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K Band in Colored Alkali Halide Crystals*

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Recently the results of a number of experiments relating to the *K* band in colored alkali halides have been reported and several new speculations have been put forth concerning this absorption. A comparison of the known properties of the band with the predictions of various theories leads to the conclusion that the available experimental evidence supports the original suggestion of Mott and Gurney that the *K* band is an absorption of the *F* center to a series of higher excited states. To provide a semiquantitative theoretical test of this explanation the Simpson model for the *F* center was investigated in detail. The model problem was solved for the most important higher bound states, and transition energies and oscillator strengths for transitions to these states were calculated. It was found that for reasonable choices of parameters the model predicts an optical absorption spectrum that is strikingly similar to the composite *F*- and *K*-band absorption. Several experimental tests of the Mott-Gurney model are suggested and the possibility of *K*-band-like absorptions associated with other centers is discussed.

I. INTRODUCTION

IN the past year a number of experimental studies of the *K* band[1,2] in colored alkali halides have been reported. This work includes research on photoconductivity,[3,4] the effect of crystal purity,[5] the shape of the optical absorption,[4] the effect of uniaxial stress[6] and external magnetic fields[7] on the band, and the modulation of the *K*-band absorption by optical pumping.[8] In addition, several theoretical studies have been reported suggesting various mechanisms to account for the transitions involved.[9–11]

The aim of the present work is to consider the various theories in light of the known properties of the *K* band. Particular emphasis is devoted to the original suggestion of Mott and Gurney[12] that the *K* band arises from transitions of the *F* center to highly excited states and the relation of this model to some recent speculations.

Since Kleinschrod's observation of the *K* band[13] the following prominent features of this absorption have been reported:

1. In all salts in which a *K* band has been resolved,[4,5,13–16] the band is always found toward the high-energy side of the *F* band and it is always much weaker than the *F*.[17] In experiments in which precautions are taken to use highly purified crystals and to eliminate absorptions due to *F*-aggregate centers, the ratio of the maximum of the absorption coefficient of the *K* band to that of the *F* band is found to be a concentration-independent constant for each of the alkali halides.[5,14,18]

2. The *K*-band width appears to be relatively temperature-independent with a width at half-maximum that is roughly equal to that of the *F* band at room temperature.[4,5,14] The peak position of the *K* band is also relatively independent of temperature over the range in which the band can be resolved.[4,14] This is to be compared with the appreciable temperature shift of the *F*-band peak with temperature.[19]

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[13] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

[14] F. Lüty, Z. Physik **160**, 1 (1960).

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[16] H. W. Etzel and F. E. Geiger, Jr., Phys. Rev. **96**, 225 (1954); F. E. Geiger, Jr., *ibid.* **97**, 560 (1955).

[17] The possibility that polarization effects in the lithium halides could alter the *F*-center potential so that some excited states lie below the state responsible for the main *F* band has been raised by W. B. Fowler. At present there is little evidence either for or against this speculation. W. B. Fowler (private communication).

[18] B. J. Faraday and W. D. Compton, Phys. Rev. **138**, A893 (1965).

[19] See, for example, the often quoted result for the KBr *F* center, R. W. Pohl, Proc. Phys. Soc. (London) **49**, (extra part), 3 (1937); or Ref. 2, p. 54.

3. Careful measurements of the K band in RbCl at low temperatures show that the band is considerably more asymmetric than the F band and that it has a long high-energy tail that may be detected at least half an electron volt beyond the peak of the band.[4]

4. Photoconductivity studies of colored KCl,[20] KBr,[3] and RbCl[4] show that there is relatively little photoconductivity in the F band, in the low-energy side of the K band, and near the peak of the K band. There is, however, a sharp increase in photoconductivity toward short wavelengths in the high-energy side of the K band and the quantum efficiency for photoconductivity is generally thought to be unity in the high-energy tail.[3]

5. Schnatterly has found that the application of uniaxial stress to crystals containing F centers yields linear dichroism in both the F and the K bands.[6] Furthermore, he has found that the area under the F band decreases under stress while the area under the K band increases. The area under the composite F-K band decreases somewhat, but this effect is smaller by a factor of three than the change in area of the individual bands. From the data on the effect of stress-induced lattice distortions on the K band Schnatterly has estimated the effect of similar thermal distortions. He concludes that if the transitions involved are assumed to be forbidden in the static lattice there should be a stronger dependence of area and peak position than is observed. If the transitions are assumed to be allowed, the predictions are consistent with experiment.

6. Magneto-optical experiments of Henry[7] on colored KCl show that the F and K bands also exchange area when a magnetic field is applied. In addition, it was found that the paramagnetic circular dichroism in both the F and K bands have the same spin relaxation time.

