

Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 20, No. 2, April 1977

APPLICATION OF THE EXTENDED EFFECTIVE MASS THEORY TO THE EXCITON SPECTRA OF Cu_2O

MOHAMMAD ALI KHATTAK

Physics Department, University of Peshawar, Peshawar

RALP R. GOODMAN

U. S. Naval Research Laboratories, Washington, D. C., U.S.A.

(Received February 13, 1977; revised April 14, 1977)

Abstract. The Extended Effective Mass Theory, as reported in our earlier communication, is applied to the exciton spectra of cuprous oxide. The information available about the crystal structure and the band structure of this crystal is utilised to calculate the various parameters that enter our extended theory. Since the screening parameters k_e and k_h of the electron and hole charges are so far not known experimentally, the exciton spectra of Cu_2O is itself used to choose them in such a manner that there is agreement between the theory and experiments for the $n = 1$ state. The resultant dielectric function is plotted and compared with the unscreened coulomb potential as well as the potential diluted by the static dielectric constant ϵ_0 . The relative magnitudes of the ∇^4 and the dielectric response corrections are calculated separately. The calculations also show that the hydrogenic $n-1$ degeneracy is removeable to the extent of optical resolution. The expected shape of the dielectric response curve and the concordance between the calculated and the experimental exciton energy levels indicate the success of our proposed theory.

An extension of the conventional Effective Mass Theory (EMT) for excitons was presented in our earlier communication. In the present article we intend to apply it to the exciton spectra of cuprous oxide. For the sake of ready reference and continuity the important equations are reproduced in the following section. The salient features of the extended EMT are: (i) incorporation of the dielectric response of the crystal by replacing the static dielectric constant by electron-hole separation dependent dielectric function, (ii) inclusion of the ∇^4 terms of the expansion of the effective hamiltonian, (iii) the solution of the resultant effective Schrodinger equation by a variational method for the $n = 1$ excitons and by perturbation method for the states $n \geq 2$.

In order to apply the extended EMT to a particular crystal we need to know the band structure parameters m_e^* , m_h^* , the crystal structure parameters C_c , C_v , k_e , k_h and the static dielectric constant ϵ_0 . Unfortunately these parameters are not all known independently of one and other. However, we calculated the parameter C_c and C_v . We used in our calculation the values of m_e^* and m_h^* based on the presently available experimental results.^{3,4,5,6} To the best of our knowledge the experimental values of k_e and k_h are not yet known. Since we know the observed values of the exciton energy levels, in particular the $n = 1$ level, we varied k_e (consequently k_h) over a range

of values. By this method we determined not only the best set of values for k_e and k_h , but also the relationship between the exciton energy levels and constants k_e and k_h . Knowing the values of k_e , k_h and ϵ_0 the dielectric response curve is drawn and compared with the bare coulomb potential and the potential $\frac{1}{\epsilon_0 \beta}$. Then the relative magnitudes of the corrections due to ∇^4 terms and the dielectric term were calculated. It is also revealed that the hydrogenic $n-1$ degeneracy is optically resolveable. The energy difference between the 2p and 2s states in Cu_2O is calculated to be about 10 cm.^{-1} Finally the correction terms are added to the zero order energies to obtain the energy levels of the exciton spectra of Cu_2O . These results are tabulated in Tables 1, 2. The procedure carried out for determining the various parameters is given in the following sections.

Equations of the Extended Effective Mass Theory

The extended EME for exciton is ^{1,2}

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

TABLE 1. THE VARIOUS CONTRIBUTIONS TO THE BINDING ENERGY OF EXCITONS IN Cu_2O .

n,l	ϵ_{nl}°	$\epsilon_{nl}^{k^4}$	ϵ_{nl}^d	ϵ_{nl}	
	in R_{ex}	in R_{ex}	in R_{ex}	in R_{ex}	in eV
1,0	0.0016	0.0029	0.0204	0.0249	0.1387
2,0	0.0043	33.31×10^{-6}	3.11×10^{-4}	0.0046	0.0256
2,1	0.0043	5.97×10^{-6}	18.0×10^{-6}	0.0043	0.0240
3,0	0.0019	10.62×10^{-6}	1.25×10^{-4}	0.0020	0.0111
3,1	0.0019	2.53×10^{-6}	0.36×10^{-6}	0.0019	0.0105
3,2	0.0019	0.91×10^{-6}	$\approx -10^{-10}$	0.0019	0.0105

$$\epsilon_{nl} = \epsilon_{nl}^{\circ} + \epsilon_{nl}^{k^4} + \epsilon_{nl}^d$$

$$R_{ex} = 5.774 \text{ eV}$$

TABLE 2. CALCULATED AND OBSERVED³ EXCITON ENERGY LEVELS IN Cu_2O AT 4.2°K.

