

Note on the Absorption Spectra of Pure and Colored Alkali Halide Crystals*

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The absorption cross section per electron is calculated for ultraviolet radiation in NaCl at the first exciton band, at the exciton series limit, at the *F*-band, and at its series limit. The assumed models lead to qualitative agreement with experimental results. The conclusions are briefly extended to other crystals.

I. INTRODUCTION

THE near ultraviolet absorption spectra of pure alkali halide crystals have been the subject of many theoretical and experimental investigations.¹ The low energy peak is believed to represent the transition from the ground state of a negative halide ion to the first optically allowed "exciton" level,² during which process an outer halide (*p*) electron from the closed shell is photo-excited to a higher bound level. The second, higher energy peak probably indicates the transitions into all the other allowed exciton levels, and, at its high energy side, into the continuum of states; there is some evidence that the series limit is at the second maximum.³ The actual magnitude of the absorption coefficient is too large to measure accurately, but is of the order⁴ of 10^5 or 10^6 cm⁻¹ at both peaks.

The *F*-band in alkali halide crystals has likewise been extensively studied.⁵ It consists of a single absorption peak decreasing rapidly on both sides of the maximum. No structure is apparent on the high energy side of most of the experimental absorption spectra; however, Kleinschrod⁶ has performed an accurate measurement on KCl and found a secondary plateau at about 0.7 ev above the main peak. The absorption at this plateau is about one-seventh that of the maximum. The main

peak is interpreted as the absorption of an *F*-center electron into its first allowed excited state, and the secondary plateau probably contains the absorption lines of higher discrete transitions and transitions into the continuum of states in the crystal.^{1(a)}

Tibbs⁷ has calculated an oscillator strength for the lowest allowed transition of the *F*-center electron, using wave functions numerically computed for a sawed-off coulomb potential. He obtained an oscillator strength of 0.6, presumably making use of his calculated transition energy, 1.26 ev, rather than the observed energy, 2.72 ev. His matrix elements were presumably integrated numerically with the free electron functions mentioned above and without modulation by lattice functions.

The purpose of the present paper is to calculate the absorption cross sections at the exciton band, the exciton series limit, at the *F*-band, and at the *F*-center series limit. Some of Tibbs' *F*-center wave functions will be used in calculating the cross section at the *F*-band. Further, the use of the Schrödinger equation here is similar to that of Tibbs in his attempt to take account of the lattice structure in calculating the *F*-center energy levels. The early part of the present calculation will nevertheless be presented in some detail to serve for the exciton calculations as well, to emphasize the similarity between the *F*-center and exciton wave functions,⁸ and to point out explicitly the differences between them.

II. CALCULATION OF ABSORPTION CROSS SECTIONS

Let us consider a pure NaCl crystal with one additional electron introduced into the lowest state in the first unfilled band; let the hamiltonian operator for this electron be H_0 . Clearly, H_0 is periodic with the period of the lattice; then

$$H_0 g(\mathbf{r}) = E_0 g(\mathbf{r}). \quad (1)$$

Tibbs⁷ has calculated the function $g(\mathbf{r})$ for the (1,0,0)

⁷ S. R. Tibbs, *Trans. Faraday Soc.* **35**, 1471 (1939).

⁸ Several discussions of excitons (see, for example, E. Rabinowitch, *Revs. Modern Phys.* **14**, 112 (1942), A. von Hippel reference 2, 1(b), p. 411) have suggested that an exciton wave function can be written as a sum of wave functions describing the motion of an electron about one of the surrounding positive ions. In the present discussion the author wishes to emphasize the attraction between the electron and the positive hole, just as between an electron and a negative ion vacancy.

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¹ The absorption spectra of a number of alkali halide crystals are presented and discussed in (a) N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), Chapter III; and in (b) F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapter XII.

² J. Frenkel, *Phys. Rev.* **37**, 17, 1276 (1931); R. Peierls, *Ann. Physik* **13**, 905 (1932); J. C. Slater and W. Shockley, *Phys. Rev.* **50**, 705 (1936); G. H. Wannier, *Phys. Rev.* **52**, 191 (1937); A. von Hippel, *Z. Physik* **101**, 680 (1936).