7. In an attempt to see if the K and L bands arise from complexes involving the F center, Klick and Kabler have studied the absorption spectra of crystals colored by different methods at low temperatures.[21] Although the different methods of coloration produce different populations of complexes, no differences of the L and K bands relative to the F band were observed. The investigators concluded that both the K and L bands must arise from the isolated F center.

8. Chiarotti and Grassano have studied the K and L bands in crystals in which the population of the ground state of the F center is modulated by optical pumping.[8] Their experiment consists of illuminating a colored crystal with modulated F-band light and simultaneously measuring the absorption spectrum. They observed that the F, K, L_1, L_2, and L_3 bands all exhibit the same modulation indicating that they all arise from excitations from the same ground state.

The fact that the ratio of the absorption constants of the F and K band is a constant has largely limited theoretical speculations to models that relate the K-band absorption to the F center. However, Gold has speculated that aggregate centers may be involved.[22] Stungis and co-workers have suggested trace impurities may play an important role,[5] and Suzuki and Doyama have attributed the absorption to F centers perturbed by dislocations.[23]

The first K-band model was proposed by Mott and Gurney[12] on the basis of a dielectric continuum approximation to the de Boer model of the F center.[1,2] They suggested that the F band arises from the $1s$–$2p$ transition of the trapped electron and that the K band is the result of the $1s$–np, $n\geqslant 3$ transitions. Dexter calculated the ratio of the F-band absorption to absorption at various points in the K band on the basis of this model and found reasonable agreement with experiment.[24] A variation of this proposal has been made by Wagner[25] and later by Wang[26] who assign the K band to the $1s$–$3p$ transition as a result of detailed model calculations.

Wood, arguing from the results of his linear-combination-of-atomic-orbitals (LCAO) calculations for the F center, has recently suggested that the absorption represents a transition between the ground state and an excited state of the same symmetry[9] that is made partially allowed by lattice vibrations. An extension of these calculations suggests that two electronic transitions may be involved.[10] A somewhat similar possibility that the K band is due to a forbidden $1s$–$3d$ transition has been discussed by Kübler as a result of calculations based on a pseudopotential approximation for the ions surrounding the F center.[11]

II. F-CENTER MODELS

At the present time the weight of experimental evidence, particularly the results of Klick and Kabler,[21] Schnatterly,[6] Henry,[7] and Chiarotti and Grassano[8] indicate that the K band is an absorption of the isolated F center. The lack of strong temperature dependence of the K band is consistent with the transitions being allowed in the static lattice[6] and the band's asymmetry and long high-energy tail suggest that more than one transition is probably involved.[4] Thus, the present experimental situation supports the original speculation of Mott and Gurney.

In an effort to extend Dexter's treatment of this model,[24] we have attempted to fit the transition energies and oscillator strengths of the F and K bands of RbCl from the solution of a physically reasonable Simpson-type F-center model.[27] This model is particularly well suited to the study of the gross features of the F center

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[20] R. L. Wild and F. C. Brown, Phys. Rev. **121**, 1296 (1961).

[21] C. C. Klick and M. N. Kabler, Phys. Rev. **131**, 1075 (1963).

[22] A. Gold, Phys. Rev. **123**, 1965 (1961).

[23] T. Suzuki and M. Doyama, J. Phys. Chem. Solids **10**, 77 (1959).

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

[25] M. Wagner, Z. Naturforsch. **15a**, 889 (1960); **16a**, 302 (1961).

[26] S. F. Wang, Phys. Rev. **132**, 573 (1963).

[27] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949). See also K. Lehovec, Phys. Rev. **92**, 253 (1953).

in the one-electron approximation because it is consistent with both the tightly bound ground state and the more loosely bound higher excited states having large orbits.

The Simpson-model potential, Fig. 1, is a combination of potentials for the dielectric-continuum–effective-mass model and the point-ion model with provision for crystal polarization effects. Alone, either of these models is misleading. The dielectric-continuum–effective-mass model generally accounts for polarization effects correctly and is appropriate for describing diffuse states that extend over many lattice sites.[28,29] However, it does not take the details of the solid near the defect into account and so it is not useful in treating localized states. On the other hand, point-ion, LCAO and similar models that include details of the defect are capable of giving good representations of localized states, particularly energy differences.[29,30] However, they generally do not include polarization effects and so energy-level predictions may not be good on an absolute energy scale and models neglecting polarization are fundamentally inconsistent for highly extended states in polarizable crystals.