n,l	λ_n^{obs}	E_{nl}^{obs}	E_{nl}^{cal}	E_{nl}^{cal}	$E_{nl}^{\circ} - E_{nl}^{obs}$	$E_{nl} - E_{nl}^{obs}$
		in eV	in eV	in eV	in eV	in eV
1,0	6095.8	2.0332	2.0732	2.0332	+0.0400	0.0000
2,0				2.1463		-0.0014
	5770.8	2.1477	2.1479		0.0002	0.0002
2,1				2.1479		
3,0				2.1608		0.0003
3,1	5735.0	2.1611	2.1614	2.1614	0.0003	0.0003
3,2				2.1614		0.0003
4	5722.8	2.1657	2.1659	2.1659	0.0002	0.0002
5	5716.8	2.1679	2.1680	2.1680	0.0001	0.0001
6	5713.1	2.1694	2.1694	2.1695	0.0001	0.0001
:						
∞	5706	2.1719	2.1719	2.1719	0.0000	0.0000

In excitonic units,

$$\hbar = 2\mu = \frac{e^2}{2} = 1$$

(2)

$$\left[\frac{1}{\left(1 + \frac{k_e}{2\alpha_o}\right)^2 + \left(1 + \frac{k_h}{2\alpha_o}\right)^2} \right], \quad (3)$$

Its solutions ^{1,2} for the state $n=1$ and states $n > 2$ are respectively

$$\epsilon_1 = \alpha_o^2 - \frac{2\alpha_o}{\epsilon_o} + 5C_{cv}\alpha_o^4 - \frac{\epsilon_o - 1}{\epsilon_o}$$

$$\epsilon_{nl} = -\frac{1}{\epsilon_o^2 n^2} - \frac{4C_{cv}}{\epsilon_o^4 n^3} \left[\frac{3}{4n} - \frac{1}{1+\frac{1}{2}} \right] -$$

$$\epsilon_{nl}^{(d)}(k_e, k_h), \quad (4)$$

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

where $R_{nl}^{\epsilon_0}$ are the radial hydrogenic functions modified^{1,2} by the static dielectric constant ϵ_0 .

It is convenient to recapitulate the following definitions:^{1,2}

$$\text{the binding energy of excitons } \epsilon_n = E_n - E_g \quad (6)$$

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

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

The variation parameter α is so chosen as to minimise ϵ_1 i.e.

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

or

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

The expansion of the band energies up to k^4 , with k now replaced by $-i \nabla$, is

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

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

where

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

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

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

Calculations and Results

Exciton Spectrum of Cu_2O - Reduced Mass of Excitons and the Static Dielectric Constant of the

Crystal. The exciton spectrum of Cu_2O has been studied very thoroughly by Gross^{3,5}, Nikitine⁴, Hadley⁷ etc. It forms probably the best known example of Wannier excitons, obeying almost a hydrogenic law except for the $n=1$ exciton where there is a variation of about 340 cm^{-1} for the yellow series of lines. For the purpose of illustration, the results of Apfel⁷ and Hadley are reproduced here in Fig. 1. We attempt to interpret these results more accurately by applying the EMT proposed in our earlier communication and as summarised above.

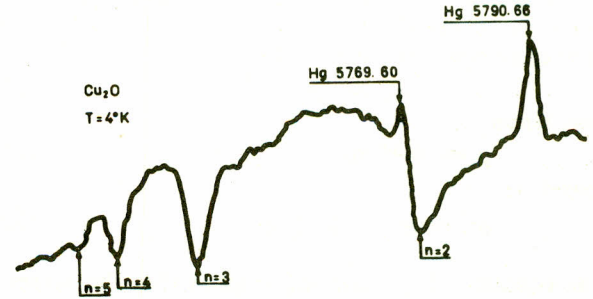


Fig. 1. Spectrometer record of exciton series in Cu_2O at a temperature of 4°K (after Apfel and Audley).

