_{(\gamma)}$$
$$\ldots(14)$$

where $\Sigma = E - E_g$ is the binding energy of an exciton.

Making the following transformations,[11]

$$x = x_e - x_h, \quad y = y_e - y_h, \quad z = (z_e - z_h)\left(\frac{\epsilon_s}{\epsilon_p}\right)^{\frac{1}{2}}$$

$$\epsilon_0 = \sqrt{\epsilon_s\epsilon_p}, \quad \frac{1}{\mu_s} = \frac{1}{m_e^*} + \frac{1}{m_{hs}^*}, \quad \frac{1}{\mu_p} = \frac{1}{m_e^*} + \frac{1}{m_{hp}^*}$$

$$\frac{1}{\mu} = \frac{2}{3}\frac{1}{\mu_s} + \frac{1}{3}\frac{1}{\mu_p}\frac{\epsilon_s}{\epsilon_p}, \quad \gamma = \mu\left(\frac{1}{\mu_s} - \frac{1}{\mu_p}\frac{\epsilon_s}{\epsilon_p}\right)$$
$$\ldots(15)$$

one obtains the zero-order reduced mass equation

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{\hbar^2}{2\mu}\left(\frac{2\gamma}{3}\right)\left(\frac{1}{2}\frac{\partial^2}{\partial x^2}+\frac{1}{2}\frac{\partial^2}{\partial y^2}-\frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{\epsilon_0\gamma}\right]$$
$$U_{(\gamma)} = \mathcal{E}\,U_{(\gamma)} \qquad \ldots(16)$$

The zero-order energy levels are thus determined by a mean reduced mass μ, a mean static dielectric constant ϵ_0 and a single anisotropy parameter γ.

The zero-order equation 16 is now modified by introducing γ-dependent dielectric function. If one of the components of the effective mass tensor (say m_{hp}^*) is much greater than the other (m_{hs}^*), then to a good approximation the effective interaction potential energy is given by

$$V_{(\gamma)} = -\frac{e^2}{\gamma}\left[\frac{1}{\epsilon_0} - \frac{\epsilon_0-1}{\epsilon_0}\left(\frac{e^{-\kappa^\gamma e}+e^{-\kappa_{sh}^\gamma}}{2}\right) \right] \ldots(17)$$

In excitonic units

$$\hbar = 2\mu = \frac{e^2}{2} = 1\;; \qquad \ldots(18)$$

then the EWE 16 becomes

$$\left[-\nabla^2 - \frac{2\gamma}{3}\left\{ \nabla_{xy}^2 - \frac{\partial^2}{\partial z^2} \right\} - \frac{2}{\epsilon_0\gamma} - \frac{2(\epsilon_0-1)}{\epsilon_0\gamma} \right.$$
$$\left. \left(\frac{e^{-\kappa^\gamma e}+e^{-\kappa_{sh}^\gamma}}{2}\right) \right] U_{(\gamma)} = \mathcal{E}U_{(\gamma)} \qquad \ldots(19)$$

Solution of Effective Wave Equation for Excitons in the Anisotropic Crystals

The solution of the EWE 19 for the model anisotropic crystal considered here will now be obtained by a procedure similar to that for isotropic crystals. For the $n=1$ state, the solution will be obtained by the variation and for the higher states by the perturbation method.

(a) *Solution for n=1 state by the variational method.* It is easy to see that as γ approaches smaller values, the potential energy term in equation 19 approaches the value $-\frac{2e^2}{\gamma}$ which is the same as for a hydrogen atom. Therefore, for the state $n=1$, we try the hydrogenic function :

$$U_1(\alpha\gamma) = R_{10}(\alpha\gamma)\,Y_0^0 \qquad \ldots(20)$$

as a solution to equation 19 with α as a variation parameter. Normalization of equation 20 gives

$$U(\alpha\gamma) = 2\alpha^{3/2}\,e^{-\alpha\gamma}\,Y_0^0 \qquad \ldots(21)$$

The expectation value of the anisotropic term in equation 19 in the state of the trial function 21 is

$$\langle U_1 | -\frac{2\gamma}{3}\left(\frac{1}{2}\nabla_{xy}^2 - \frac{\partial^2}{\partial z^2}\right) | U_1\rangle$$
$$= \frac{-2\gamma}{3}\left[-\frac{\alpha^2}{6} - \frac{\alpha^2}{6} + \frac{\alpha^3}{3} \right] = 0^* \qquad \ldots(22)$$

