PHYSICAL REVIEW VOLUME 186, NUMBER 3 15 OCTOBER 1969

Electronic Transitions of the F Center in Alkali Halides

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(Received 14 October 1969)

Topological wave functions, in the form of localized free-electron orbitals, are used to describe the F center in alkali halides of the NaCl structure. Previous calculations on the F-band transition energies are extended to the K and L bands, confirming that these are higher-energy trnasitions of the F center. Oscillator strengths are calculated for the F and K bands. The model treats these bands as tangential excitations of the free-electron orbitals, and shows that the allowed radial transition correlates well with the β band. The low transition energy and long lifetime of F emission follows directly from the theory.

I. INTRODUCTION

The F-band absorption in alkali halides is caused by an electron trapped at an anion vacancy. There are many theoretical investigations of this absorption,[1–3] but the higher-energy transitions of the F center, now experimentally well documented,[4,5] have not been easily incorporated into the existing theories. It has recently been suggested[6] that the use of localized free-electron orbitals combines the advantages of both the molecular model and the point-ion approach in the calculation of energy levels, and this free-electron model was applied to F-band absorption.[6] The problem common to all calculations has been that of the polarization of the surrounding lattice, and whether by the use of gross dielectric properties[3] or the inclusion of localized pseudopotentials,[7] the calculations have basically regarded the surrounding lattice as a perturbation of the F electron. If, however, the polarization is strong, then the one-electron approximation breaks down and transitions of a localized system need to be considered. The localized free-electron model takes account of several ion shells by including the most labile electrons in the trap explicitly as part of the free-electron system. It is, thus, somewhat similar to the theory developed for the π electrons of planar aromatic molecules[8] and has a rough mathematical equivalence to an approach based on a linear combination of atomic orbitals. The calculations below are based on a static undistorted lattice. The details of the assumptions in the model have been discussed previously.[6]

II. THEORY AND RESULTS

The model for the F center[6] involves the ions on and within a radius of $2a$, where a is the crystal nearest-neighbor distance. This volume contains 19 electrons (including the F electron) which are sufficiently labile to be considered in the F-center absorption pattern. The bulk of the electron distribution, that which determines the energy levels, is within a shell describable in terms of a parameter Δ, where

$$\Delta=(r_1-r_2)/a\,, \tag{1}$$

with r_1 and r_2 the limiting radii of the shell. The radial wave solutions are solved for the two boundary conditions at r_1 and r_2, using spherical Bessel and Neumann functions; the energies are given by

$$E_{mn}=(h^2/8\pi^2\mu a^2)\lambda_{mn}^2\,, \tag{2}$$

where μ is the mass of the electron, λ_{mn} is the eigenvalue determined for a particular value of Δ, and the wave function has $n-1$ radial nodes and m angular nodes. The eigenvalues, in their dependence on Δ, are most suitably calculated in terms of parameters x_1 and x_2, where

$$x_1=\lambda(1+\tfrac{1}{2}\Delta)$$

and

$$x_2=\lambda(1-\tfrac{1}{2}\Delta)\,. \tag{3}$$

These have previously been tabulated[6] for $n=1$ and $m=0$, 1, 2, and 3. The calculations have been extended to $n=1$ and $m=4$ and 5, and $n=2$ and $m=0$, 1, and 2. The results are summarized in Fig. 1.

The appropriate eigenfunctions are a combination of the radial solutions and the corresponding spherical harmonics. The transition energies are calculated as one-electron transitions within the set of eigenvalues; the free-electron wave functions, reflecting the topology of the possible states of the system, minimize the need to allow for electron correlation and suggest that the one-electron transition is a good approximation. The energies of the F center are, thus, simply regarded as a summation of one-electron energies.

Strongly allowed transitions will be those obeying the spherical harmonic selection rule of $\Delta m=\pm1$, while those with $\Delta m=\pm2$ will be weak and dependent for their intensity on the nonstatic nature of the real lattice.