The best empirical series relation representing the yellow series of excitons in Cu_2O is

$$E_n = \left[2.1719 - \frac{0.0968}{n^2} \right] \text{ eV; } n = 1, 2, 3, \dots \infty \quad (14)$$

Comparing this equation with equation

$$E_n = E_g - \frac{\mu e^4}{2 \epsilon_0^2 \hbar^2 n^2} \quad (15)$$

of the zeroth order effective mass theory we infer that

$$E_g = 2.1719 \text{ eV} \quad (16)$$

and

$$\frac{\mu e^4}{2 \epsilon_0^2 \hbar^2} = 0.0968 \text{ eV} = \text{exciton Rydberg } R_{ex}^0 \quad (17)$$

Knowing ϵ_0 accurately, μ can be calculated to the same accuracy. However, there is a considerable uncertainty in the value of ϵ_0 quoted in the literature. Gross takes

$$\epsilon_0 \approx (\text{index of refraction})^2 \approx (2.25)^2 = 6.25$$

and therefore finds from the exciton Rydberg R_{ex}^0

$$\mu = 0.25 m$$

Nikitine uses

$$\epsilon_0 = 8.5$$

and finds

$$\mu = 0.52 m$$

This uncertainty seems to have been partially removed by Halpern and Zakharchenya⁶ who have somewhat carefully measured the reduced electron-hole mass of the yellow series of Cu_2O at 1.5°K by magneto-oscillatory absorption experiment. We

adopt for μ this somewhat recent value of

$$\mu = 0.41 m \quad (18)$$

Then it follows that

$$\epsilon_0 = 7.6 \quad (19)$$

Gross and Zakharchenya⁵ have shown that the members of the exciton series in Cu_2O do not display the ordinary linear Zeeman effect proportional to the magnetic field, but exhibit an effect proportional to the square of the magnetic field. From theoretical investigations of Samojlovic and Korenblit⁸, the magnetic splitting ∇^- in the exciton spectrum must be proportional to $(m_e^* - m_h^*)$ and one may conclude that in Cu_2O

$$m_e^* = m_h^* \quad (20)$$

and since

$$\mu = 0.41 m \quad (21)$$

therefore

$$m_e^* = m_h^* = 0.82 m \quad (22)$$

The equality of m_e^* and m_h^* implies that the screening parameters

$$k_e = k_h = k \quad (23)$$

Calculation of C_c , C_v and C_{cv} for Cu_2O Crystal and Band Structure of Cu_2O . The lattice of the Cu_2O crystal can be visualised as constructed from two sublattices⁹—a face centered cubic lattice of all copper ions and a body centered cubic of all oxygen ions, inserted and displaced relative to each other. The elementary cell of the crystal contains four copper ions and two oxygen ions. The Cu—Cu distance⁹ is 3.01 Å, Cu—O distance is 1.84 Å and the O—O distance is 3.69 Å. The electron configuration for the Cu^+ ion in the crystal is $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^{10}$ and for O^{2-} ion is $(1s)^2 (2s)^2 (2p)^6$. C 's which are the coefficients of the k^4 term in equations (11) depend on the mechanism of excitation. They depend on whether the excitation process corresponds to the excitation of the cations Cu^+ , the anions O^{2-} or an electron transfer from O^{2-} to the Cu^+ ions. From the energy band point of view the synonymous question is, whether the highest filled band is provided by the occupied 3d levels of Cu^+ or by the 2p levels of O^{2-} ions. The conduction band or the lowest empty band is provided by the 4s levels of Cu^+ ions^{10,11}. Energy band calculations^{11,12} and the study of the symmetry^{10,11} of excitons in Cu_2O has established that the exciton formation in this crystal is associated with the excitation of an electron from a 3d Cu^+ state to a 4s Cu^+ state. The electron and the hole thus both reside on the sub-lattice of Cu^+ ions. Making use of this information the coefficients C_n are calculated in terms of the Cu—Cu distance and the effective masses of the electron and the previous section hole. The result from is