In the case of the composite Simpson-model potential the ground state and to a lesser extent the first few excited states are determined primarily by the details of the defect. The higher excited states, particularly non-s-like states, are determined by the Coulomb tail. An important consequence of this particular long-range part of the potential is that it leads to an infinite number of bound states leading up to the bottom of the conduction band as a limit regardless of the details of the potential near the vacancy.[31] It should also be stressed that this potential is an *equivalent* one-electron potential and that by allowing for polarization, electronic many-body effects appropriate to an insulator (in which screening occurs because of virtual interband transitions) have been accounted for.[32]

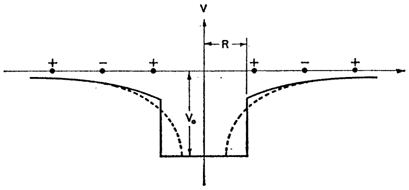

FIG. 1. F-center model potentials. Solid curve: the Simpson model. Dashed curve: the Tibbs model (see Ref. 2).

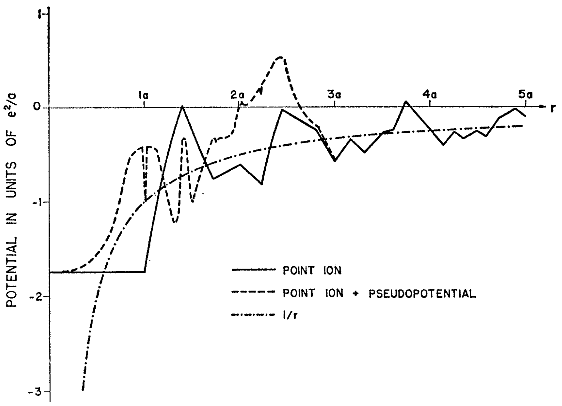

FIG. 2. F-center model potentials. Solid curve: the spherically symmetric component of the point-ion potential. Dashed curve: the spherically symmetric component of Kübler's pseudopotential modification of the point-ion model. Dot and dash curve: the potential for a unit point charge at the origin with no screening.

In the Simpson model only the spherically symmetric component of the crystal field, i.e., the angular average, is considered. Kübler has shown that terms with higher angular dependence are important in detailed energy-level calculations,[11] but since we are concerned with the over-all features of the problem, this approximation should be satisfactory. Another important omission in this model is the neglect of lattice vibrations. This necessarily restricts the calculation to crystals at low temperatures because terms in the electronic energy involving the phonon field are ignored.[33]

Originally Simpson[27] and later Krumhansl and Schwartz[34] derived the parameters for this model by considering the F center to be a positively charged cavity, of radius equal to the Mott-Littleton radius, within a dielectric continuum. The effective mass of the electron in the dielectric was generally taken as unity and the dielectric constant ϵ was assumed to be the high-frequency one.

Subsequent calculations have shown that several effects may alter this picture somewhat. Haken and Schottky have shown that in the exciton problem the "dielectric constant" can vary from unity for an electron and hole at small distances to the static value at large electron-hole separations.[35] This variation of dielectric constant with distance has been included in F-center calculations by Fowler.[36] The finite size of the ions neighboring the F center has been considered by Kübler who has included pseudopotential terms in an F-center energy-level calculation to take account of the Pauli principle "repulsion" of the F-center electron from the region of the ion cores.[11] His model potential

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[28] See for example, W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

[29] B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnball (Academic Press Inc., New York, 1960), Vol. 10.

[30] See for example, D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vols. 8 and 9.

[31] See the discussion starting on p. 80 in Ref. 12.

[32] D. Pines, *Elementary Excitations in Solids*, (W. A. Benjamin, Inc., New York, 1963).

[33] See for example D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

[34] J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953); J. A. Krumhansl, *ibid.* **93**, 245 (1954).

[35] H. Haken, Z. Naturforsch. **9a**, 228 (1954); Nuovo Cimento **3**, 1230 (1956); H. Haken and W. Schottly, Z. Physik. Chem. (Frankfurt) **16**, 218 (1958).

[36] W. B. Fowler, Phys. Rev. **135**, A1725 (1964).

TABLE I. Calculated energy eigenvalues, transition energies, and oscillator strengths for the F center in RbCl.