The expectation value of the effective Hamiltonian in equation 19 in the state of trial function 21 is therefore

$$\mathcal{E}_1(\alpha) = \langle U_1 | -\nabla^2 - \frac{2}{\epsilon_0\gamma} - \frac{2(\epsilon_0-1)}{\epsilon_0\gamma} \cdot$$
$$\frac{e^{-\kappa^\gamma e}+e^{-\kappa_{sh}^\gamma}}{2} | U_1\rangle$$

*It will be seen shortly that for the anisotropic term vanishes (accidentally) for all s-states. For other states it does not vanish.

$$= \alpha^2 - \frac{2\alpha}{\epsilon_0} - \frac{2(\epsilon_0 - 1)}{\epsilon_0}\left(\frac{2\alpha^3}{(2\alpha + \kappa_e)^2} + \frac{2\alpha^3}{(2\alpha + \kappa_{sh})^2}\right)$$
$$\ldots(23)$$

If α_0 is the particular value of the parameter which minimizes $\mathcal{E}_1(\alpha)$ then the energy of the $\underline{n=1}$ exciton state is given by

$$\mathcal{E}_1(\alpha_0) = \alpha_0^2 - \frac{2\alpha_0}{\epsilon_0} - \frac{\epsilon_0 - 1}{\epsilon_0}\left[\left(1 + \frac{\kappa e}{2\alpha_0}\right)^3 + \left(1 + \frac{\kappa_{sh}}{2\alpha}\right)^{-2}\right]$$
$$\ldots(24)$$

where α_0 is the appropriate root of the equation

$$\frac{\partial \mathcal{E}_1}{\partial \alpha} = \mathcal{E}' = 2\alpha - \frac{2}{\epsilon_0} - \frac{\epsilon_0 - 1}{\epsilon_0}$$
$$\left[3\left(1 + \frac{\kappa_e}{2\alpha}\right)^{-2} + 3\left(1 + \frac{\kappa_{sh}}{2\alpha}\right)^{-2}\right]$$
$$+ \frac{\epsilon_0 - 1}{\epsilon_0}\left[2\left(1 + \frac{\kappa_e}{2\alpha}\right)^{-3} + 2\left(1 + \frac{\kappa_{sh}}{2\alpha}\right)^{-3}\right] = 0$$
$$\ldots(25)$$

(b) *Solution for $n \geqslant 2$. Perturbation Approach.* For $Y \gg$ the lattice constant, the exponential terms in equation 10 approach zero. For a moment, ignoring the anisotropy, the remaining terms approach the zero order effective Hamiltonian $-\triangle^2 - 2/\epsilon_0 Y$ in equations 5 and 16. Therefore for the model anisotropic semiconductor considered here, the perturbation approach is justified. The zero order energies are $-1/\epsilon_0^2 n^2$. The first corrections due to dielectric response are given by:

$$\Sigma_{nl}^d(\kappa_e, \kappa_{sh}) = \frac{\epsilon_0 - 1}{\epsilon_0}\langle R_{nl} | \frac{e^{-\kappa_e Y} + e^{-\kappa_{sh} Y}}{Y} | R_{nl}\rangle$$
$$\ldots(26)$$