$$C_c = - \frac{\hbar^2 d^2}{80 m_e^*}$$

$$C_v = + \frac{\hbar^2 d^2}{80 m_h^*}$$

$$C_{cv} = C_c - C_v = - \frac{\hbar^2 d^2}{80 \mu}$$

where

$$d = \text{Cu—Cu distance} = 3.01 \text{ \AA}$$

Determination of the Screening Parameters for Cu_2O . As far as we know no reliable experimental results are available for this characteristic constant of the crystal. Using the values of m_e^* , m_h^* , μ , ϵ_0 and C_{cv} mentioned above, we now set out to try, as roots of the Eq. (9) the various values of k ranging from 1.22 to 8.00 \AA^{-1} . For each value of k , α was varied from 0.12 to 0.80 \AA^{-1} . This enables us to find the roots α_0 of this equation. All the numerical computations were carried out using a desk calculator.

The roots were determined graphically by plotting $\epsilon'_k(\alpha; k)$ versus α with k as a parameter. A few sample graphs are presented in Fig. 2. It is found that for $k < 1.8$ there is no real value of α for which $\epsilon'_k(\alpha, k) = 0$. For $k > 1.85$ two roots α_0 and α'_0 occur in pairs. Additional calculations readily reveal that the roots α'_0 are not the minimising roots because the energy values obtained from them are much higher and even positive for some of the higher values of α'_0 . Having a set of the appropriate roots α_0 and the corresponding set of K , α_0 was plotted versus k . This graph is presented in Fig. 3. Each point on this curve mini-

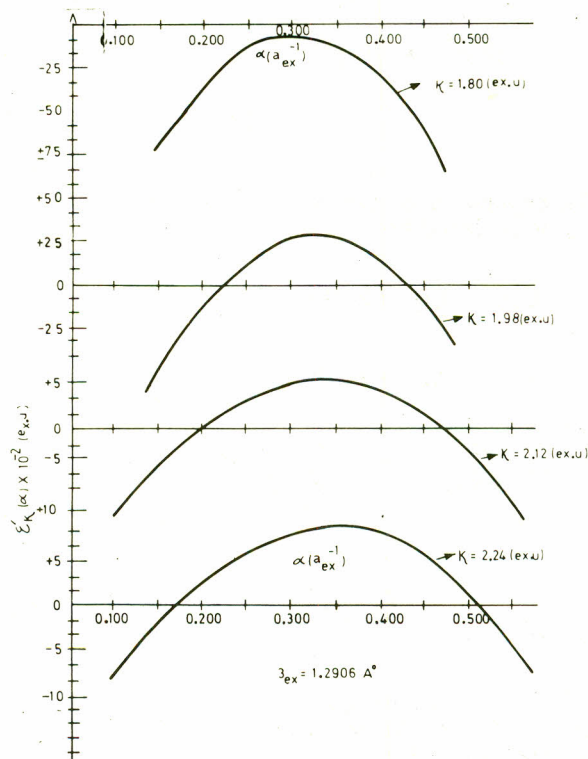
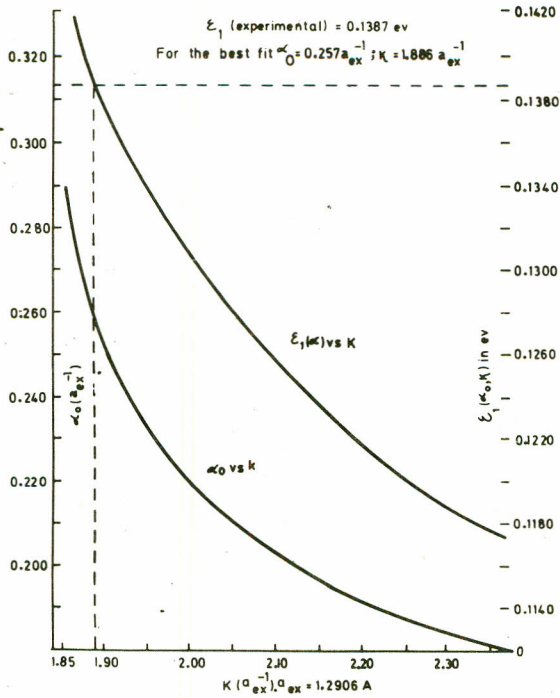


Fig. 2. Representative graph of $\epsilon'_k(\alpha)$ vs the variation parameter α for a few values of the parameter K for finding the roots of $\epsilon'_k(\alpha) = 0$ for the case of Cu_2O .