³ N. F. Mott, *Trans. Faraday Soc.* **34**, 500 (1938).

⁴ See, for example, E. G. Schneider and H. M. O'Bryan, *Phys. Rev.* **51**, 293 (1937).

⁵ The absorption spectra caused by *F* and similar centers are shown for many crystals in reference 1(a), Chapter IV, 1(b) Chapter XIII, and in F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946). In addition, these sources contain thorough discussions of the considerable theoretical and experimental researches on *F*-centers, and give references to the original papers. See also R. W. Pohl, *Proc. Phys. Soc. (London)* **49**, extra part, 3 (1937). For evidence that an *F*-center is an electron trapped at a negative ion vacancy, see in particular J. H. De Boer, *Rec. Trav. Chim. Pays-Bas.* **56**, 301 (1937), J. J. Markham and F. Seitz, *Phys. Rev.* **74**, 1014 (1948), and Estermann, Leivo, and Stern, *Phys. Rev.* **75**, 627 (1949).

⁶ F. G. Kleinschrod, *Ann. Physik* **27**, 97 (1936).

direction in NaCl. Near each Cl^- ion it behaves like a $\text{Cl}^- 4s$ function and near each Na^+ ion like a $\text{Na}^+ 3s$ function. Throughout most of the volume of the unit cell the magnitude of $g(\mathbf{r})$ does not vary greatly.

Now let us remove one entire Cl^- ion from the crystal and investigate how the hamiltonian of the additional electron is changed after equilibrium is again reached. This, of course, corresponds to the case of an F -center. The perturbations will be discussed in three parts,

$$H = H_0 + eV_1 + eV_2 + eV_3. \quad (2)$$

V_1 is the perturbation due to the removal of the Cl nucleus and 17 electrons, that is, to the removal of a Cl atom, and so for large distances ($r \approx 5a_0$, where $a_0 = \hbar^2/mc^2$) is negligibly small. V_2 is the potential term caused by the removal of the remaining Cl^- ion $3p$ electron:

$$V_2(\mathbf{r}) = -e \int |\psi_{3p}(\mathbf{r}')|^2 d\tau' / |\mathbf{r} - \mathbf{r}'|. \quad (3)$$

For large r ($r \approx 5a_0$) V_2 becomes $-e/r$ and for small r V_2 is a constant. V_3 is the potential introduced by the changes in the equilibrium positions and wave functions of all the surrounding nuclei and electrons. This term will have the effect of inserting a dielectric constant into the denominator of V_2 , and for large distances $V_2 + V_3 = -e/K_0 r$, where K_0 is the high frequency dielectric constant. (For NaCl K_0 is 2.25.) For small distances $V_2 + V_3$ is approximately constant.

Then the total hamiltonian of the additional electron at large distances is $H_0 - e^2/K_0 r$, and thus there exists an infinite number of bound states in the field of the negative ion vacancy.⁹ Writing the Schrödinger equation $H\psi = E\psi$ and attempting to find a solution of the form $\psi = fg$ we subtract Eq. (1) and obtain for large distances,

$$(\hbar^2/2m)\nabla^2 f + (\hbar^2/m)(\nabla f \cdot \nabla g/g) + [(e^2/K_0 r) + E_1]f = 0.$$

But for large distances $|\nabla f|$ is small and slowly varying, and $\nabla g/g$ is an odd function of r in any unit cell. The average value of $\nabla f \cdot \nabla g/g$ throughout a unit cell is then approximately zero and we may neglect it. The functions f are thus hydrogenlike atomic functions with an effective nuclear charge of e/K_0 ; and the lowest energy state, that is, the ground state of the F -center electron, behaves at large distances like

$$\psi_{1s} = g(\mathbf{r}) \exp(-r/K_0 a_0).$$

There are two remarks that should be made about this result. At very small distances we do not expect ψ_{1s} to vary at all like $g(\mathbf{r})$; $g(\mathbf{r})$ for small r is determined almost entirely by a Cl nucleus, and is similar to a $4s$ function. If no positive charge is present at $r=0$, the wave function ψ_{1s} must be a slowly varying function near $r=0$. Secondly, we have neglected entirely the fact that the coulomb well must change to a square