They have been calculated in Appendix A for those values of n and 1 which really matter for the Wannier

excitons. Their representation by a closed-form function has not been attempted. The first-order corrections due to anisotropy, γ, are calculated in ref. 11. Collecting the various contributions, the energies Σ_{nlm} for $\underline{n \geqslant 2}$, are given by the following:

$$\mathcal{E}_{200} = -\frac{1}{4\epsilon_0^2} - \mathcal{E}_{20}^d(\kappa_e, \kappa_{sh}) \qquad \ldots(27a)$$

$$\mathcal{E}_{211} = -\frac{1}{4\epsilon_0^2}\left(1 - \frac{2\gamma}{15}\right) - \mathcal{E}_{20}^d(\kappa_e, \kappa_{sh}) \ldots(27b)$$

$$\mathcal{E}_{300} = -\frac{1}{9\epsilon_0^2} - \mathcal{E}_{30}^d(\kappa_e, \kappa_{sh}) \qquad \ldots(28a)$$

$$\mathcal{E}_{310} = -\frac{1}{9\epsilon_0^2}\left(1 + \frac{4\gamma}{15}\right) - \mathcal{E}_{31}^d(\kappa_e, \kappa_{sh}) \ldots(28b)$$

$$\mathcal{E}_{311} = -\frac{1}{9\epsilon_0^2}\left(1 - \frac{2\gamma}{15}\right) - \mathcal{E}_{31}^d(\kappa_e, \kappa_{sh}) \ldots(28c)$$

$$\mathcal{E}_{320} = -\frac{1}{9\epsilon_0^2}\left(1 + \frac{4\gamma}{21}\right) - \mathcal{E}_{32}^d(\kappa_e, \kappa_{sh}) \ldots(28d)$$

$$\mathcal{E}_{321} = -\frac{1}{9\epsilon_0^2}\left(1 + \frac{2\gamma}{21}\right) - \mathcal{E}_{32}^d(\kappa_e, \kappa_{sh}) \ldots(28e)$$

$$\mathcal{E}_{322} = -\frac{1}{9\epsilon_0^2}\left(1 - \frac{4\gamma}{21}\right) - \mathcal{E}_{32}^d(\kappa_e, \kappa_{sh}) \ldots(28f)$$

$$\mathcal{E}_{400} = -\frac{1}{16\epsilon_0^2} - \mathcal{E}_{40}^d(\kappa_e, \kappa_{sh}) \text{ etc.} \qquad \ldots(29)$$

Equations 24, 25 and the set of equations 27 through 29 will now be applied to the exciton spectrum of CdS.

Calculations and Results for Exciton in CdS

The exciton spectrum of CdS has been studied extensively by Gross,[3] Dutton,[13] Thomas and Hopfield[11] at liquid nitrogen and liquid helium temperatures. Three series of exciton lines A, B, have been definitely identified. These series are formed by an electron in the conduction band and a hole in each of the three valence bands. The three valence bands result from a lifting of the degeneracy of the three p-like bands at $\underline{k=0}$, under the influence of crystal field and spin-orbit coupling effects. Series which arises from the top valence band and the conduction band is strongly active only for light polarized with its $\underline{E}$-vector perpendicular to the hexagonal $\underline{c}$-axis of the crystal. Series B and C are active for both modes of polarization of the light and only the A series will be considered here. Its members $\underline{n=1}$, 2, 3, 4 have been identified to obey the hydrogenic series relationship.[11]

$$E_{-n} = 2.5826 - \frac{0.0270}{n^2} \text{ eV} \quad \underline{n} = 1, 2, 3 \ldots(30)$$

CdS is anisotropic. Its top valence band is also anistropic. This anisotropy lifts the hydrogen $1 - \underline{m}$ degeneracy. The dielectric correction lifts the $\underline{n-1}$ degeneracy. Bquation 30 above gives only the gross features of the exciton lines and not the fine structure of these lines.