Electronic state	Simpson potentials with			Hydrogenic potential with		
	$R=4.1a_0$	$V_0=-5.92$ eV	$\epsilon=3.0$	$\epsilon=3.00$		
nl	E_{nl} eV	$(E_{np}-E_{1s})$ eV	$f_{1s\to np}$	E_{nl} eV	$(E_{np}-E_{1s})$ eV	$f_{1s\to np}$
$1s$	−2.574	...	...	−1.512	...	...
$2p$	−0.493	2.081	0.5757	−0.378	1.134	0.4162
$3p$	−0.201	2.372	0.0857	−0.168	1.344	0.0791
$4p$	−0.108	2.466	0.0284	−0.095	1.418	0.0290
$5p$	−0.067	2.507	0.0130	−0.061	1.452	0.0139
$6p$	−0.046	2.527	0.0070	−0.042	1.470	0.0078
$7p$	−0.033	2.541	0.0042	−0.031	1.481	0.0048
$8p$	−0.025	2.549	0.0028	−0.024	1.489	0.0032
$9p$	−0.020	2.555	0.0019	−0.019	1.494	0.0022
$10p$	−0.016	2.557	0.0014	−0.015	1.497	0.0016
$11p$	−0.013	2.560	0.0010	−0.013	1.500	0.0012
$n=12$ to ∞	...	...	0.0052[a]	...	...	0.0059
Continuous spectrum	...	...	0.2737[a]	...	...	0.4350

[a] Estimated by using asymptotic form appropriate for the dielectric continuum model.

is compared with the point-ion potential in Fig. 2. Notice that the effective radius of the potential well at the vacancy has been reduced in size and that the average depth of the well has decreased in the pseudopotential model.

These developments suggest that an improvement over the potentials of Simpson, and Krumhansl and Schwartz could be made by using at small distances a potential of the form found by Kübler with appropriate corrections for the shielding effect of polarization. At large distances the potential should reflect the variation of dielectric constant with distance from the vacancy. The determination of such a potential is not the object of the present work, but these considerations suggest that an empirical Simpson-type potential developed by fitting the absorption of the F center will have a central well smaller than the Mott-Littleton radius and a dielectric constant that might be larger than the observed high-frequency one ϵ_∞.

III. CALCULATIONS AND RESULTS

To study the solutions of the Simpson F-center model a computer program was developed to solve the pertinent electronic Schrödinger equation for the ground $1s$ state and the first 10 excited p states.[37] From these solutions the oscillator strengths of the various $1s$–np transitions were calculated.[33] To compare these predictions with the observed spectra, the transitions were clothed with Gaussians of area equal to the calculated oscillator strength and a width of the order of the F-band half-width and then summed to yield the predicted spectrum.

It was found that for a very wide range of potential parameters the spectrum consisted of a single strong transition similar to the F band and a second band with a high-energy tail made up of transitions to highly excited, but still bound p states. As anticipated above, it was found that to fit the observed spectra, it was necessary to use values of R less than the Mott-Littleton radius, a well depth V_0, shallower than the Madelung energy, and a dielectric constant ϵ somewhat larger than the observed high-frequency dielectric constant.

Table I gives representative values of eigenvalues, transition energies, and oscillator strengths for the first 10 transitions of a potential with $R=4.1\ a_0$, $V_0=-5.92$ eV, and $\epsilon=3.0$. In this calculation the effective mass was assumed to be unity for all space.[38] Also included in Table I are predictions for a dielectric continuum model with $\epsilon=3.0$.[39] A comparison of the potential parameters for the present calculation with RbCl crystal constants and theoretical predictions is given in Table II.[40] In Table III the observed peak positions and oscillator strengths for the principal bands in colored NaCl and RbCl are listed for comparison with the calculated energies and oscillator strengths. In calculating the oscillator strengths for transitions to the

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[37] The method of solution was based on the Schrödinger equation subroutine written by Sherwood Skillman, reported in F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[38] It should be noted that the choice of potential parameters and the effective mass are not independent. For example, in the simpler dielectric continuum model the energy spectrum is determined by the ratio m^*/ϵ^2. In the alkali halides, experiment indicates an effective mass for conduction electrons of roughly unity and we have used this value for simplicity. At present the best experimental values are given by cyclotron resonance measurements in KBr. These yield an effective mass of 1.1±0.1, M. Mikkor, K. Kanazawa, and F. C. Brown, Phys. Rev. Letters **15**, 489 (1965).

[39] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957).

[40] The values of the crystal constants are taken from Ref. 2. The values of R and V_0 for the Simpson potential were calculated by W. A. Smith, Jr., and are listed in AEC Report, KAPL-1720 (unpublished). The Mott-Littleton radius depends on the value of the ionic polarizabilities and two sets of parameters are listed for the polarizabilities reported by L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927); and by J. R. Tessman, A. H. Kahn and W. Shockley, Phys. Rev. **92**, 890 (1953). In calculating the Krumhansl-Schwartz correction, the electron affinity was taken to be 0.5 eV for both cases. For further details see W. A. Smith, Jr., and A. B. Scott, Phys. Rev. **91**, 219 (1953); and W. A. Smith, Jr., *ibid.* **136**, A243 (1964).

