Theory of the Beta Band in Alkali Halide Crystals*

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It is shown that the β band in alkali halides with the NaCl lattice consists of six components. Their energies are estimated in NaCl. It is suggested that the observed β band is the component with the lowest energy and that the other components are not easily observed because they lie in the fundamental band. The calculated oscillator strength is 0.10, which is probably too small by a factor of 5. The final state for the β-band transition undergoes autoionization with the rate 1.8×10^{13} sec^{-1}. The width of the β band is increased by only 0.012 ev or about 10% by this process.

INTRODUCTION

AN optical absorption band called the β band appears on the tail of the fundamental band in alkali halide crystals which contain F centers. The assumption that the β band is due to the formation of an exciton in the neighborhood of an F center is supported by the observation that the intensity of the β band is proportional to the intensity of the F band when the concentration of F centers is varied, and by the calculation of Bassani and Inchauspé on the separation of the β band from the first peak of the fundamental band.[1] This combination of an exciton in the vicinity of an F center, to which we given the name "β center," has a total energy which lies in the conduction band. That is, an energy of about 6 ev must be added to the crystal to create the exciton, whereas only about 3 ev is required to ionize the F center. Therefore the β center can undergo autoionization, the final state being a bare negative-ion vacancy and an electron about 3 ev above the bottom of the conduction band. Since the finite lifetime of the β center causes a broadening of the β band, it is of interest to calculate this lifetime in order to determine whether the broadening due to this process is comparable to the broadening due to the interaction with phonons. It will be shown that the model of the β center which we use implies that the β band should consist of six peaks. Since only one peak is observed, we shall make an attempt to explain this discrepancy.

MODEL OF THE β CENTER

We use a model of the β center which is an extension of that used by Dexter[2] in his calculation of the oscillator strengths of the α and β bands in NaCl. He assumes that the transition associated with the β-band absorption involves the excitation of an electron from the filled $3p$ shell of one of the twelve Cl$^-$ ions which are next nearest neighbors to the Cl$^-$ vacancy. This electron is then bound to the vacancy together with the F-center electron. In other words, the β center consists of two electrons bound to a Cl$^-$ vacancy and a hole on the next nearest neighbor Cl$^-$ ions. It is necessary to distribute the hole over these Cl$^-$ ions in such a way that the spatial wave functions of the β center belong to the irreducible representations of the cubic group of rotations and reflections about the vacancy site. The initial state for the optical transition, which is the ground state of the F center, is essentially an S state, and belongs to the unit representation Γ_1. x, y, and z, the components of the electric dipole operator, belong to the 3×3 representation Γ_4'. Therefore the only states of the β center which can be reached by an optical transition are those which belong to $\Gamma_1 \times \Gamma_4' = \Gamma_4'$. The hole state must also belong to Γ_4', since the two electrons bound to the vacancy are in a spatial state which belongs to Γ_1.

In the Heitler-London approximation, the wave function which represents a hole localized on the μth atomic orbital on the ith ion is

$$\Psi_{i\mu} = A \prod_{k,q} \frac{\psi_{kq}}{\psi_{i\mu}} \psi_{F\mu} \psi_{Fb}, \qquad (1)$$

where ψ_{kq} is the qth atomic orbital on the kth ion, $\psi_{F\mu}$ and ψ_{Fb} are the wave functions of the two electrons bound to the vacancy, and A is the antisymmetrization operator. $\prod_{k,q}$ runs over all ions and atomic orbitals in the crystal with the exception of the missing ion at the origin, the $\psi_{i\mu}$ in the denominator signifies that $\psi_{i\mu}$ is left out of $\prod_{k,q}$, and the μ and b in $\psi_{F\mu}$ and ψ_{Fb} are spin indices which signify that these two functions have opposite spins and that $\psi_{F\mu}$ has the same spin as the missing $\psi_{i\mu}$. With regard to the Cl$^-$ $3p$ atomic orbitals, we let $\mu = 1, 2, 3$ represent the x, y, z directed atomic orbitals with a given spin, and $\mu = 4, 5, 6$, the corresponding orbitals with opposite spin. Confining i to the next nearest neighbor Cl$^-$ ions, the 36 functions $\Psi_{i\mu}$ with a given spin belong to a reducible representation of the cubic group which contains Γ_4' three times. Therefore we can form the linear combinations

$$\Psi_\nu^{\sigma,m} = \sum_{i,\mu} c_{i\mu,\nu}{}^{\sigma,m} \Psi_{i\mu}, \qquad (2)$$

[1] F. Seitz, Revs. Modern Phys. **26**, 7 (1954); F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957).
[2] D. L. Dexter, Phys. Rev. **83**, 1044 (1951).