The chosen system consists of 19 electrons, and the ground state is $(0,1)^2$, $(1,1)^6$, $(2,1)^{10}$, and $(3,1)^1$, where (m,n) symbolizes the eigenfunction. The F-band

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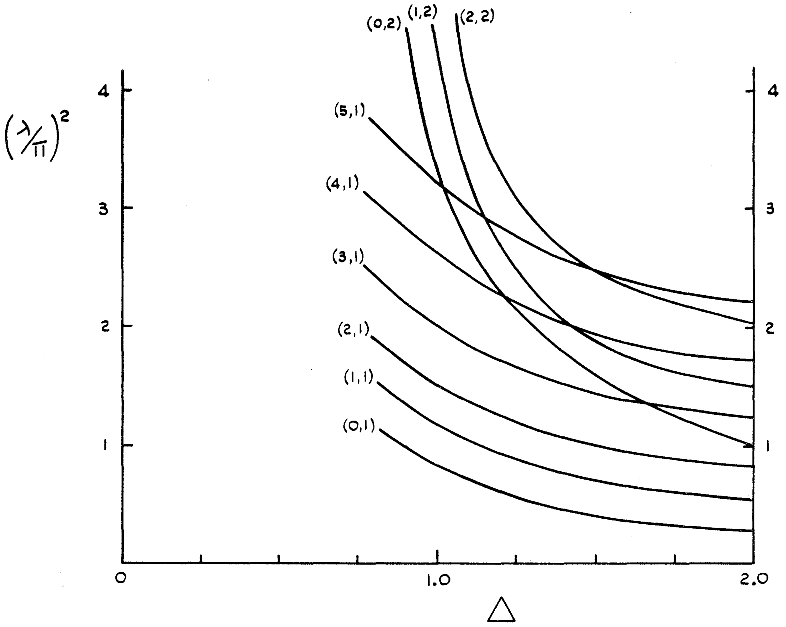

FIG. 1. Variation of eigenvalues (λ) with shell width (represented by Δ) for the lowest-energy levels in the free-electron model.

absorption was found[6] to be in accord with the one-electron transition $(2,1) \rightarrow (3,1)$ at values of Δ varying from 1.15 to 1.50. The dependence of the eigenvalues on Δ, and the individual values of Δ for each of the alkali halides have been previously discussed[6] for the F-band absorption. Values of Δ, Δ_e, which are required to yield experimental F bands are listed in Table I.

It should be noted that calculations on the F band[6] were initially carried out without any assumption about Δ and yielded agreement with experiment to 2 or 3%. Exact agreement is obtained using the Δ_e's listed, and these are used for the calculation of the higher-energy transitions to test the consistency of the derived eigenvalues. Experimentally, the higher-energy transitions of the F center are designated, in order of increasing energy, the K, L_1, L_2, L_3, and L_4 bands. These have been measured mainly[4,5] at around 90°K and the values, for room temperature, listed in Table I are derived assuming the same temperature dependence as the F band has. This is done for reasons of comparison with the F band, since lattice parameters are more reliably known at room temperature.

The higher-energy transitions of the F center are treated similarly to the F band itself; for a particular crystal all transitions have the same ground-state configuration, and, thus, the same value of Δ is used. This is essentially a statement of the Franck-Condon principle, and will only be valid for absorption. The self-consistency of the theoretical model is tested, since the only parameters required are the crystal nearest-neighbor distances and the Δ_e values from the F band.

A. *F* Band

The transition energies of the F band have previously been discussed,[6] but it is of interest to use the model to calculate oscillator strengths. Experimental oscillator strengths have been measured using a variety of techniques, and these have tended to yield a spread of results.[2,3] However, for all alkali halides of NaCl structure the F band has an oscillator strength (f_F) certainly between 0.5 and 1.0. The measured values of f_F may not give the theoretical f, because: (i) of the many assumptions in the derivation of Smakula's equation and (ii) of the experimental measurement which does not represent the pure electronic transition, but includes changes in lattice quanta. Nevertheless, the calculated values should yield an extra test of the general validity of the theory.