⁹ Reference 1(a), p. 83, contains a discussion of this theorem.

well at small distances. Tibbs¹⁰ has taken this effect into account in his calculations of F -center wave functions. He found that for the first two excited states the effect is unimportant, so that the functions f may be written as hydrogenlike functions with a "nuclear charge" e/K_0 . This result will be true *a fortiori* for any more highly excited state and we shall make use of this fact in writing continuum wave functions. He presented his wave functions in graphical form and his ground state wave function may be approximated, where $r^2 f^2$ is sizable, by an exponential with damping length $3a_0$. Accepting this result, we assume the F -center electron ground-state wave function to be $\exp(-r/3a_0)$ at small distances and to be $g(\mathbf{r}) \exp(-r/3a_0)$ at large distances.

The ground, first-excited, and continuum wave functions then are hydrogenlike functions at small distances and are modified by the factor $g(\mathbf{r})$ at larger distances. In normalizing each of these functions it will be necessary to take account of $g(\mathbf{r})$; but since $|g(\mathbf{r})|^2$ is not a rapidly changing function over most of the unit cell, we may remove it from the normalizing integral and normalize f and g separately. That is, we obtain

$$1 = \int |f|^2 |g|^2 d\tau = \langle g^2 \rangle_{\text{av}} \int |f|^2 d\tau = \int |f|^2 d\tau.$$

Similarly, in computing dipole matrix elements to obtain absorption cross sections, in each integral will appear $|g(\mathbf{r})|^2$, and the same procedure may be followed. All of this is merely to say that in this approximation we may neglect $g(\mathbf{r})$ entirely.

With this understanding we may write for the ground state,

$$\psi_{1s}(\mathbf{r}) = 2\alpha^{-3/2} e^{-r/\alpha}, \quad (4)$$

where $\alpha = 3a_0$, and for the radial part of the first optically allowed excited state,

$$\psi_{2p}(\mathbf{r}) = r e^{-r/2a} / a^{5/2} (24)^{1/2}, \quad (5)$$

where $a = 2.25a_0$. The square of the radial part of the dipole matrix element of Eq. (4) with Eq. (5) is

$$|R_{1s,2p}|^2 = \left| \int_0^\infty \psi_{1s}(r) r^3 \psi_{2p}(r) dr \right|^2 = 96 \alpha^7 a^5 / (a + \frac{1}{2}\alpha)^{10}. \quad (6)$$

The absorption cross section per electron per unit frequency range at the absorption maximum is¹¹

$$\sigma = (4\pi^2 e^2 / 3\hbar c) (2\nu / \pi \Delta\nu) |R|^2 \quad (7)$$

for s - p transitions. Here, ν is the frequency of the absorption maximum, and $\Delta\nu$ is the width of the line at half-maximum. Inserting Eq. (6) into Eq. (7) and

¹⁰ Reference 7. See also J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

¹¹ See, for example, W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, London, 1944), second edition, Chapter III.

neglecting the local field correction, we find

$$\sigma_{1s,2p} = [128\pi^2 e^2 \alpha^7 a^5 / \hbar c (a + \frac{1}{2}\alpha)^{10}] 2\nu / \pi \Delta\nu. \quad (8)$$

The wave functions in the continuum of states for an r^{-1} potential, ψ_{cl} , have been calculated by Gordon.¹²

Using these wave functions normalized according to the wave number, κ , scale with an effective nuclear charge e/K_0 , we evaluate¹³ the radial part of the dipole matrix element $R_{1s,2p}$. Then the absorption cross section per electron per unit frequency range becomes

$$\sigma_{1s,2p}(\lambda) = \frac{2^{11}\pi^3 \alpha^7 (2a - \alpha)^2}{3\lambda a_0 a^5} \frac{1 + \kappa^2 a^2}{(1 + \kappa^2 \alpha^2)^6} \times \frac{\exp[-(4/\kappa a) \tan^{-1} \kappa \alpha]}{1 - \exp(-2\pi/\kappa a)}.$$