TABLE I. The levels of the β center which can be reached by optical dipole transitions and the oscillator strengths of these transitions.

State		Energy ev	Oscillator strength f
E_1	$J=\frac{3}{2}$	−1.68	0.10
E_1	$J=\frac{1}{2}$	−1.58	0.05
E_2	$J=\frac{1}{2}$	0.69	0.25
E_2	$J=\frac{3}{2}$	0.75	0.51
E_3	$J=\frac{1}{2}$	0.89	0.01
E_3	$J=\frac{3}{2}$	0.94	0.02

which belong to the νth row of Γ_4' and have the spin magnetic quantum number $m=\pm\frac{1}{2}$. $\sigma=1, 2, 3$ specifies the three possible independent linear combinations corresponding to the triply repeated representation Γ_4'. $\Psi_x^{\sigma,m}$, $\Psi_y^{\sigma,m}$, and $\Psi_z^{\sigma,m}$ are essentially $L=1$ functions written in the cubic symmetric form.

Each of the twelve next nearest neighbor Cl$^-$ ions lies on the midpoint of an edge of a cube with the vacancy at the center and with edge length $2a$, where a is the Na-Cl distance. The distribution of the hole over these twelve ions for the functions $\Psi_\nu^{\sigma,m}$ can be specified by stating the direction of the hole on each ion, since an arbitrary linear combination of x-, y-, and z-directed holes is equivalent to a single hole in a suitable direction. The three trial hole functions which belong to a given row of Γ_4' have been chosen in such a way that they are orthogonal. Taking the z-directed functions $\Psi_z^{\sigma,m}$ as an example, the trial hole functions are: for $\sigma=1$, the four ions in the plane $z=a$ have holes directed away from the vacancy, the four ions in the plane $z=0$ have no holes, and the ions in the plane $z=-a$ have holes directed towards the vacancy; for $\sigma=2$, the holes at $z=a$ are directed towards the point $(0,0,2a)$ and the holes at $z=-a$ are directed away from the point $(0,0, -2a)$; for $\sigma=3$, only the ions on the plane $z=0$ have holes, and they are all in the $+z$ direction.

The total Hamiltonian can be divided into a part which contains the kinetic energy and electrostatic interaction terms and a part which contains the spin-orbit interaction:

$$H=H_e+H_{\text{s.o.}} \quad (3)$$

If $H_{\text{s.o.}}$ is neglected, the energy levels of the β center are found by diagonalizing the 3×3 matrix

$$H_e^{\sigma\sigma'}=\langle\Psi_\nu^{\sigma,m}|H_e|\Psi_\nu^{\sigma',m}\rangle. \quad (4)$$

$H_e^{\sigma\sigma'}$ is independent of m and ν. Therefore in this approximation the β center has three energy levels, each of which is sixfold degenerate.

The addition of $H_{\text{s.o.}}$ splits each of these levels into a twofold and a fourfold degenerate level. The $\Psi_\nu^{\sigma,m}$ transform like $L=1$, $S=\frac{1}{2}$ functions under the operations of the cubic group. Therefore it is possible to form functions $(J,M)^\sigma$ with $J=\frac{1}{2}$ and $J=\frac{3}{2}$ which are eigenfunctions of J^2 and J_z and which diagonalize $H_{\text{s.o.}}$. Since the $(J,M)^\sigma$ are degenerate with respect to M, we may choose any convenient value of M, such as

$M=J$, in carrying out the calculation. We find

$$(\tfrac{3}{2},\tfrac{3}{2})^\sigma=-[\Psi_x^{\sigma,\frac{1}{2}}+i\Psi_y^{\sigma,\frac{1}{2}}]/\sqrt{2},$$
$$(\tfrac{1}{2},\tfrac{1}{2})^\sigma=[\Psi_z^{\sigma,\frac{1}{2}}+(\Psi_x^{\sigma,-\frac{1}{2}}+i\Psi_y^{\sigma,-\frac{1}{2}})]/\sqrt{3}. \quad (5)$$

