

## APPLICATION OF THE EXTENDED EFFECTIVE MASS THEORY TO THE EXCITON SPECTRA OF CuCl

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**Abstract.** The extended effective mass theory (EMT) is applied to the interpretation of the exciton spectrum of CuCl. The coefficients of the  $\nabla^4$  terms in the effective Hamiltonian are calculated from the known band structure and crystal structure of the crystal. The screening parameters are as yet not known experimentally. The exciton spectrum of CuCl was, therefore, used itself to choose the parameters in such a manner that there is agreement between the theory and experiments for the  $n=1$  state. The zero order exciton energies and the relative magnitudes of the  $\nabla^4$  and dielectric corrections are then calculated. The proposed theory and experimental findings are found to converge to the same result. It is also found that the empirical series formulas suggested by previous workers are defective. They need to be replaced by series relationships suggested in the present article.

An extension of the conventional effective mass theory (EMT) for excitons, as proposed<sup>1,2</sup> by the author and Prof. Goodman, has already been applied to the interpretation of the exciton spectrum of  $\text{Cu}_2\text{O}$ .<sup>1,3</sup> There, one finds an excellent agreement between the proposed theory and the experimental results.  $\text{Cu}_2\text{O}$  has closed packed F.C.C. structure<sup>4</sup> and its exciton spectrum is first class forbidden<sup>5,6</sup> i.e., direct inter-band transitions at the band edges are forbidden. CuCl has zinc blende structure<sup>7,8</sup> and its exciton spectrum is first class allowed.<sup>5,6</sup> In the present article we wish to supplement further the validity and consistency of our proposed theory by applying it to the successful interpretation of the exciton spectrum of CuCl. For the sake of ready reference and continuity of the present paper, the salient features and the important equations of the extended<sup>1,2</sup> EMT will be reproduced here. The salient features of the extended EMT are: (1) Incorporation of the dielectric response of the crystal by replacing the static dielectric constant by electron-hole separation dependent dielectric function; (2) Inclusion of the  $\nabla^4$  terms of the expansion of the effective Hamiltonian; (3) Solution of the resultant effective Schrodinger equation by a variational method for the  $n=1$  excitons and by perturbation method for the states  $n \geq 2$ . The important equations of the extended theory are given in the next section.

In order to apply the extended EMT to a particular crystal one needs to know the band structure parameters  $m_e^*$ ,  $m_h^*$ , the crystal-cum-band structure parameters  $C_c$ ,  $C_v$ , the screening parameters  $k_e$ ,  $k_h$  and the static dielectric constant  $\epsilon_0$ . Unfortunately, all these parameters are not known independently. A method of calculating  $C_c$  and  $C_v$  has, however, been presented in our references.<sup>1,2</sup> The values of  $m_e^*$  and  $m_h^*$  are taken from the available information about the band structure of the crystal. To the best knowledge of author,

the experimental values of  $k_e$  and  $k_h$  are not yet known. Since we know the observed values of the exciton energy levels, we varied  $k_e$  (consequently  $k_h$ ) over a range of values. By this method, the best set of values of  $k_e$  and  $k_h$  as well as the relationship between the exciton energy levels and the screening parameters are established. Knowing the values of  $k_e$ ,  $k_h$  and  $\epsilon_0$ , the dielectric response function, and the relative magnitudes of the  $\nabla^4$  and dielectric correction terms are calculated. The calculations reveal that the hydrogenic  $n-1$  degeneracy is resolvable only in the case of  $n=2$  states. Finally the correction terms are added to the zero order energies to obtain the energy levels of the excitons of CuCl. The results are tabulated in Tables 2-3. The procedure carried out for determining the various parameters, is given in the following sections.

### *Important Equations of the Extended EMT.*

The extended EME for exciton is (1,2)

$$\left\{ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{\beta} + C_{cv} \nabla^4 + \frac{e^2 \nabla \epsilon}{\epsilon_0} \left[ 1 - \frac{e^{-k_e \beta} - e^{-k_h \beta}}{2} \right] \right\} U(\beta) = (E - E_g) U(\beta) \quad (1)$$

In excitonic units,

$$\hbar = 2\mu = U = \frac{e^2}{2} = 1 \quad (2)$$

its solutions for the state  $n=1$  and states  $n \geq 2$  are respectively<sup>1,2</sup>

$$\epsilon_1 = \alpha_0^2 - \frac{2\alpha_0}{\epsilon_0} + 5C_{cv}\alpha_0^4 - \frac{\epsilon_0 - 1}{\epsilon_0} \left[ \frac{1}{\left(1 + \frac{k_e}{2\alpha_0}\right)^2 + \left(1 + \frac{k_h}{2\alpha_0}\right)^2} \right] \quad (3)$$

$$\epsilon_{nl} = -\frac{1}{\epsilon_0^2 n^2} - \frac{4 C_{cv}}{\epsilon_0^4 n^3} \left[ \frac{3}{4n} - \frac{1}{l+\frac{1}{2}} \right] - \epsilon_{nl}^{(d)}(k_e, k_h) \quad (4)$$

$$\epsilon_{nl}^{(d)}(k_e, k_h) = \frac{\epsilon_0 - 1}{\epsilon_0} \left\langle R_{nl} \left| \frac{e^{-k_e \beta} - e^{-k_h \beta}}{2} \right| R_{nl} \right\rangle \quad (5)$$

where  $R_{nl}$  are the radial hydrogenic functions modified <sup>1,2</sup> by the static dielectric constant  $\epsilon_0$ .