The effective mass of the electron in the conduction band of CdS is isotropic. The hole mass per-

pendicular to the $\underline{k}_z$-axis is different from the hole mass parallel to the $\underline{k}_z$-axis by one order of magnitude. The static dielectric constants ϵ_p and ϵ_s are not very different and so this anisotropy is small. The solutions of the wave equation developed in the solution of the effective wave equation for excitons in anisotropic crystals is thus applicable to the exciton spectrum of CdS. From an analysis of the magnetooptic absorption spectrum of CdS near the fundamental band edge, Thomas and Hopfield have established the following value for the parameters needed for our calculations.

$$m_e^* = 0.205 \, \underline{m} \quad \text{(isotropic)} \qquad \ldots(31)$$

$$m_{hp}^* = 5 \, \underline{m} \; ; \; m_{hs}^* = 0.7 \, \underline{m} \qquad \ldots(31)$$

$$\epsilon_p = 9.53, \; \epsilon_s = 9.02 \qquad \ldots(31c)$$

$$\gamma = 0.222$$

From equation (30)

$$\underline{R}_{ex}^0 = 0.0270 \, \underline{eV}. \qquad \ldots(31d)$$

From the above equations

$$\frac{1}{\underline{\mu}_p} = \frac{1}{m_e^*} + \frac{1}{m_{hp}^*} = \frac{5.078}{\underline{m}}$$

$$\frac{1}{\mu_s} = \frac{1}{m_e^*} + \frac{1}{m_{hs}^*} = \frac{6.306}{\underline{m}}$$

$$\frac{1}{\mu} = \frac{1}{3} \frac{\epsilon_s}{\epsilon_p} \frac{1}{\underline{\mu}_p} + \frac{2}{3} \frac{1}{\underline{\mu}_s} = \frac{5.80}{\underline{m}}$$

$$\mu = 0.17 \, \underline{m}$$

$$\epsilon_0 = \sqrt{\epsilon_s \, \epsilon_p} = 9.27$$

The remainder of the procedure is exactly the same as for Cu_2O and CuCl given in refs. 8 and 9. Equation 25 was solved for its roots α_0 by computer (CDC 6400) for values of κ ranging from 1.000,000 to 5.000,000 in steps of $\Delta \underline{\kappa} = 0.10$. For the sake of convenience, 2α instead of α was varied between the limits 0.200,000 and 0.400,000. The roots α_0 of $\mathcal{E}'(\alpha, \kappa)^{25}$ were then plotted versus $\underline{\kappa}$. This graph is shown in Fig. 1. The energy of the $\underline{n}=1$ exciton state $\mathcal{E}_1^{\kappa}(\alpha_0)$ was then computed by a desk calculator for the appropriate pair α_0 and $\underline{\kappa}$. The graph of $\mathcal{E}_1(\underline{\kappa})$ is shown alongside the $\alpha_0 - \underline{\kappa}$ graph in Fig. 1.

The best value of and the corresponding α_0 obtained are

$$\underline{\kappa} = \underline{\kappa}_e = 2.160 \, \underline{a}_{ex}^{-1} = 0.694 \times 10^8 \, cm^{-1} \quad \ldots(32a)$$

$$\underline{\kappa}_h = \sqrt{\frac{m_{sh}^*}{m_e^*}} \, \underline{\kappa}_e = 3.996 \, \underline{a}_{ex}^{-1} = 2.773 \times 10^8 cm^{-1}$$
$$\ldots(32b)$$

$$\alpha_0 = 0.1260 \, \underline{a}_{ex}^{-1} \qquad \ldots(32c)$$

where

$$\underline{a}_{ex} = \frac{m}{\mu} \, \underline{a}_H = 3.11206 \, \overset{\circ}{A} \qquad \ldots(32d)$$

The energy of $\underline{n}=1$ exciton state obtained from equation 24 for the above parameters of CdS is of course (by best fit) the experimental value

$$\mathcal{E}_{100} = 0.0298 \, eV \qquad \ldots(33)$$

whereas from zero order EMT one obtains for this state the energy

$$\mathcal{E}_{100}^0 = 0.0270. eV \qquad \ldots(34)$$

The energies of the states $\underline{n} \geqslant 2$ were calculated with the help of equations 27a through 29. The results are presented in the Table. For the sake of convenience we have included in this table the spectroscopic notation for the designation of the various states along with the quantum number notations, $\underline{n} \, \underline{l} \, \underline{m}$.