Evaluating σ at λ_K , the wavelength of the series limit, we obtain

$$\sigma_{1s,2p}(\lambda_K) = 2^{11}\pi^3 \alpha^7 (2a - \alpha)^2 e^{-4\alpha/a} / 3\lambda_K a_0 a^5. \quad (9)$$

Let us now consider the wave functions pertinent to the absorption calculations in the pure NaCl crystal. Hartree and Hartree¹⁴ have solved the Fock equations including exchange for a free Cl^- ion, and Fock and Petrashen¹⁵ have done the same for Na. Using these wave functions, Landshoff¹⁶ calculated the cohesive energy of NaCl; the good agreement with experiment is an indication that use of the free ion wave functions in the crystal is a good approximation to the true one-electron functions.¹⁷ The author has found by curve-fitting that the Cl^- $3p$ wave function of Hartree and Hartree can be approximated analytically by

$$\psi_{3p}(r) = [r/(24)^{1/2} (A/2)^{5/2}] (e^{-r/A} - 23.2e^{-r/B}), \quad (10)$$

where $A = a_0/1.1$ and $B = a_0/8$.

To find an exciton wave function, it will be instructive to return to the Schrödinger equation. The hamiltonian of an additional electron introduced into a perfect crystal is H_0 . Removing from a Cl^- ion one $3p$ electron, let us investigate how the hamiltonian of the additional electron is changed in this exciton model. As before, we have

$$H = H_0 + eV_1 + eV_2 + eV_3,$$

¹² W. Gordon, Ann. Physik (5) 2, 1031 (1929). For further discussion see also M. Stobbe, Ann. Physik (5) 7, 661 (1930), and H. Bethe, Handbuch der Physik (1933), (2) 24/1, p. 273.

¹³ The summation in the resulting expression for $R_{1s,2p}(\kappa)$ can be evaluated by the following device:

$$R_{1s,2p}(\kappa) = B(\alpha, \kappa, a) \sum_{n=0}^{\infty} \frac{\Gamma(n+2-i/\kappa a)(n+4)}{\Gamma(2-i/\kappa a)\Gamma(n+1)} \left(\frac{-2i\kappa\alpha}{1-i\kappa\alpha} \right)^{n+3} \\ = B'(\alpha, \kappa, a) \left[\frac{d}{ds} \left\{ s^4 \left(1 + \frac{2i\kappa\alpha s}{1-i\kappa\alpha} \right)^{-2+i/\kappa a} \right\} \right]_{s=1}.$$

¹⁴ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A156, 45 (1936).

¹⁵ V. Fock and M. J. Petrashen, Physik. Z. Sowjetunion 6, 368 (1934).

¹⁶ R. Landshoff, Z. Physik 102, 201 (1936); Phys. Rev. 52, 246 (1937).

¹⁷ For a discussion of this point, see reference 1(b), p. 385.

where now V_1 arises just from the changes in the wave functions of the electrons in the Cl atom. V_2 is the negative of the potential due to a $3p$ electron, and is given by Eq. (3). V_3 is due to the changes in the wave functions of all the surrounding electrons. (By the Franck-Condon principle we consider times short compared with that necessary for the surrounding nuclei to move.) Again V_3 can be taken into account by putting a dielectric constant into the denominator of V_2 ; so for large distances, $H = H_0 - e^2/K_0 r$, and for small distances, $H = H_0$ plus a constant. Writing the Schrödinger equation as before, we seek a solution of the form $\psi(\mathbf{r}) = f(\mathbf{r})g(\mathbf{r})$; subtracting the wave equation for the unperturbed crystal, we obtain for large distances $(\hbar^2/2m)\nabla^2 f(\mathbf{r}) + (e^2/K_0 r)f(\mathbf{r}) + E_1 f(\mathbf{r}) = 0$. Thus the exciton wave functions at large distances are hydrogenlike functions times $g(\mathbf{r})$, and the lowest exciton wave function $\psi_{\text{exc}}(\mathbf{r}) = f(\mathbf{r})g(\mathbf{r})$ is the same at large distances as the F -center ground-state wave function; furthermore the damping length in the lowest energy state $f(r)$ is changed from $K_0 a_0$ to $3a_0$ for the same reason as in the case of the F -center wave function. There is an important distinction between these wave functions, however. Whereas we expected the F -center ground-state wave function to be slowly varying at small distances because no Cl nucleus was present, we now expect ψ_{exc} to behave very much like a $4s$ function at small distances. That is, we expect ψ_{exc} to be approximated by $g(\mathbf{r}) \exp(-r/\alpha)$ throughout the crystal. As with the F -center wave functions, we normalize $f_{1s}(r)$ separately and obtain