TABLE II. Crystal constants and F-center model parameters for NaCl and RbCl.

Crystal parameters	NaCl	RbCl
Nearest-neighbor distance	5.325 a_0	6.187 a_0
Madelung energy	−8.93 eV	−7.69 eV
Optical dielectric constant	2.25	2.19
Static dielectric constant	5.62	5.0
Potential based on Pauling ionic polarizabilities		
R	5.005 a_0	4.880 a_0
V_0—Simpson model	−5.91 eV	−4.66 eV
V_0—Krumhansl-Schwartz model	−6.92 eV	−5.67 eV
Potential based on Tessman *et al.* polarizabilities		
R	4.724 a_0	4.550 a_0
V_0—Simpson model	−5.74 eV	−4.44 eV
V_0—Krumhansl-Schwartz model	−6.84 eV	−5.56 eV
Empirical potential for best energy fit		
R	···	4.1 a_0
V_0	···	−5.92 eV
ϵ	···	3.00

continuum reported in Table I, the f-sum rule for a one-electron system or monovalent atom was assumed. This is valid to the extent that the F-center one-electron wave functions can be derived from an effective field.[41]

As expected, only the ground- and the first excited-state eigenvalues differ appreciably for the Simpson and dielectric continuum models. There is, however, a significant difference in oscillator strengths and transition energies. Physically the difference in oscillator strengths arises largely from the change in the ground s-state wave function relative to those for the p states. Truncation of the Coulomb well near the origin causes an expansion of the wave functions from their hydrogenic form. This is more pronounced for the s states (which have nonzero density at the origin) than for p states. In the region of parameters of interest this has the effect of increasing the oscillator strengths of the first transition and decreasing the oscillator strength of transition to both higher bound states and the continuum.

To compare these results with experiment we have chosen the width at half-maximum of the Gaussian for the $1s$–$2p$ transition to be the observed F-band width at half-maximum 0.145 eV.[42] To choose the widths for the higher transitions we observed that, if the skewness of the K band is indeed due to a series of transitions, the first transition in the series should have a width at half-maximum roughly twice the low-energy semi-half-width of the skewed K band. This leads to a width at half-maximum of 0.22 eV for the $1s$–$3p$ transition[43] and for simplicity we have assumed that this value is appropriate for all higher transitions.

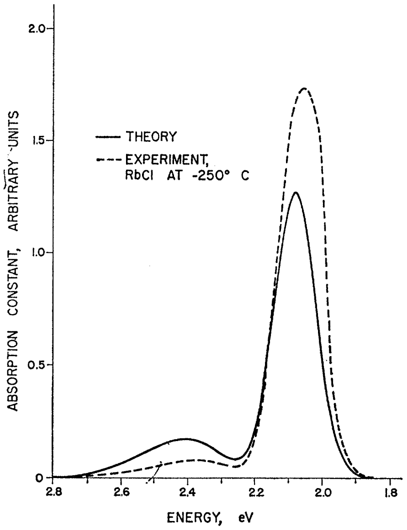

FIG. 3. Predicted and observed F and K bands in RbCl. The solid curve is the prediction of the Simpson model for $R=4.1\ a_0$, $V_0=-5.92$ eV, $\epsilon=3.0$, and $m^*=1.0$. The full widths at half-maximum of the individual Gaussians are assumed to be 0.145 eV for the $1s$–$2p$ transition and 0.22 eV for all higher transitions. The dashed curve is the experimental observation of F. Lüty (see Ref. 14).

Using the predictions for the Simpson model given in Table I and the above assumptions for half-widths, the calculated spectra for all allowed F-center transitions to bound excited states is found to be that shown by the solid curve in Fig. 3. The experimentally observed absorption for the F and K bands in RbCl as measured by Lüty is given for comparison by the dashed curve.[14] In drawing these graphs the normalization was chosen so that the area under the absorption bands is proportional to their calculated or observed oscillator strength.[44] The general form of the two spectra is similar although the predicted and observed K-band heights differ by a factor of two or so. However, considering the

TABLE III. Observed transition energies and oscillator strengths for the F center in NaCl and RbCl.

	NaCl (78°K)		RbCl[c] (−180°C)	
Band	Peak energy eV	Oscillator strength	Peak energy eV	Oscillator strength
F	2.758[a]	0.81[b]	2.04	0.85
K	···	···	2.37	0.095
L_1	···	···	3.08	0.007
L_2	···	···	3.70	0.024
L_3	···	···	4.60	0.024

[a] Reported by J. J. Markham *et al.*, Ref. 15.
[b] An average of various experimental determinations given by W. T. Doyle. Values ranging from 0.58 to 0.87 have been reported. See Ref. 45.
[c] Reported by F. Lüty, Ref. 14.