$$f_F = (8\pi^2 c\mu E/3he^2)\left(\sum M_{df}\right)/g, \tag{4}$$

where E is the F transition energy, g is the degeneracy of the initial state in the one-electron transition, i.e., the (2,1) state, and M_{df} is the transition moment between two sublevels d and f of the (2,1) and (3,1) states. The summation is over all the allowed transitions between components of the initial and final states.

$$M_{df} = \bar{m}_{df} \int_\theta \psi(\theta)_{21}\psi(\theta)_{31}\sin\theta d\theta \times \int_\phi \psi(\phi)_{21}\psi(\phi)_{31}d\phi \int_{r_1}^{r_2} R(r)_{21}R(r)_{31}r^2 dr,$$

where $\psi(\theta)$ and $\psi(\phi)$ indicate the appropriate angular parts of the spherical harmonics for each eigenfunction (2,1) or (3,1); the function $R(r)$ represents the radial part of the eigenfunction, and $\bar{m}_{df}$ is the transition moment operator.

In the actual calculation, the total wave function for each state was first normalized, and M_{df} calculated for $d=0$ and $f=0$. All the values of M_{df} were then calcu-

TABLE I. Experimental band positions (eV) at room temperature (corrected if necessary) and transitions energies (eV) in the free-electron model. Experimental Δ_e's are used to make the F band correspond exactly to the $(2,1)\rightarrow(3,1)$ transition.

	Experimental						Theoretical[a]							
MX	F^b	K^c	$L_1{}^d$	$L_2{}^d$	$L_3{}^d$	$L_4{}^e$	Δ_e	$(2,1)\rightarrow(3,1)$	$(3,1)\rightarrow(4,1)$	$(4,1)\rightarrow(5,1)$	$(3,1)\rightarrow(1,2)$	$(1,1)\rightarrow(3,1)$	$(2,1)\rightarrow(4,1)$	$(3,1)\rightarrow(5,1)$
LiF	4.96						1.42	4.96	5.99	7.30	5.81	8.80	10.95	13.29
LiCl	3.22						1.33	3.22	3.91	4.74	4.41	5.63	7.13	8.65
LiBr														
LiI														
NaF	3.64	4.27					1.49	3.64	4.32	5.35	3.68	6.42	7.96	9.67
NaCl	2.71						1.29	2.71	3.24	4.00	4.05	4.75	5.95	7.24
NaBr	2.30						1.39	2.30	2.74	3.37	2.84	4.03	5.04	6.11
NaI	2.11						1.22	2.11	2.58	3.10	3.76	3.70	4.69	5.68
KF	2.72						1.50	2.72	3.25	4.00	2.74	4.75	5.97	7.25
KCl	2.23	2.63	3.50	4.19	4.82	~6.0	1.23	2.23	2.71	3.28	3.91	4.02	4.94	5.99
KBr	1.98	2.29	3.22	3.83	4.38		1.28	1.98	2.35	2.91	3.15	3.58	4.34	5.27
KI	1.80	2.05	2.70	3.16	3.70	~4.6	1.19	1.80	2.19	2.65	3.01	3.24	3.99	4.84
RbF														
RbCl	2.04	2.29	3.00	3.61	4.48		1.24	2.04	2.48	3.00	3.30	3.66	4.52	5.48
RbBr	1.79	2.02	2.77	3.34	4.01		1.35	1.79	2.17	2.64	2.45	3.22	3.96	4.81
RbI	1.64	1.86	2.39	2.92	3.57		1.23	1.64	1.98	2.41	2.72	2.95	3.61	4.39

[a] Correspondence between theory and experiment is suggested as $F \leftrightarrow (2,1)\rightarrow(3,1)$, $K \leftrightarrow (3,1)\rightarrow(4,1)$, $L_1 \leftrightarrow (4,1)\rightarrow(5,1)$ or $(3,1)\rightarrow(1,2)$, $L_2 \leftrightarrow (1,1)\rightarrow(3,1)$, $L_3 \leftrightarrow (2,1)\rightarrow(4,1)$, $L_4 \leftrightarrow (3,1)\rightarrow(5,1)$.