It has been discussed earlier that the dielectric correction removes the hydrogenic $\underline{n}-1$ degeneracy and anisotropy, γ, removes the $\underline{m}-1$ degeneracy. Both these effects are well exemplified by this table for the exciton states of CdS. It is clear from the table that the anisotropic term $\mathcal{E}_{nlm}^{\gamma}$ is zero for all $\underline{S}$-states. This is a consequence of using hydrogenic functions as the zero order solutions of the extended effective Schrödinger equation for excitons. It is also important to note that the 2$\underline{S}$ state for which $\mathcal{E}_{200}^{\gamma}$ is zero, $\mathcal{E}_{200}^{d}$ is appreciable and bring an improvement on the zero order energy $\mathcal{E}_{200}^0$ constant dielectric coefficient).

For states beyond $2P_{-o}$, $\mathcal{E}_{nlm}^{d}$ is small compared to $\mathcal{E}_{nlm}^{\gamma}$ except for $\underline{S}$-states. However $\mathcal{E}_{nlm}^{d}$ is then

itself very small compared to the zero order energy.

For state $3D_{1\pm}$ and higher states both $\varepsilon_{nlm}^{\gamma}$ and ε_{nlm}^{d} are negligible compared with ε_{nlm}^{0}, that is, the energies predicted by the extended theory converge to that of the zero order theory.

Discussion

The theory as well as the calculations presented in the preceding sections is an attempt to extend the effective mass theory for excitons so as to cover the excitons in slightly anisotropic crystals and also to incorporate the corrections brought about by the replacement of the static dielectric constant of a crystal by a dielectric function. The anisotropics in crystal structure and band structure are assumed to be small enough to be treated as perturbations on a model semiconductor which, in the zero order, has isotropic crystal and band structures. Only uniaxial anisotropy is considered but it is clear from the theory that, for all practical purposes, it will not be advantageous to develop a formalism for a general anisotropy represented by a second-order tensor. Each type of special anisotropy needs to be considered separately. It is admitted that the exciton spectra of CdS have been studied extensively. The study is well documented. It was chosen, however, as an example, for testing our proposed theory as well as for indicating the procedure and the method for calculating the relative magnitudes of the various corrections to the zero order theory. This author believes there is considerable scope for pursuing further studies in this regard.

Appendix A

The Hydrogen-like Radial Wave Functions R_{NLM} (r/ϵ_0). In a system of units $\hbar = 2\mu = e^2/21$ and an interaction potential energy $-e^2/\epsilon_0\gamma$ the radial functions are listed below.

$$R_{10} = \epsilon_0^{-3/2} \, 2 \, e^{-\gamma/\epsilon_0}$$

$$R_{20} = \frac{\epsilon_0^{-3/2}}{\sqrt{8}} (2 - \gamma/\epsilon_0) \, e^{-\gamma/2\,\epsilon_0}$$

$$R_{21} = \frac{\epsilon_0^{-3/2}}{\sqrt{24}} \, \gamma/\epsilon_0 \, e^{-\gamma/2\,\epsilon_0}$$

$$R_{30} = \frac{2\,\epsilon_0^{-3/2}}{81\sqrt{3}} (27 - 18\,\gamma/\epsilon_0 + 2\,(\gamma/\epsilon_0) \, e^{-\gamma/3\,\epsilon_0}$$

$$R_{31} = \frac{4\,\epsilon_0^{-3/2}}{81\sqrt{6}} \, \gamma/\epsilon_0 \, (6 - \gamma/\epsilon_0) \, e^{-\gamma/3\,\epsilon_0}$$

$$R_{32} = \frac{4\,\epsilon_0^{-3/2}}{81\sqrt{30}} \, \gamma^2/\epsilon_0^2 \, e^{-\gamma/3\,\epsilon_0}$$

Pawling and Wilson or Condon and Shortley are recommended for the continuation list.

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