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[41] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[42] W. Gebhardt and H. Kühnert, Phys. Letters **11**, 15 (1964).

[43] The ratio of this $1s$–$3p$ transition half-width to that for the $1s$–$2p$ transition is roughly 1.5. This is in line with the value of 1.21 predicted by Wagner on the basis of his theory of the F center. See Ref. 25.

[44] The observed oscillator strengths for RbCl used in Table III and Fig. 3 are taken from Lüty's assignments given in Ref. 14. These are based on the assumption that all possible F-center transitions are represented by the F, K, L_1, L_2, and L_3 bands. If other absorptions are associated with the F center, including them would decrease the value of oscillator strengths reported.

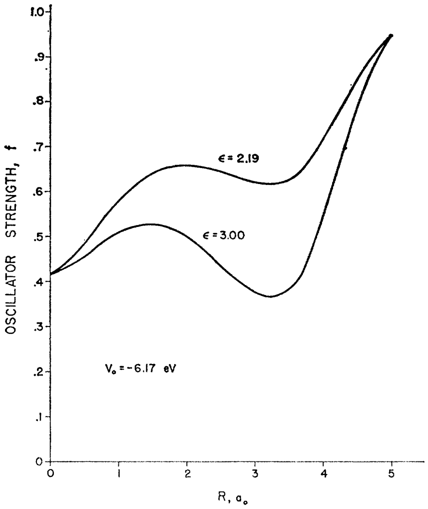

FIG. 4. The variation of oscillator strength for the $1s$–$2p$ transition for a Simpson-model potential with cavity radius R and a constant well depth of -6.17 eV.

oversimplified potential employed in the calculation, the agreement between the spectra is felt to be good. It should be noted that in the present calculation absorption to the continuum has been neglected. Inclusion of this term would tend to lengthen the high-energy tail of the K band.[24]

The dependence of oscillator strength on the parameters of a Simpson-type potential is shown in Fig. 4. The curves shown are for a well depth of $V_0=-6.17$ eV and two values of dielectric constant: $\epsilon=2.19$ and $\epsilon=3.00$. In the region in which agreement with experiment is good, i.e., $4.0\,a_0<R<5.0\,a_0$, there is a very rapid variation of oscillator strength while, as Fig. 5 shows, there is a much less rapid change of transition energies with R. Considering this relatively strong dependence of oscillator strength on well shape, it is not surprising that the model we have used yields good transition energies, but somewhat poorer oscillator strengths. The important point is that a reasonable set of F-center potential parameters yields the general form of *both* the F and the K bands.

These general considerations should hold for all alkali halides and indeed both the rubidium and potassium halides show distinct K bands. On the other hand, neither the sodium nor the lithium salts do, but in these salts the F-band breadth is relatively large and it seems reasonable to suppose that the K band is buried under the wings of the F.[15] To test this hypothesis the absorption spectrum calculated with parameters for RbCl was clothed with bands using half-widths appropriate to the NaCl F band. The results are shown (after translation along the energy scale) in Fig. 6 together with Markham and Konitzer's observations for the F band in NaCl at 78°K.[15] In this calculation the half-width of the F-band Gaussian was taken to be 0.278 eV as reported by Markham and Konitzer. The half-width of the Gaussians for the higher transitions was taken to be 0.545 eV since smaller values yielded a bump in the high-energy tail. The latter half-width is roughly twice the F-band width, a somewhat greater ratio than that assumed for RbCl. However, the difference is not considered significant since no search for potential parameters to give a fit to the NaCl F band was made. As in Fig. 3, the curves are drawn so that the area under the bands is proportional to the observed or calculated oscillator strength.[45] The similarity of the calculated band to the NaCl F band is encouraging and tends to substantiate Markham and Konitzer's conjecture that the long high-energy tail of the NaCl F band is part of an unresolved K band. This is also in line with Schnatterly's observation that a more consistent picture of the effect of stress on the NaCl F band can be made if it is assumed that the absorption consists of two overlapping bands.[6]

In RbCl the calculated series limit for transitions to bound states occurs at 2.57 eV for the Simpson-model potential parameters given in Table I. In the static lattice, optical absorption above this energy would lead to photoconductivity with 100% efficiency while below this energy the efficiency would be zero. In an actual crystal the onset of direct transitions to conduction states would be broadened by lattice vibrations to a

