cubes of the odd integers now is of higher order in $1/k$ than are already neglected terms, and hence it may also be neglected. In the second series we make the transformation (A3), add and subtract the terms from 1 to k, and cancel the final term of (A2). The high frequency contribution is now:

$$2e^2\left[\frac{L}{2\pi^2\nu_0 m}\left\{\sum_1^k \frac{1}{(n-\frac{1}{2})^2-(\nu_0 L/\pi)^2}+\sum_{k+1}^{\infty}\frac{1}{(n-\frac{1}{2})(n-\frac{1}{2}+\nu_0 L/\pi)}\right\}+\frac{1}{8\nu_0{}^3 m^2}\right]. \quad \text{(A10)}$$

In the first series we may neglect the first term in the denominator in comparison with the second, because of the assumption that the coupling constant e is small compared with the fundamental oscillator frequency ν_0. The resulting expression may be summed and it is of order e^3 and thus is to be neglected. We add and subtract the terms from 1 to k in the remaining series. The sum from one to infinity is equal to the middle term in (A5). In the sum from 1 to k that we subtract, the $n-\frac{1}{2}$ may be neglected compared with $\nu_0 L/\pi$. This last sum then becomes

$$-\frac{1}{2\pi\nu_0{}^2 m}\sum_1^k \frac{1}{(n-\frac{1}{2})}=-\frac{1}{2\pi\nu_0{}^2 m}[\log(eL)+\log 2+C]. \quad \text{(A11)}$$

Hence the total contribution from high frequency terms is;

$$2e^2\left[\frac{\log(\nu_0 L/\pi)+2\log 2+C}{2\pi\nu_0{}^2 m}-\frac{\log(eL)+\log 2+C}{2\pi\nu_0{}^2 m}+\frac{1}{8\nu_0{}^3 m^2}\right]$$

$$=e^2\left[\frac{\log(2\nu_0/\pi e)}{\pi\nu_0{}^2 m}+\frac{1}{4\nu_0{}^3 m^2}\right]. \quad \text{(A12)}$$

When this is combined with the low frequency contribution (A9), the formula (30) is obtained.

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Oscillator Strengths for the α- and β-Bands in Alkali Halide Crystals*

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The oscillator strengths for the α- and β-absorption bands are calculated for NaCl. These bands, investigated experimentally by Delbecq, Pringsheim, and Yuster in KI, lie on the long-wavelength tail of the first fundamental absorption band and are interpreted by use of a model according to which valence electrons of the adjacent halide ions are raised to bound states in the fields of negative ion vacancies (α-transitions) and F-centers (β-transitions). The oscillator strengths turn out to be only slowly varying with the assumed wave functions and are about 1.9 and 0.6 for the α- and β-bands, respectively.

I. INTRODUCTION

RECENT experiments of Delbecq, Pringsheim, and Yuster[1] have shown the existence of two new absorption bands in the long-wavelength tail of the first fundamental absorption band in KI. Pringsheim *et al.* point out the unlikelihood that the α- and β-bands are caused by V-centers[2] and suggest that "The presence of certain well-defined singularities in sufficient numbers, such as negative ion vacancies or F-centers, may affect the first fundamental frequency of the crystal in such a way that new well-defined absorption bands corresponding to perturbed transitions of the valency electrons of the adjacent halide ions appear superimposed on the tail of the fundamental absorption band."[1]

In the present paper the oscillator strengths of the α- and β-bands are evaluated for NaCl, assuming models in which Cl⁻ ion $3p$ electrons make transitions to bound levels in the field of a negative ion vacancy for the α-band and in the field of an F-center for the β-band. It is found that the oscillator strength of each band is of the order unity and that the results are rather insensitive to the assumed final-state wave functions.

II. DISCUSSION OF WAVE FUNCTIONS

In order to determine the dipole matrix elements needed for the calculation of the oscillator strengths, the following four wave functions will be required.

Let ψ_1 be the wave function of an otherwise perfect crystal of NaCl containing a single negative ion vacancy. As discussed in a previous paper[3] the wave function of a $3p$ electron in a Cl^- ion may be written as an analytical approximation of the Hartree wave function[4]

$$\varphi_{3p}=r(e^{-r/A}-Ce^{-r/B}), \quad (1)$$

where $A=a_0/1.1$, $B=a_0/8$, $C=23.2$, and $a_0=\hbar^2/me^2$; ψ_1 may be approximated by a permutation of the products of such functions. Specific changes in these one-electron functions due to the presence of the vacancy will be neglected, and the presence of the positive ions may be ignored for the moment.

The excited state of this crystal is described by a wave function, ψ_2, representing a configuration in which any one of the 72 surrounding $3p$ electrons is in a $1s$

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[1] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951). See also, E. Burstein and J. J. Oberly, Phys. Rev. **79**, 903 (1950), and H. Dorendorf, Z. Physik **129**, 317 (1951).