$$\psi_{\text{exc}}(\mathbf{r}) = (2/\alpha^3) e^{-r/\alpha} g(\mathbf{r}). \quad (11)$$

In computing the matrix element of Eqs. (10) and (11), though, we may not ignore $g(\mathbf{r})$. Since the changes in sign in $g(\mathbf{r})$ do not coincide with those in $\psi_{3p}(r)$ and since f_{1s} is a relatively short-ranged function, there will be considerable cancellation in the matrix element in the vicinity of the Cl atom caused by the changes of sign in $g(\mathbf{r})$. Extrapolation of $g(\mathbf{r})$ for all directions and numerical integration¹⁸ of the matrix element indicates that $|R_{3p}^{\text{exc}}|^2$ is approximately $1.1a_0^2$. The absorption cross section per electron per unit frequency range at the absorption maximum is

$$\sigma_{3p}^{\text{exc}} = (4\pi^2 e^2 / 9\hbar c) (2\nu / \pi \Delta\nu) |R_{3p}^{\text{exc}}|^2. \quad (12)$$

Transitions can occur from the $3p$ state to both s and d states of the continuum. The hydrogenic continuum wave functions¹² are normalized separately, as before, without reference to $g(\mathbf{r})$. Investigation of the shapes of the wave functions shows that because the first loops of the hydrogenic continuum wave functions are so extended and because the maximum of $r^2\psi_{3p}$ is so far out ($\sim 3a_0$) and broad, the effect of $g(\mathbf{r})$ on the matrix element is unimportant and we may omit it from the integrand. Stating this again in a slightly

¹⁸ The variation of $g(\mathbf{r})$ with angle has been taken into account by suitably reducing the magnitude of R .

different way, if $g(\mathbf{r})$ were included in the matrix element integral, it would cause very little cancellation because most of the contribution to the matrix element occurs where $g(\mathbf{r})$ keeps the same sign (except over small volume elements). An approximation to the matrix element can be obtained then by integrating \mathbf{r} with ψ_{cl} and Eq. (10). Evaluating σ at the series limit, where $\kappa=0$ and $\lambda=\lambda_M$, we obtain

$$\begin{aligned} \sigma_{3p^c}(\lambda_M) &= \sigma_{3p^{cd}}(\lambda_M) + \sigma_{3p^{cs}}(\lambda_M) \\ &= \frac{2^{13}\pi^3 A^5 e^{-4A/a}}{27a_0\lambda_M a} \left\{ \left[2\left(\frac{A}{a}\right)^4 \left(3 - \frac{A}{a}\right)^2 \right] \right. \\ &\quad \left. + \left[3 - 9\frac{A}{a} + 6\frac{A^2}{a^2} - \frac{A^3}{a^3} \right]^2 \right\}. \quad (13) \end{aligned}$$

In obtaining this expression we have performed summations by methods similar to that shown in reference 13. The expression in the first square brackets comes from the d states of the continuum. It is found that the second term in Eq. (10) is so short-ranged as to contribute only negligibly to σ .

III. DISCUSSION OF RESULTS

It should be noted in connection with Eq. (13) that $A/a \sim 0.4$ and the absorption into the d states of the continuum is only 4.7 times that into the s states. For an isolated hydrogenlike atom in a $3p$ state, the effective nuclear charge is the same in all states, and the absorption into the continuum d states is 18 times that into the s states.¹² This decrease from 18 to 4.7 is brought about by the tight compression of the Cl^- ion wave function relative to the continuum wave functions.