It is convenient to recapitulate the following definitions.<sup>1,2</sup>  
The binding energy of excitons  $\epsilon_n = E_n - E_g$  (6)

$$\text{The Exciton Rydberg, } R_{ex} = \frac{\mu e^4}{2\hbar^2} = \frac{\mu}{m} R_H \quad (7)$$

$$\text{Bohr radius of exciton, } a_{ex} = \frac{\hbar^2}{\mu e^2} = \frac{m}{\mu} a_H \quad (8)$$

The variation parameter  $\alpha$  is so chosen to minimise  $\epsilon_1$  i. e.

$$\frac{\partial \epsilon_1}{\partial \alpha} = 0$$

or

$$2\alpha - 2 + 20C_{cv}\alpha^3 + \frac{2\nabla \epsilon}{\epsilon_0} \left[ 1 - \frac{6\alpha^2}{(2\alpha + k_e)^2} - \frac{6\alpha^2}{(2\alpha + k_h)^2} \right] + \frac{2\nabla \epsilon_0}{\epsilon_0} \left[ \frac{8\alpha^3}{(2\alpha + k_e)^3} + \frac{8\alpha^3}{(2\alpha + k_h)^3} \right] = 0 \quad (9)$$

The expansion of the band energies upto  $k^4$ , with  $\underline{k}$  now replaced by  $-i\nabla$  is

$$E_c(-i\nabla) = E_c(0) - \frac{\hbar^2 \nabla^2}{2m_c^*} + C_c \nabla^4 \quad (10)$$

$$E_v(-i\nabla) = E_v(0) + \frac{\hbar^2 \nabla^2}{2m_h^*} + C_v \nabla^4 \quad (11)$$

where

$$C_c = \frac{-\hbar^2 d^2}{80 m_c^*}, C_v = \frac{\hbar^2 d^2}{80 m_h^*}, C_{cv} = C_c - C_v = -\frac{\hbar^2 d^2}{80 \mu} \quad (12)$$

$$\frac{1}{\epsilon(\beta)} = \frac{1}{\epsilon_0} + \frac{\epsilon_0 - 1}{\epsilon_0} \left[ \frac{e^{-k_e \beta} - e^{-k_h \beta}}{2} \right] \quad (13)$$

H stands for hydrogen atom, d for nearest neighbour distance, and  $E_g$  for band gap at  $k=0$   
 $\nabla \epsilon$  will be used for  $\epsilon_0 - 1$ .

## Calculations and Results

### Exciton Spectrum of CuCl. Reduced Mass and Rydberg for Excitons

The exciton spectrum of CuCl has been studied by Reiss<sup>9</sup>, Nikitine<sup>9</sup>, Khan and Hadley.<sup>10</sup> Its lines consist of two different kinds of series. Nikitine has represented them by the following empirical expressions<sup>6,9</sup>

Sharp Series :\*

$$E_n^s = 3.41578 - \frac{0.21317}{n^2} \text{ eV; } n = 1, 2, \dots \infty \quad (14)$$

Diffuse Series :

$$E_n^d = 3.42730 - \frac{0.19830}{n^2} \text{ eV; } n = 1, 2, \dots \infty \quad (15)$$

The existence of the two series is not yet clear. It is presumably due to the splitting of the hole energy state ( $j=3/2, j=1/2$ ) in the  $\text{Cl}^-$  ion. When one electron of the  $p^6$  configuration of the chlorine ion is excited, the  $p^5$  configuration can be left in a state with  $j=3/2$  or  $j=1/2$ . Transitions from both of these states to the  $p^5$  excited states are allowed ( $1S_0 \rightarrow 1P_1, 3P_1$ ) and thus produces a splitting. A slightly different proposal for the existence of two series of excitons is that they are due to the difference in energy states of longitudinal and transverse excitons. The details of such types of excitons can be found in references.<sup>11,12,13</sup> Here the result is quoted "when electrons and holes of given symmetry types are coupled via a given envelope function,<sup>11</sup> symmetry, one can obtain different sets of exciton states: longitudinal transverse and of other symmetries". The energy difference between exciton states of different symmetries, (say longitudinal and transverse) give rise to different exciton series.