 Fig. 3. Binding energy of the 1s exciton in Cu_2O .

mizes the energy of the $n = 1$ exciton state. There is then plotted $\mathcal{E}_1(k)$ as a function of K and this graph is also given in Fig. 3. Comparing the experimental value of $\mathcal{E}_1 = 0.1387$ eV with the curve we obtain the best value of K to be

$$K = K_e = K_h = 1.886 a_{\text{ex}}^{-1} = 1.4613 \times 10^8 \text{ cm}^{-1}$$

where

$$a_{\text{ex}} = h / e^2 = 1.2906 \text{ \AA}$$

Calculations of Energy Levels of Excitons.

The energy levels calculated by using above parameters and eqs. 3, 4, 5 are tabulated in Tables 1 and 2. Contribution to the binding energy of an exciton by the k^4 term and the dielectric correction are given respectively by $\mathcal{E} k^4$ and \mathcal{E}^d . \mathcal{E}_0^n gives the results of the zero-order theory. \mathcal{E}_0^n denote exciton energies with reference to the bottom of the conduction band as the zero of energy, while E_s are energies with reference to the ground state of the crystal as the zero of energy.

In Table 1 we have denoted part of the energy $\mathcal{E}_1(\alpha_0)$ given by (3) as \mathcal{E}_1^0 . In fact $\mathcal{E}_1^0 = \alpha_0^2 - \frac{2\alpha_0}{\epsilon_0} = \text{Kinetic Energy} + \text{Part of the Potential Energy of the exciton in the state } n = 1$. Besides bringing a symmetry in the Table, \mathcal{E}_1^0 corresponds to the zero order energy of this state. If in eq. 1 we put $C_n = 0$ (no k^4 correction) and $K_e = K_h = \infty$ (static dielectric constant), then the variational method gives $\alpha_0 = \frac{1}{\epsilon_0}$ and

$$\mathcal{E}_1^0 = \alpha_0^2 - \frac{2\alpha_0}{\epsilon_0} = -\frac{1}{\epsilon_0^2}, \quad (24)$$

This is the same result as one would obtain from the rigorous solution of the Schrodinger equation of the problem. Therefore, when C is not zero and K 's are not infinite, we call $\alpha_0^2 - \frac{2\alpha_0}{\epsilon_0}$ as \mathcal{E}_1^0 .

However, we note that \mathcal{E}_1^0 differs significantly from \mathcal{E}_1 , while for the states $n \geq 2$, \mathcal{E}_n^0 differs from \mathcal{E}_n only by the amount of perturbation present.

It is obvious from Table 1 that the hydrogenic l -degeneracy is lifted—levels of the same n but different l have slightly different energies. The energy difference between the 2p and 2s states is

$$3.11 \times 10^{-4} R_{\text{ex}} \text{ or } \nabla \nu_{2p, 2s} = 13.8 \text{ cm}^{-1}. \quad (25)$$

This corresponds to a wave length difference of,

$$\nabla \lambda_{2p, 2s} = 4.5 \text{ \AA} \quad (26)$$

at the mean or unresolved wave length of λ_2 equal to 5770.8 \AA . Similarly from Tables 1 and 2 we find that

$$\nabla \nu_{3p, 3s} = 5.5 \text{ cm}^{-1} \quad (27)$$

$$\nabla \lambda_{3p, 3s} = 1.8 \text{ \AA} \quad (28)$$

at

$$\lambda_3 = 5735.0 \text{ \AA}$$

and

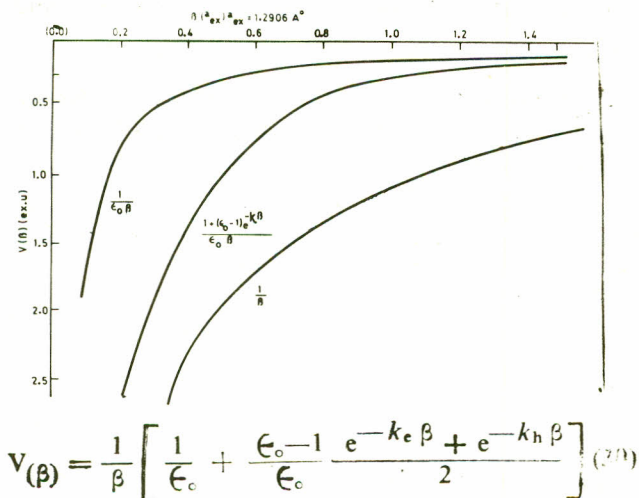
$$\nabla \nu_{3d, 3p} < 0.1 \text{ cm}^{-1}. \quad (29)$$

For higher values of n the degeneracy is hardly lifted, and there is a perfect agreement between the observed values, and the values calculated by the zero order theory and by the present theory to which it converges.