The matrix elements of $H_{\text{s.o.}}$ between the foregoing functions can be written in terms of $\lambda=0.11$ ev, the spin-orbit splitting between the $J=\frac{1}{2}$ and $J=\frac{3}{2}$ levels of the ground configuration of the Cl atom. We obtain two different 3×3 matrices for the two values of J:

$$\langle(J,M)^\sigma|H|(J,M)^{\sigma'}\rangle$$
$$=\begin{cases} H_e^{\sigma\sigma'}-\tfrac{1}{6}\lambda\begin{bmatrix}0&1&1\\1&0&1\\1&1&0\end{bmatrix}, & J=\tfrac{3}{2}, \\[2mm] H_e^{\sigma\sigma'}+\tfrac{1}{3}\lambda\begin{bmatrix}0&1&1\\1&0&1\\1&1&0\end{bmatrix}, & J=\tfrac{1}{2}. \end{cases} \quad (6)$$

In the calculation of $H_e^{\sigma\sigma'}$, it is assumed that no relaxation of the ions surrounding the vacancy takes place and that the atomic orbitals on different ions are orthogonal. Under these assumptions, an expression for $H_e^{\sigma\sigma'}$ can be obtained which involves primarily the Cl$^-$ $3p$ atomic orbitals $\psi_{i\mu}$ and the wave functions $\psi_{F\mu}$ and ψ_{Fb}. Löwdin's analytic expression[3] for the Hartree Cl$^-$ atomic orbital with exchange has been used for $\psi_{i\mu}$. The spatial part of $\psi_{F\mu}$ and ψ_{Fb} is approximated by the function $Cg(\mathbf{r})\exp(-\gamma r)$ with $\gamma=0.3$ atomic unit, a form which has also been used by Dexter.[2] C is the normalizing constant and $g(\mathbf{r})$ is the wave function for an electron at the bottom of the conduction band. Since $g(\mathbf{r})$ varies slowly over most of the unit cell, we set $g(\mathbf{r})=1$. We find

$$H_e^{\sigma\sigma'}=\begin{bmatrix} 0.81 & -0.48 & -0.85 \\ -0.48 & 0.82 & -0.95 \\ -0.85 & -0.95 & 0.02 \end{bmatrix} \text{ ev.} \quad (7)$$

The diagonalization of $\langle(J,M)^\sigma|H|(J,M)^{\sigma'}\rangle$ yields the energy eigenvalues listed in Table I. Since only the terms in H_e which contribute to the splitting have been kept, the position of these levels with respect to the fundamental band is not known. Because of the assumptions made in calculating $H_e^{\sigma\sigma'}$, these energy levels are only approximate. It is certain, however, that H_e causes a splitting into three levels which are relatively widely separated, and that $H_{\text{s.o.}}$ causes only a small additional splitting.

The energy levels in bromides and iodides can be estimated if we assume that $H_e^{\sigma\sigma'}$ is the same as in chlorides and use only a different spin-orbit splitting constant λ. For bromine, $\lambda=0.46$ ev, from which we find that the two lowest levels are split by 0.4 ev. In iodides the splitting is even greater.

The β band has not yet been observed in chlorides, since it lies in the ultraviolet, an inconvenient spectral region. In bromides and iodides, the β band typically

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[3] Per-Olov Löwdin, Phys. Rev. **90**, 120 (1953).

has a width of 0.1 to 0.2 ev and lies about 0.3 ev on the low-energy side of the first peak of the fundamental band. If we assume that the observed β band is due to transitions to the lowest level of the β center, the appearance of only a single peak is explained, since the peaks arising from transitions to the five higher energy levels would be masked by the fundamental band. In NaCl, we would expect the two lowest levels to contribute to the β band, since they are separated by only 0.1 ev. If the peak with the lower energy has about the same width and position with respect to the fundamental band as in the case of bromides and iodides, it may be possible to observe this doublet structure. The higher-energy peak may, however, be masked by the tail of the fundamental band to such an extent that its detection would be difficult.