It is admitted that the present calculations will be carried out in specifically for the sharp series of excitons. The effects of the proximity of two sets of energy states and/or longitudinal and transverse splitting will not be explicitly considered. Their effects will be lumped together in the screening parameters  $k_e$  and  $k_h$ .

Table 1 gives the positions of the absorption line of the sharp series of excitons in CuCl at 4.2°K. In this table the calculated values refer to those obtained from equation (14).

The agreement between the calculated and the observed energies is very good. However, this agreement seems to be a forced one by selecting the exciton

\*We have converted Nikitine's expressions

$$v_n^s = 27560 - \frac{1720}{n^2} \text{ cm}^{-1}$$

$$v_n^d = 28016 - \frac{1600}{n^2} \text{ cm}^{-1}$$

from wave numbers to eV

TABLE 1. SHARP SERIES OF EXCITONS IN CuCl.

n	$\lambda_n$	obs	cal	cal	obs
	( $\text{\AA}$ )	(eV)	(eV)	(eV)	(eV)
1.	3870	3.20268	3.20261	0.00003	
2.	3685	3.36336	3.36249	-0.00087	
3.	3657	3.38910	3.39210	+0.00299	
...					
$\infty$	—	—	3.41578	—	

Rydberg and the ionization energy in such a way that no deviations occur from the  $n=1$  line. Since only three lines are observed the energy deviations of the lines  $n=2$  and  $n=3$  are obscured by the above choice of  $R_{ex}^{\circ}$  and  $E_{\infty}$ . Since generally one would expect an excellent agreement between the theory and experiment only for large quantum numbers  $n$ , we therefore have modified the series relation (14). If we accept Nikitine's value for  $E_{\infty}$  equal to 3.41578 eV and choose  $R_{ex}^{\circ}$  such that no deviation occurs for the  $n=3$  line then we find

$$R_{ex}^{\circ} = 0.24003 \text{ eV}^*$$

With this choice of  $R_{ex}^{\circ}$  and  $E_{\infty}$  quoted by Nikitine (3.41578 eV)

$$E_1^{\text{cal}} - E_1^{\text{obs}} = -0.02679 \text{ eV} \quad (16)$$

$$E_2^{\text{cal}} - E_2^{\text{obs}} = -0.00757 \text{ eV} \quad (17)$$

These energy differences are not compatible with EMT. Excitons are bound somewhat tighter than the binding predicted by the theory. The calculated values should lie above the observed values and thus the above energy differences should be positive rather than negative.

Since only three lines are observed, the best one can do is to assume that the  $n=2$  and  $n=3$  lines are both represented accurately by the hydrogenic relation

$$E_n = E_{\infty} - \frac{R_{ex}^{\circ}}{n^2} \quad (18)$$

Substituting the observed values of  $E_2$  and  $E_3$  in this equation we obtain

$$R_{ex}^{\circ} = 0.18540 \text{ eV} \quad (19)$$

$$\text{and } E_{\infty} = 3.40971 \text{ eV} \quad (20)$$

$$R_{ex}^{\circ} = \frac{\hbar^2 e^4}{2\mu \epsilon_0^2}, \quad R_{ex} = \frac{\hbar^2 e^4}{2\mu^2}$$

$$R_{ex} = R_{ex}^{\circ} / \epsilon_0^2$$

We, therefore, suggest that the sharp series of exciton lines in CuCl be represented by

$$E_n = 3.40971 - \frac{0.18540}{n^2} \text{ eV}; \quad n = 1, 2, 3, \dots \infty \quad (21)$$

and not by the relation (14) proposed by Nikitine. The energy difference between the calculated and the observed value for  $n=1$  line is then 0.02163 eV, whereas by the choice of  $R_{ex}^{\circ}$  and  $E_{\infty}$  energy the difference is zero for the lines  $n=2$  as well as  $n=3$ . Taking Nikitine's results for  $\epsilon_0 = 5$  and the equality of  $m_e^*$  and  $m_h^*$  it is easy to find from the exciton. Rydberg suggested by the present work that

$$\mu = 0.34 m$$

$$m_e^* = m_h^* = 0.68 m$$

$$k_e = k_h = k \quad (22)$$

$$\epsilon_0 = 5$$

Calculations of the Parameters  $C_{cv}$  and  $k$

To find the parameter  $C_{cv}$  we have to consider the structure of the crystal and the mechanism of the excitation of excitons in the crystal. CuCl has zinc blend structure<sup>7,8</sup> i.e., it is composed of an F.C.C.  $\text{Cu}^+$  sublattice displaced from F. C. C.  $\text{Cl}^-$  sublattice by one quarter of the body diagonal of the overall cubic lattice. The cube edge length is 5.41  $\text{\AA}$ . The formation of excitons in CuCl corresponds<sup>6</sup> to the excitation of an electron from the 3p to the 4s state in  $\text{Cl}^-$ . The electron and hole thus reside on the F. C. C. sublattice of the chlorine