[b] References 2 and 3.

[c] References 4 and 5.

[d] Reference 4.

[e] M. Hirai and M. Ikezawa, J. Phys. Soc. Japan **22**, 810 (1967).

lated using comparison with M_{00} and standard angular momentum relationships.[9] The integration over the radial part of the function (using values of r_1 and r_2 corresponding to Δ_e) was simplified by taking the trigonometric approximation to both the Bessel and Neumann functions. For the values of Δ, i.e., r_1 and r_2, of interest in the present calculation this was a good approximation.

F-band f values calculated in this way are given in Table II for NaCl, KCl, and KBr, for which a number of experimental determinations have been made using a variety of techniques.

The model suggests that all F-band f values should be similar in magnitude, since the main lattice dependences are $f \sim CEa^2$, and $E \sim D/a^2$, where C and D are constants, and thus f is independent of the actual lattice. However, because of the dependence of λ_{mn} on a [see Eq. (2) and Ref. 6] and also the details of the radial integration, they vary in the small way shown in Table II.

B. *K* Band

Other than that corresponding to the F band, the only other allowed tangential transition ($\Delta m=1$) is $(3,1)\rightarrow(4,1)$. Transitions involving changes in n are at much higher energies and are discussed below. The $(3,1)\rightarrow(4,1)$ transition energies are listed in Table I and are seen to correspond to the experimental K band. Calculation of the K-band oscillator strengths followed the same procedure as in Sec. II A and they were found to be down from the F-band oscillator strength by a factor of approximately 0.3 for all the alkali halides. Experimental ratios of f_K to f_F are all in the region 0.1–0.4, and thus agreement is reasonable.

In Fig. 1, we see that the (0,2) state crosses the (4,1) state at $\Delta=1.22$, and similarly the (1,2) state crosses (4,1) at $\Delta=1.40$. Although mixing of these states should be small owing to the necessary high symmetry of the perturbing vibrations, some observable effect on oscillator strengths may be present. Two such observables are suggested:

(i) Lüty[4] suggested in studying the strengths of the K bands in KCl, KBr, KI, RbCl, RbBr, and RbI that the bromide crystals showed rather higher f_K values than the chlorides and iodides. The Δ_e values for these six crystals are such that the chloride and iodide transitions are at Δ_e values very close to 1.22, whereas the bromide Δ_e values are higher, at or above 1.3, but still well below 1.4. The result of this would be much less mixing of (0,2) and (1,2) with (4,1) for the bromides and, thus, higher measured oscillator strengths, provided that the perturbation is strong enough to separate the resulting states.

(ii) The F band is often found to be asymmetric with a buildup in intensity at high energy[3]; this is referred to

TABLE II. Theoretical and experimental oscillator strengths for the F bands of NaCl, KCl, and KBr.

	f_F (Calc.)	f_F (Expt.)
NaCl	0.75	0.81[a]
KCl	0.70	0.90[a]
KBr	0.75	0.80[a]

[a] A weighted mean of several determinations using a variety of techniques [W. T. Doyle, Phys. Rev. **111**, 1072 (1958)].

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as the B band. It is suggested that a possible cause for this is the presence of the split K band owing to (0,2) or $(1,2) \leftrightarrow (4,1)$ mixing. The low-energy component of the K band will be weak but could well be sufficiently strong to show up as asymmetry in the F band. The present model indicates that for the six crystals studied by Lüty[4] this asymmetry would be least marked for the bromides.

C. L_2, L_3, and L_4 Bands

These bands are very weak ($f \sim 0.01$) and have not been observed for all alkali halide crystals as is shown in Table I. In many crystals their observation has been impaired by the presence of impurity bands[4] or V bands.[5] The present model suggests that these bands are due to $\Delta m = 2$ tangential excitations, formally forbidden on orbital angular momentum considerations and only weakly allowed by the nonstatic nature of the lattice. L_2 is $(1,1) \rightarrow (3,1)$, L_3 is $(2,1) \rightarrow (4,1)$, and L_4 is $(3,1) \rightarrow (5,1)$.