[2] F. Seitz, Phys. Rev. **79**, 529 (1950), and references therein.

[3] D. L. Dexter, Phys. Rev. **83**, 435 (1951).

[4] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).

state about the negative ion vacancy and a positive hole is left on one of the 12 nearest Cl^- ions (at distance $7.5a_0$). This configuration is similar to that of an F-center in a photochemically excited crystal, but differs in one important respect. The usual F-center electron's wave function is determined by an effective "nuclear charge" characteristic of the crystal with the surrounding ions in the equilibrium positions they take when an electron is present; however, in the present case, according to the Franck-Condon principle, the nuclear charge will be characteristic of the ionic configuration before the absorption act. The potential due to a negative ion vacancy in an otherwise perfect crystal[5] is e/Kr, where K is the static dielectric constant (5.62 for NaCl); and hence the wave function of the excited electron is

$$\varphi_{F^*}(\mathbf{r})=g(\mathbf{r})\exp(-r/Ka_0), \qquad (2)$$

where $g(\mathbf{r})$ is the lattice function in the conduction band.[6] Thus, ψ_2 may be written as one of 72 sums of products of Eq. (2) with the functions (1). We shall use ψ_1 and ψ_2 for calculating the oscillator strength for the α-band.

The function ψ_3 is the wave function describing a crystal in the vicinity of a normal F-center. According to this model, it is the ground-state wave function for the transition corresponding to the β-band and can be written as a sum of products of Eq. (1) and an F-center wave function,

$$\varphi_F(\mathbf{r})=g(\mathbf{r})\exp(-r/\gamma_F). \qquad (3)$$

Tibbs[7] has calculated an F-center wave function in NaCl, and for small distances the coefficient of $g(\mathbf{r})$ can be approximated by $\exp(-r/3a_0)$. For large distances, however, φ_F must have its high frequency dielectric constant value[3] $\exp(-r/K_0a_0)g(\mathbf{r})$ ($K_0=2.25$ in NaCl). We shall approximate φ_F by a single function (3) and examine the variation of oscillator strength with γ_F.

The crystal with a positive hole in one of the surrounding Cl^- ions and an extra electron in the F-center is described by ψ_4. As in the discussion of ψ_2, however, this is not a usual F'-center, because the surrounding ions have not yet moved to new equilibrium positions for times of interest here. If we assume both electrons to be bound to the negative ion vacancy in $1s$ orbits, an estimate of ψ_4 can be made by use of the variational method[8] as applied to the He atom. Minimizing the expectation value of the hamiltonian with respect to the binding parameter Z, we find

$$Z=\tfrac{1}{2}(2z-5/8K_0), \qquad (4)$$

where z is the effective nuclear charge of the vacancy for binding one electron and Z is defined by

$$\varphi_{F'^*}(\mathbf{r})=g(\mathbf{r})\exp(-Zr/a_0). \qquad (5)$$

From the discussion of φ_F and consideration of the fact that $\varphi_{F'^*}$ has a larger spread than φ_F it appears that $z=1/K_0$ is a good approximation, so that $Z=1/3.27$. It will be shown that the oscillator strength is insensitive to choice of Z. Thus, ψ_4 can be written as one of a sum of products of the functions (1) and two functions (5).

III. MATRIX ELEMENTS AND OSCILLATOR STRENGTHS

The matrix elements we need for the oscillator strengths[9] are of the form $\int\psi_0^*\mathbf{r}\psi_jd\tau$, where ψ_0 is the initial wave function and ψ_j a final-state wave function. For the α-band this becomes $\int\psi_1^*(\mathbf{r})\mathbf{r}\psi_2(\mathbf{r})d\tau$, which reduces to $\int\varphi_{3p}^*\mathbf{r}\varphi_{F^*}d\tau$. These two center integrals have been evaluated analytically by using elliptic coordinates and by treating the function $g(\mathbf{r})$ as a constant. From inspection of $\varphi_{3p}^*\mathbf{r}\varphi_{F^*}$ it is clear that there is a roughly spherical region about each ion (although not about the vacancy) in which cancellation occurs because of $g(\mathbf{r})$ so that to take $g(\mathbf{r})$ into account it is necessary to subtract the contribution to the integral arising from each of these regions. In view of the approximate constancy of $g(\mathbf{r})$ in the important parts of the crystal (except for these small regions) it is felt that this method is sufficient to give a good approximation to the matrix elements. These small contributions were evaluated analytically by treating $\exp(-r/Ka_0)$ as constant over each small region.

TABLE I. Values of f_β for various choices of wave functions (3) and (5).