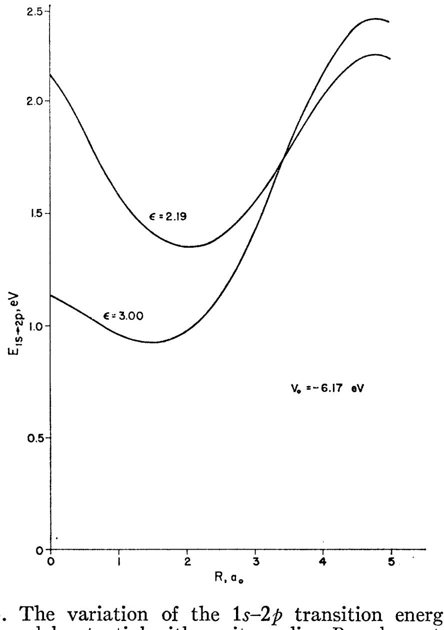

FIG. 5. The variation of the $1s$–$2p$ transition energy for a Simpson-model potential with cavity radius R and constant well depth of -6.17 eV.

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[45] The oscillator strength for the NaCl F band was taken as 0.81 as suggested by W. T. Doyle, Phys. Rev. **111**, 1072 (1958). This value was derived assuming Smakula's equation for a Lorentzian line shape. Assumption of a Gaussian line shape leads to oscillator strengths 0.675 times smaller or 0.55 for the present case. See D. L. Dexter, Phys. Rev. **101**, 48 (1956). The latter value is in somewhat better agreement with the calculated oscillator strength for the $1s$–$2p$ transition, but is in somewhat worse agreement with the calculated oscillator strength for transitions to all bound states.

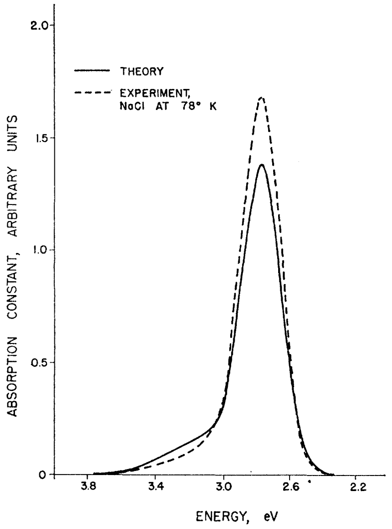

FIG. 6. Predicted and observed "*F* band" in NaCl. The solid curve is based on the predictions of the same Simpson-model potential as used for RbCl, but with the zero of potential energy shifted to bring the peak of the observed and predicted *F* bands into coincidence. The predicted transitions are clothed with Gaussians appropriate for NaCl. The full widths at half-maximum used were 0.278 eV for the $1s$–$2p$ transition and 0.545 eV for all higher transitions. The dashed curve is the experimental observation of Markham and Konitzer (see Ref. 15).

region roughly as wide as the half-width of bands near the series limit. In the present approximation this would be somewhat greater than 0.2 eV. Spinolo's measurements show a sharp increase in photoconductivity from 2.5 to 2.8 eV for RbCl at liquid-helium temperature.[4] This is felt to be consistent with the qualitative features suggested by the present calculation.

IV. DISCUSSION

Considering the available experimental evidence and the over-all agreement of the qualitative theory just outlined with the observed optical spectra, it would seem that the most tenable viewpoint at present is that the Mott-Gurney picture of the *K* band is correct. This leaves to be explained the many reports of a variable *F* to *K* band ratio,[16,46] differences in optical absorption in the *K*-band region of strained crystals,[23,47] and effects of impurities on the *K* band.[5] The simplest explanation for these observations is that there are a number of absorptions due to various defects that underlie the *K* band. As Lüty has pointed out,[14] *F*-center aggregates have absorptions in the *K*-band region. Since the measurements of Etzel and Geiger, and Geiger[16] show *M* absorption,[48,49] their observation of a variable *K* to *F* ratio is probably attributable, at least in part, to absorption of *F*-aggregate centers. Stungis and coworkers have found that the absorption in the *K*-band region also depends on the purity of the crystals.[5] This is likely a result of additional absorptions either of the impurities themselves or of *F* centers perturbed by them. Similarly, dislocations and the strong electric fields in their vicinity may perturb color centers and lead to the reported dislocation-dependent absorption.[50]

An as yet incompletely understood problem is that of the origin of the *L* bands. Luty,[14] Klick and Kabler,[21] and Chiarotti and Grassano[8] have presented convincing evidence that these are also *F*-center transitions. The present picture suggests that these bands are analogous to the transitions of an atom to the continuum of unbound states. However, in the case of the *F* center, the periodic crystal potential may modify the problem so that these transitions cluster into bands. This point of view has support in the measurements of Nakazawa and Kanzaki on KCl[51] and Crandall and Mikkor's study of KBr[3] which indicate that the quantum efficiency for photoconductivity throughout the *L* bands is unity. These results are consistent with the idea that the *L* bands arise from transitions to conduction-band states or at least to localized states degenerate with the conduction band. Further support for this picture is given by calculations of Knox and Dawber that indicate a perturbation such as that produced by the *F* center can give rise to in-band resonances that could yield *L* band-like transitions.[52] Similar calculations have also been reported by Kojima,[53] and by Bassani.[53a] A somewhat related interpretation has been developed by Klick and Kabler to explain their observation of a similarity between the spectra of alkali atoms and the *L* bands.[21,54] Their suggestion is that the *L* spectra may arise from transitions to states made up of *F*-center excited states associated with conduction bands higher than the first.