ions. The  $\text{Cl}^-$   $\text{Cl}^-$  distance is  $\frac{5.41}{\sqrt{2}} \text{\AA}$ . Since

for an F. C. C. lattice  $C_{cv} = \frac{\hbar^2 d^2}{80\mu}$

we have

$$C_{cv} = - \frac{d^2}{40 a_{ex}^2} = -0.15 \text{ ex. units} \quad (23)$$

The rest of the procedure is similar to that for  $\text{Cu}_2\text{O}$ ; whose details are given in our references 1 and 3. The best value of  $k$  and the corresponding  $\alpha_0$  to be inserted in equations (3) and (4) for evaluating the energies of exciton state are

$$k_e = k_h = k = 4.24 a_{ex}^{-1} = 2.73 \times 10^8 \text{ cm}^{-1} \quad (24)$$

$$\alpha_0 = 0.246 a_{ex}^{-1} \quad (25)$$

$$a_{ex} = 1.5526 \text{\AA}$$

Energy Levels of Exciton in CuCl

The results for the energy levels of excitons and contributions from the various terms, i.e. zero order value  $\mathcal{E}_{nl}^{(0)}$  and the  $k^4$  (or  $\nabla^4$ ) correction  $\mathcal{E}_{nl}^{k^4}$  and the non-static dielectric correction are tabulated  $\mathcal{E}_{nl}^4$  in Tables 2 and 3.

TABLE 2. CALCULATED VALUES OF THE VARIOUS CONTRIBUTIONS TO THE BINDING ENERGY SHARP SERIES OF EXCITONS IN CuCl

n,l	$\epsilon_{nl}^{10}$	$\epsilon_{nl}^{k^4}$	$\epsilon_{nl}^d$	$\epsilon_{nl}$	
	in $R_{ex}$	in $R_{ex}$	in $R_{ex}$	in $R_{ex}$	in eV
1,0	0.0379	0.0027	0.0042	0.0448	0.2072
2,0	0.0200	$1.95 \times 10^{-4}$	$2.77 \times 10^{-4}$	0.0104	0.0484
2,1	0.0100	$3.49 \times 10^{-5}$	$2.40 \times 10^{-7}$	0.0100	0.0462
3,0	0.0044	$6.22 \times 10^{-5}$	$8.19 \times 10^{-6}$	0.0045	0.0208
3,1	0.0044	$1.48 \times 10^{-5}$	$1.0 \times 10^{-7}$	0.0044	0.0203
3,2	0.0044	$5.3 \times 10^{-6}$	$2.2 \times 10^{-11}$	0.0044	0.0203

TABLE 3. CALCULATED AND OBSERVED  $6^9$  POSITIONS OF THE SHARP SERIES OF EXCITON ABSORPTION LINES. IN CuCl AT 4.2°K

n,l	Observed wave length	$E_{nl}^{obs}$ in eV	$E_{nl}^{cal}$ in eV	$E_{nl}^{cal} - E_{nl}^{obs}$ in eV
1,0	3870 Å°	3.2026	3.2026	0.0000
2,0			3.3613	-0.0020
	3685 Å°	3.3633		
2,1			3.3635	+0.0002
3,0			3.3889	-0.0002
3,1	3657 Å°	3.3891	3.3894	+0.0003
3,2			3.3894	+0.0003
⋮				
∞	—	—	3.40971	—

It is clear from the Tables that  $n-1$  degeneracy is lifted. The splitting of the  $n=2$  state is  $22 \times 10^{-4}$  eV. This splitting corresponds to a wave length difference of 3 Å. In fact Reiss and Nikitine did observe two lines at 3677 Å and 3685 Å corresponding to transitions to the  $n=2$  state. The wave-length difference is 8 Å. Since the line 3677 Å is very weak, the above authors did not include this weak line in suggesting their empirical hydrogenic formula (14).

#### Discussion

Comparing equations (14) and (21) and the more sophisticated nature of the extended EMT; our claim is justified that Nikitine's formula (14)

is defective. It should be replaced by our suggested series relation(21).

It is admitted that in the present calculations  $k_e$  and  $k_h$  were determined from experimental data

of the exciton spectrum of CuCl which we wish to interpret in terms of a theory. It is desirable and, in fact, would be a good problem to calculate theoretically, the above constants from the energy band structure of CuCl. Another suggestion that is made concerns the experimental study of the fine structure of the  $n=2$  excitons. According to present calculations the wave length difference corresponding to the 2P and 2S states is 3 Å°. It seems feasible that this fine structure is resolvable by current methods of spectroscopy even if one of the lines is very weak.

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