Z γ_F	1/3.00	1/3.27	1/5.62
2.25	0.605	0.612	0.544
3.0	0.646	0.680	0.748

The energy of the α-transition, according to a simple cycle and by comparison with the experimental results on KI, should be about 6.8 ev. Then, using this energy and the matrix elements described in the preceding paragraph, we can evaluate f_α, the oscillator strength between a state with a vacancy and no holes and a state with an electron of either spin in the vacancy and a hole on any adjacent Cl^- ion, for $K=5.62$ in Eq. (2). It turns out to be $f_\alpha=1.89$. To show how f_α varies with damping length in Eq. (2) we may state the values of f_α for $K=3$ and $K=7.3$, i.e., 1.23 and 1.22, respectively. The reason for the slow variation is that the two centers are $7.5a_0$ apart, so that the magnitude of the function (2) near the Cl^- ion site is

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[5] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), p. 85.

[6] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939). For further use and discussion of this function see reference 3.

[7] See reference 6 and J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[8] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 172.

[9] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 148.

not strongly dependent on damping length in this size range of K. The oscillator strengths for transitions to excited states are negligibly small because of the very wide extent of the excited state wave functions.

The β-band matrix elements were treated similarly except that in this case only half of the electrons can make transitions, because of the spin of the electron already in the F-center, and except that each one-electron integral is multiplied by the overlap integral of φ_F and $\varphi_{F'}*$. The value of f_β is the oscillator strength between a state with an F-center and no holes and a state with 2 electrons in the vacancy and a hole on any adjacent Cl^- ion, γ_F is the damping length of the F-center wave function (3), and Z/a_0 is the inverse damping length in Eq. (5). The energy of the β-band is taken to be 7.2 ev for NaCl. Table I shows the oscillator strength f_β for wave functions in the interesting size range. There is very little variation of f_β with wave functions of this approximate extent, because as $1/Z$ increases and the one-electron dipole matrix element increases (until $Z \sim 1/6$), the overlap integral decreases. This calculation then indicates that $f_\alpha = 1.9$ and $f_\beta = 0.6$.

It does not seem advisable at this time to attempt to compare these results with the experimental data obtained for KI, because the oscillator strength of the F-band is not known for KI and because comparison of areas in the α-, β-, and F-bands is made difficult with the steep rise of the fundamental absorption band superimposed on the α- and β-bands. Nevertheless, assuming the oscillator strength of the F-band to be about 0.6 or 0.7 in KI, the experimental areas of the α- and β-bands are not inconsistent with oscillator strengths of the order of those calculated here. At first sight, it might seem surprising that f_α and f_β should be as large as f_F, but the relative smallness of the matrix elements for the β- and α-band transitions are compensated for by the large numbers of electrons that can take part in these transitions and by the high energy of the transitions.

The author is indebted to Dr. W. R. Heller for bringing the work of Delbecq, Pringsheim, and Yuster to his attention and for helpful discussions. He would also like to express his appreciation to Professor Pringsheim for a discussion of the experimental results before their publication and to Professor Seitz for his kind interest in this work.

Note added in proof: Dr. LeRoy Apker has kindly informed me of evidence, obtained by himself and Dr. E. Taft from the photoelectron emission experiments, which has a bearing on the β-bands in Rb I and KI. In their paper on Rb I near 85°K [Phys. Rev. 81, 698 (1951)] they show a separate peak (a few tenths of an ev removed from the position of the maximum yield) which they suggested might be associated with the decreasing transparency of the film. Further preliminary results on KI near 85°K also show this separate peak. However, their additional experiments on optical interference appear to rule out the optical effect as being important in this region; in view of the absorption measurements described in reference 1, Apker and Taft now interpret the separate peak as being associated with the β-band. One would expect to find a peak in the photoelectric yield corresponding to the β-band for two reasons: (1) Because of the increase in the absorption coefficient on the tail of the fundamental band, the light is absorbed closer to the surface, so that the electrons which are eventually released have a shorter distance to travel within the crystal, and thus have a higher probability of getting out of the crystal; (2) inasmuch as F′ centers, containing electrons of lower binding energy than F center electrons, are formed by irradiation in the β-band, subsequent ionization of the F′ centers by excitons results in electrons of relatively high energy in the conduction band, which again increases the external photoelectric yield.

It should perhaps be emphasized at this point that this calculation has neglected entirely the effects of the positive hole left at the Cl^- ion site adjacent to the vacancy, and has assumed that the positive hole diffuses away. A more exact calculation, which appears difficult to perform, should take into account the effect of the positive hole on the electrons' wave functions. As Professor Seitz first pointed out to Drs. Apker and Taft, if the positive hole remains in the vicinity of the vacancy, one of the F′-center electrons could perhaps recombine with the positive hole, the energy of the transition being used to ionize the remaining electron. This two-center Auger process would likewise increase the photoelectric yield at an energy close to that of the β-band, and could perhaps be distinguished from the two-quanta process mentioned above by the temperature and light intensity dependence of the external yield.