D. L_1 Band

The L_1 band lies in energy between the K and L_2 bands and is even weaker than the other L bands showing an f value of ~ 0.005. Lüty[4] also suggests that its bandwidth is considerably less than for the other L bands. The transition energies for the L_1 band do not fit so easily into the present theoretical model, and *two possible* one-electron transitions are suggested:

(i) Change in quantum number n has so far not been considered, although this will be looked at in Sec. II E with $\Delta n = 1$ and $\Delta m = 1$, which is an allowed transition. However, transitions of the type $\Delta n = 1$ and $\Delta m = 2$, although formally forbidden, should show up with an oscillator strength of the same order as observed for the L_1 band (see Sec. II C). Three such transitions are possible: $(2,1) \rightarrow (0,2)$, $(3,1) \rightarrow (1,2)$, and $(4,1) \rightarrow (2,2)$, and for the six observed L_1 bands given in Table I, having Δ_e values between 1.2 and 1.35, only $(3,1) \rightarrow (1,2)$ is of the correct order of magnitude. For these six crystals the transitions $(2,1) \rightarrow (0,2)$ and $(4,1) \rightarrow (2,2)$ are higher in energy and would lie at longer wavelengths than L_3, thus almost certainly not being observed by Lüty who reports[4] impurity bands in that region. The $(3,1) \rightarrow (1,2)$ transition energies are given in Table I. If this is indeed the L_1 transition, then for crystals with $\Delta_e > 1.4$ it will be at lower energy than the K band (e.g., LiF, NaF, and KF) and would only be observed as asymmetry in the F band (i.e., B-band structure).

(ii) A very good energy match between L_1 and the transition $(4,1) \rightarrow (5,1)$ exists as shown in Table I. This gives a better correlation than the $(3,1) \rightarrow (1,2)$ transition suggested in (i), and would also be of the correct intensity. The (4,1) level is not populated, in the free-electron energy scheme proposed, and thus $(4,1) \rightarrow (5,1)$ is not allowed in absorption. The high concentration of F centers required to study these weak transitions allows the possibility of a small concentration of multiple centers with many more labile electrons and, thus, population of the (4,1) level. The experimental finding of Lüty that the ratio of the absorption coefficients of L_1 to F bands remained constant over an absolute change in each of a factor of 50 indicates that transition (ii) is unlikely.

E. β Band

For the crystals studied, the ratio of the transition energies K/F, L_2/F, etc., is roughly a constant; the reason for this in the present model is that both ground-state and excited-state energies vary with Δ in very similar ways. This is not true for transitions involving change in n when ground- and excited-state energy gradients with respect to Δ are quite different. The β band is regarded[2,3] as being a perturbed absorption of the crystal because of the imperfection of the F center in the lattice, and is situated close to the crystal absorption edge. Basically, the transition has been interpreted as an electron movement from an anion adjacent to an F center into the trap to form an F' center. In the present model it should be one of the transitions of the perturbed system represented by the localized free-electron trap. Further, the ratio of the transition energies β/F varies from crystal to crystal (i.e., varies with Δ), and this, from above, would indicate a radial transition. Three fully allowed transitions are possible: $(1,1) \rightarrow (0,2)$, $(2,1) \rightarrow (1,2)$, and $(3,1) \rightarrow (2,2)$.

In the range of Δ_e values pertinent to the alkali halides, $\Delta_e = 1.2–1.5$, all these transitions have essentially identical transition energies. Taken as one transition these are shown in Fig. 2 and are compared with the experimental β bands. It is seen that the model yields transition energies lower than experiment by a factor of around 17%. This represents the fact, already discussed,[6] that the free-electron model is good for tangential excitations but fairly poor for radial transitions.

Nevertheless, the change with Δ, and thus from crystal to crystal, is correctly indicated, and it is only the absolute energy of the (0,2), (1,2), and (2,2) levels which requires correcting for second-order effects.