It appears from the spectrometer record of the exciton series in Cu_2O reported by Apfel and Hadley and reproduced here in Fig. 1 for the purpose of illustration that the $n = 2$ line is broader as well as asymmetric on the long wavelength side than the $n \geq 3$ lines. The width of the $n = 2$ line is approximately 4 \AA while the lines of higher ordinal numbers have widths of about 2 \AA . We interpret the relative broadness and the asymmetry of the $n = 2$ line in terms of the absorptions by the 2p and 2s states. Were it not for the fact that optical transition to the 2s exciton state in Cu_2O is forbidden¹³, the $n = 2$ line would resolve into distinct lines. The next order allowed transitions to the 2s state seems to bring about only broadness and asymmetry in the line. Since the resolution of the optical arrangement of the above investigators is about 2 \AA , the $n = 3$ line ($\nabla \lambda = 1.8 \text{ \AA}$) is narrower and even structureless as compared with $n = 2$ line. However, it is on the verge of exhibiting the same behaviour as the $n = 2$ line.

The agreement of the present theory and the zero-order theory for large β and their disagreement for small β is best illustrated by comparing the interaction potential curve (Fig. 4) for $\frac{1}{\epsilon_0 \beta}$, the bare coulomb potential $\frac{1}{\beta}$ and the potential

Fig. 4. The screened interaction potentials seen by an electron in Cu_2O and the 'bare' Coulomb's potential.



The radius of the first Bohr orbit of the exciton in Cu_2O calculated from the wave function

$$U_1(\beta) = 2 \frac{3/2 - \alpha_0 \beta}{\alpha_0} e^{-\alpha_0 \beta} \quad y_0$$

is

$$\beta_1 = 5.021 \text{ \AA}$$

This is somewhat smaller than the values quoted in the literature (Kittle^{14,7}, 9 Å, Haken^{15,16}, 9 Å, as well as 20 Å, Nikitine⁴, 9 Å). For the observed tighter binding than the zero-order theory we would expect a smaller radius of the $n = 1$ exciton.

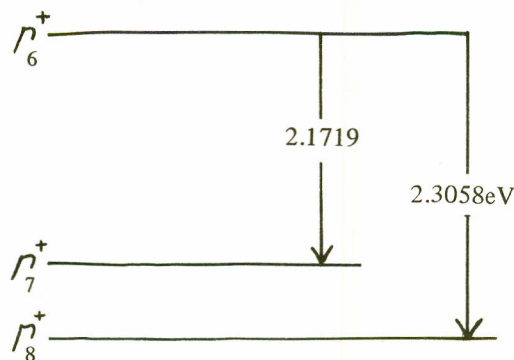
Discussion

In the preceding section we applied the extended EMT to the exciton spectrum of Cu_2O . The structure of Cu_2O is closed packed F.C.C. and its exciton spectrum is 'first class forbidden'.^{3,4} Direct interband transitions at the band edges are forbidden. In the second order they are allowed only to p-state. From the observed value of the 1S exciton energy level we determined the screening parameters K_e and K_h as well as the energies of higher states. Calculations show (Table 2) that the $n = 2$ state splits, in principle, into two optically resolvable states whereas the $n-1$ degeneracy of higher states is lifted, but not to resolvable extent. The correct magnitudes of K_e and K_h , the observed behaviour of the $n = 2$ state and the concordance between the experimental and calculated results for all exciton states, bespeak for the correctness of our proposed theory for the exciton spectra of semiconducting crystals.