Evaluating Eq. (13) for $\lambda_M = 1280A$, we find $\sigma_{3p^c}(\lambda_M) = 2.7 \times 10^{-18} \text{ cm}^2$; for $\nu/\Delta\nu = 7$, Eq. (12) becomes $\sigma_{3p^{\text{exc}}} = 4.3 \times 10^{-18} \text{ cm}^2$. This is 1.6 times as large as $\sigma_{3p^c}(\lambda_M)$, whereas the experimental ratio of the two peaks is unity for NaCl and KCl. Agreement within a factor of 2 is considered fortuitously good, but the agreement is made still better when one considers that transitions to higher exciton states are probably grouped with the continuum absorption in the experimental results. The oscillator strength of the $3p$ -exc transition is about 0.07, which is smaller by a factor of 10 than that associated with the F -band.¹⁹ Apparently, this difference again is associated largely with the tight compression of the Cl^- ion wave function relative to the other wave functions involved, which makes the cancellation due to $g(\mathbf{r})$ relatively important. The linear

¹⁹ F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946). See also reference 6.

absorption coefficient τ is σ times the number of $3p$ electrons per cm^3 . Then $\tau_{3p^{\text{exc}}} = 5.9 \times 10^6 \text{ cm}^{-1}$, which is in agreement with the probable experimental value of 10^6 or 10^6 .

A further indication that this part of the calculation is not off by a factor of more than 2 or 3 is the rough agreement with the work of Mayer, and Fajans and Joos,²⁰ who have obtained an oscillator strength of about 0.55 per Cl^- $3p$ electron. Perhaps one-third of this oscillator strength, or 0.18 is associated with the exciton band; this value is to be compared with the value 0.07 calculated here.

For the F -center case, when we set $\nu/\Delta\nu = 7$, Eq. (8) is $\sigma_{1s^{2p}} = 2.7 \times 10^{-16} \text{ cm}^2$ and for $\lambda_K = 3700A$ Eq. (9) becomes $\sigma_{1s^{cp}}(\lambda_K) = 3.5 \times 10^{-17} \text{ cm}^2$, and it is seen that the absorption into the $2p$ states is 7.5 times that at the series limit. This agrees with the experimental value⁶ for KCl of about 7. The absorption line for transitions into the $3p$ states is calculated to be about one-tenth as intense as that into the $2p$ states and is not resolved experimentally. The oscillator strength²¹ for the $1s-2p$ transition is calculated to be 1.4 using the observed energy for the transition. According to the experimental results¹⁹ this is too large by a factor of about 2; however, we might expect to be able to calculate ratios of absorption coefficients better than absolute values, because the errors introduced by the neglect of the function $g(\mathbf{r})$ would tend to cancel in taking ratios.

It is interesting to investigate qualitatively how these exciton results would be changed by an increase in dielectric constant. For silver halides K_0 is about 4 or 5 (2.25 for NaCl), and the exciton wave function, according to the present model, is spread out over a much larger volume. This would lead to a smaller dipole matrix element; and, consequently, the oscillator strength per electron for the transition to the first exciton level (0.07 for NaCl) would be lowered. The absorption spectrum of silver chloride,²² for example, shows a small bump in the ultraviolet region on a curve which steadily increases with energy for several eV. The small peak may correspond to a transition to the first exciton level; this transition seems to have a small oscillator strength as would be expected in view of the large dielectric constant.

The author would like to express his appreciation for helpful discussions to Professors N. F. Mott and F. Seitz and to Dr. E. N. Adams.

²⁰ J. Mayer, *J. Chem. Phys.* **1**, 270 (1933). K. Fajans and G. Joos, *Z. Physik* **23**, 1 (1923). See also reference 1(b), p. 658.

²¹ The apparent violation of the f -sum rule is connected with the use of the observed, rather than a calculated, energy difference between the two states.

²² H. Fesefeldt, *Z. Physik* **64**, 741 (1930).