F. Emission

Within the static model being used, it is not possible to fully discuss emission processes. Qualitatively, however, it is obvious that an excited F center will have different electron-core interactions, and that, in the free-electron model, the orbital electron distribution will be more delocalized. Thus, the energy levels for an excited F center will be characterized by having larger Δ values.

Experimentally, F-center emission has two outstanding features[2,3]: (i) a low transition energy and (ii) a

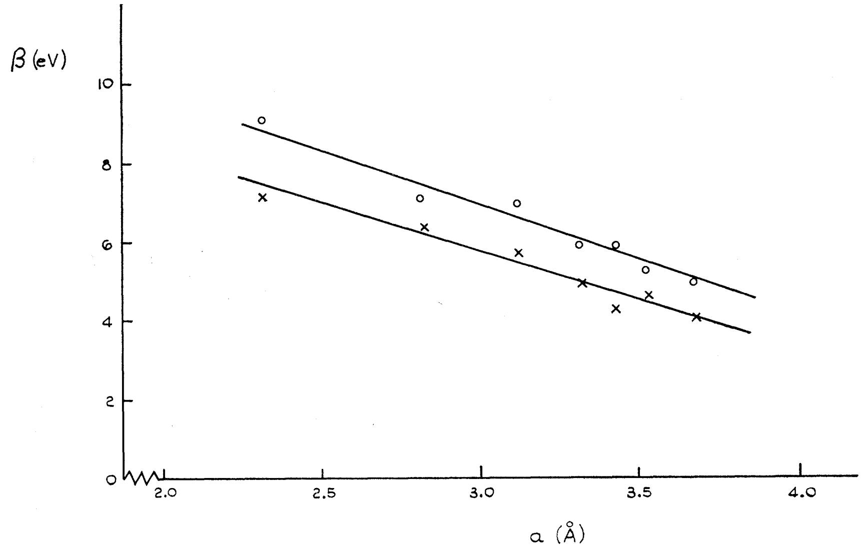

FIG. 2. Plot of experimental (*o*) and theoretical (*x*) β-band transition energies against the nearest-neighbor distance *a*. The crystals shown are NaF, NaCl, KCl, KBr, KI, RbBr, and RbI.

longer lifetime than would be expected from a fully allowed transition.[10,11]

In the present model both (i) and (ii) can adequately be explained following *F*-band absorption represented by $(2,1)\rightarrow(3,1)$. The consequent electron delocalization in the excited state means that the (0,2) level comes below (3,1). The crossover from (3,1) to (0,2) is at $\Delta=1.65$ (see Fig. 1). The emission process is then the one-electron transition $(0,2)\rightarrow(2,1)$ at much lower energy than the *F* band, and since it is largely forbidden, it shows a long lifetime. A similar explanation, linked to rapid internal conversion, is obvious for the *F* emission following absorption into the *K* or *L* bands.[12]

III. CONCLUSION

The agreement with experiment achieved by the model suggests that polarization of the most labile electrons in a localized volume exerts a dominating effect on the states of the *F* center. The extreme nature of the assumptions with regard to electron distribution could be improved by the choice of a better potential but, due to the small dependence[6] of the transition energies on Δ, this improvement would probably introduce marginal change into the calculated transition energies. The restriction of the charge distribution to a three-dimensional pattern of nodes and antinodes determined by the lattice is in accord with the strong dependence of these transitions on lattice parameters (e.g., the ratios K/F, L_1/F, etc., are roughly constant for all crystals).

The *g* factor for the ground state in the model is close to 2, there being no central field on the delocalized orbitals producing spin-orbit coupling. The spin-orbit coupling resulting from the field of the nuclei in the chosen volume is most simply expressed by examining the nature of the delocalized orbitals in the vicinity of each nucleus. The mathematical equivalence of the "linear combination of atomic orbitals" approach means that the delocalized orbitals can be expressed largely in terms of atomic *s* orbitals with a small amount of *p* (and possibly *d*) character mixed in, thus reducing the *g* factor somewhat below 2 as observed.

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