It is reminded that the present calculations have been carried out specifically for the yellow series of excitons in cuprous oxide. Cu_2O , however, has several hydrogenic series¹⁸: green, blue and violet. Calculations similar to that of the yellow series can, in fact, be performed for these series. The green series is of particular relevance to the present discussion. Its conventional series formula¹⁸ is

$$E = 2.3058 - \frac{0.1540 \text{ eV}}{n^2} \quad n = 2, 3, 4, \dots$$

The $n = 1$ line of this series has zero oscillator^{10,13} strength and is too weak to be observed so far. According to Elliot, the existence of the yellow and green series is due to the presence of two valence bands, each cooperating with the conduction band to produce a set of exciton states. At $k = 0$ the valence bands are separated by 0.1332 eV. The valence bands being so close in comparison with their separation from the conduction band, mixing is expected between the states of the two valence bands. This will be of particular importance to the most tightly bound excitons. It is admitted that our calculations did not include explicitly the possible corrections that may be introduced by mixing of the two close lying valence band states. Their effects and a number of other influencing factors such as longitudinal-transverse splitting have been lumped together in the screening parameters K_e and K_h .



Band structure of Cu_2O at $K=0$

In the present work K_e and K_h are treated as parameters. The best set of values for which they represent the experimental data is obtained. From a theoretical point of view K_e and K_h could be calculated^{1,2} from the knowledge of the band structure of Cu_2O . Since this information is now available¹⁷, it would be interesting to calculate the above constants from purely theoretical considerations. In this way one would be able to construct the interpolation formula for the dielectric response of the crystal on a more rigorous basis than presented here.

Another suggestion that we wish to make concerns the experimental study of the exciton spectra of Cr_2O . Since the energy difference of the 2p and 2s states is 14 cm^{-1} , it seems feasible to study this fine structure. It will be difficult to detect this fine structure by conventional spectroscopy because whenever transitions to one of the states are allowed, they are forbidden to the other state. If one-photon absorption experiments are supplemented with two photon absorption experiments performed with laser beams, then the positions of the split states can be determined. Perhaps with the same experimental arrangement one could study the $n = 1$ state of Cu_2O by a two-photon experiment. This would be an interesting experiment because this state has been observed⁴ by indirect transitions, i.e. photon cooperated optical transitions.

References

1. M. A. Khattak, Theory of Exciton States in Semiconductors, Doctoral Dissertation, Colo. State Univ., (1968).
2. Extension of the Effective Mass Theory of Excitons. Pakistan J. Sci. Ind. Res. (Submitted in Feb. 1977).
3. E. F. Gross, *Nuovo Cimento, Suppl.*, **4**, 672 (1956); *Soviet Phys. Uspek.* **5**, 195 (1962).
4. S. Nikitine, A. F. Gibson, *et al.*, *Progress in Semi-conductors*, Vol 6, Wiley, New York (1962).
5. E. F. Gross, *et al.*, *Soviet Phys. Tech. Phys. (English Translation)* **2**, 1802 (1957); **2**, 2018 (1957); *Phys. Chem. Solids*, **8**, 172 (1959).
6. J. Halpern and B. B. Zakharchenya, *Solid State Comm.*, **5**, 633 (1967).
7. J. H. Apfel and L. N. Hadley, *Phys. Rev.*, **100** 1689 (1955).
8. A. G. Samojlovic and L. L. Korenblit, *Dokl. Akad. Nauk, SSSR*, **101**, 55 (1955).
9. R. W. G. Wyckoff, *Crystal Structures*, Interscience Publishers, **1**, (1963).
10. R. J. Elliot, *Phys. Rev.*, **124**, 340 (1961).
11. J. P. Dahl and A. C. Switendick, *J. Phys. Chem. Solids*, **27**, 931 (1966).
12. A. G. Zhilich and V. P. Makrov, *Soviet Phys. Solid State*, **3**, 429 (1961).
13. R. J. Elliot, *Phys. Rev.*, **108**, 1384 (1957).
14. C. Kittel, *Introduction Solid State Physics*, Wiley, 2nd edition, 507 (1965).
15. H. Haken, *Theory of Excitons II. Polaron and Excitons* (C. G. Kuper and G. D. Whitfield, ed.) Plenum Press, New York, (1963).
16. H. Haken, *J. Phys. Chem. Solids*, **8**, 166 (1959).
17. M. Cordona, *J. Phys. Chem. Solids*, **24**, 1443 (1963).