OSCILLATOR STRENGTH

The oscillator strengths of the components of the β band are related to the matrix elements of the electric dipole operator between the final states, which are the states of the β center, that is, the linear combinations of the $\Psi_\nu^{\sigma,m}$ in Eq. (2) which diagonalize $\langle (J,M)^\sigma | H | (J,M)^{\sigma'} \rangle$, and the initial state

$$\Psi_I = A \prod_{k,q} \psi_{kq} \psi_{Fb}^0. \tag{8}$$

ψ_{Fb}^0 is the wave function for one electron bound to the vacancy, and therefore it is different from the corresponding functions $\psi_{F\mu}$ and ψ_{Fb} appearing in Eq. (1), which apply when two electrons are bound to the vacancy. Following Dexter, we take $\psi_{Fb}^0 = C_0 g(\mathbf{r}) \times \exp(-\gamma_0 r)$, with $\gamma_0 = 0.445$, as the wave function for a single electron bound to the vacancy, and as before, set $g(\mathbf{r}) = 1$. The results are listed in Table I. The experimental value of the oscillator strength is uncertain, but it appears to lie between $f = 0.46$ and $f = 0.9$. If the results which we have obtained for NaCl are typical also for salts in which the β band is observed, and if we interpret the transition to the lowest level as the observed β band, the calculated value is much too small. The total oscillator strength to all six levels is 0.94, a reasonable value. The small value of f for the lowest two levels is accidental, and an improved calculation of $H_e^{\sigma\sigma'}$, which would change the linear combinations of the $\sigma = 1, 2, 3$ functions which make up these levels, would probably increase f. Therefore this disagreement does not necessarily invalidate our model of the β center.

AUTOIONIZATION TRANSITION

The initial state for the autoionization transition is the β center, namely two electrons bound to a negative-ion vacancy and a hole on the next nearest neighbor Cl^- ions; the final state is the vacancy with no electrons attached and an electron in the conduction band moving away from the vacancy. In other words, roughly speaking, one of the electrons bound to the vacancy jumps into the hole, a process which releases

more than enough energy to expel the other electron into the conduction band. Wentzel[4] has shown that the autoionization rate W for a two-electron system is given by the matrix element of the Coulomb interaction energy between the two electrons:

$$W = \frac{2\pi}{\hbar} |H_{FI}|^2 \rho(E), \tag{9}$$

where

$$H_{FI} = \left\langle \Psi_{\text{final}}(\mathbf{r}_1,\mathbf{r}_2) \left| \frac{e^2}{r_{12}} \right| \Psi_{\text{init}}(\mathbf{r}_1,\mathbf{r}_2) \right\rangle, \tag{10}$$

and $\rho(E)$ is the density of final states. The result is the same in the problem under consideration, only the electrons involved in the transition appearing in the matrix element. We find

$$\Psi_{\text{init}} = A (\psi_{F\mu} \psi_{Fb}), \tag{11}$$

$$\Psi_{\text{final}} = A (\sum_{i,\mu} c_{i\mu,\nu}^{\sigma,m} \psi_{i\mu} \psi_c), \tag{12}$$

where ψ_c is the free electron function, and $\sum_{i,\mu} c_{i\mu,\nu}^{\sigma,m} \psi_{i\mu}$ is the wave function of the electron which has jumped into the hole. It can be shown that the matrix element for $\sigma = 1$ is greater than that for $\sigma = 2$ and $\sigma = 3$ by a factor of at least three; this situation arises because the p hole functions on the Cl^- ions are directed toward or away from the vacancy only for the $\sigma = 1$ function. Although the initial state of interest, the state of the β center with the lowest energy, is a mixture of all three σ functions, a rough upper limit for the autoionization rate can be found by using $\sigma = 1$ in Eq. (12).

Only the $L = 1$ term in the Legendre polynomial expansion of $1/r_{12}$ contributes to the matrix element, and ψ_c must then also be an $L = 1$ function. The $L = 0$ part of $1/r_{12}$ has in fact already been included in the Hamiltonian H_e, since screening is taken into account in finding the functions $\psi_{F\mu}$ and ψ_{Fb}. The density of final states is found by assuming that the energy of the free electron is given by the relation $E = \hbar^2 k^2 / 2m^*$ with $m^* = m_e$. E is approximately the energy of formation of the β center minus the ionization energy of the F center. For NaCl this is $E = 7.5$ ev $- 3$ ev $= 4.5$ ev.

We find $W = 1.8 \times 10^{13}$ sec^{-1}, corresponding to a line width at half-maximum of 0.012 ev. Since typical experimental widths of the β band at liquid N_2 temperature are 0.125 ev[5] and 0.20 ev,[6] we conclude that the autoionization rate of the β center is not an important factor in determining the width of the β band.

[4] G. Wentzel, Z. Physik 43, 524 (1927).
[5] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. 19, 574 (1951); 20, 746 (1952).
[6] W. Martienssen, Z. Physik 131, 488 (1952).