The essential difference between the calculations reported here and point-ion and LCAO calculations is in the choice of the asymptotic form of the model potential. The average potential in both point-ion and LCAO models is essentially $1/r$, whereas we choose $1/\epsilon r$. Hence, these models also predict a series of higher excited states for the *F* center, but with an energy separation larger by roughly a factor of the dielectric constant squared than those predicted by the present model. Furthermore, the position of the conduction band is not given in these models. Hence, it is not clear

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[46] J. D. Konitzer and J. J. Markham, Phys. Rev. **107**, 685 (1957).

[47] S. Miyamoto, S. Nakashima, and H. Mizuno, J. Phys. Soc. Japan **17**, 1076 (1962).

[48] F. Okamoto, Phys. Rev. **124**, 1090 (1961).

[49] S. Susman, Ph.D. thesis, Illinois Institute of Technology, 1962 (unpublished); and to be published.

[50] In additively colored KCl crystals formed from sintered powder a broad absorption underlying both the *F* and *K* bands has been observed. This result has not been investigated in detail, but may be due in part to highly perturbed *F* centers. H. Mizuno (private communication).

[51] F. Nakazawa and H. Kanzaki, J. Phys. Soc. Japan **20**, 468 (1965).

[52] R. S. Knox (private communication).

[53] T. Kojima, reported at the International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished).

[53a] F. Bassani, reported at the International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished).

[54] C. C. Klick and M. N. Kabler, Bull. Am. Phys. Soc. **8**, 353 (1963); C. C. Klick, Phys. Rev. **137**, A1814 (1965).

how to relate the F-center bound states to the states of the perfect crystal and if this is done incorrectly, some localized states may appear to lie in the conduction band whereas in the present model they would lie just below it.

The present calculation does not provide for coupling lattice vibrations to the electronic problem, hence, it does not predict the details of the K-band temperature dependence. However, in analogy with the F-center absorption we might expect the individual transitions making up the K band to broaden and shift toward lower energies. From Schnatterly's results that stress causes the F-band oscillator strength to decrease and the K-band oscillator strength to increase,[6] we might also expect some increase in area under the individual transitions. As we have seen, the width of the K band is determined not only by the width of the individual transition, but also by the separation of the Rydberg series of excited states. The latter presumably would not change appreciably with temperatures since it arises from an average property of the crystal. Thus, it is not unreasonable to suppose that any shift toward lower energies could combine with a small increase in area of the individual bands to produce a composite band with very little temperature dependence.

V. SPECULATIONS

The general considerations used in treating the F-center model are in no way restricted to just the F-center problem and should hold for a variety of impurity and defect centers with just a change in the details of the model potential near the origin. Thus, the absorption spectra of many types of defects should be made up of transitions to a few energy levels determined primarily by the defect followed by transitions to a quasihydrogenic series of states leading up to a continuum.

These considerations should certainly apply to the F_A center which is an F center with an impurity ion such as Li^+ as nearest neighbor.[55–57] Because of the asymmetry of the center, transitions from the s-like ground state to p states with an axis passing through the impurity occur at energies different from transitions to states with an axis passing through only normal neighbors. Thus, there should be two *series* of transitions. The principal F-band-like transitions of each series will be shifted considerably from one another because the low-lying p states are strongly perturbed by the anisotropic center. However, the higher states depend less on the details of the center and more on the host lattice so that each series should show a K band with the difference between the two bands becoming progressively smaller toward higher energies. While no detailed report of measurements in the K-band region have been given for samples containing F_A centers, the F_A-center absorption spectra for KCl:NaCl measured by Kojima and co-workers[57] shows a dichroic K band with apparently less dichroism in the tail than in the peak. Lüty has also reported dichroism in both the K- and the L-band regions.[58]

Further examples are less common since most impurity centers yield absorptions so close to the fundamental absorption edge that any K-band-like tails would be obscured. However, both the U and M bands show evidence of related K-band-like absorption. Measurements of T. Timusk and W. Martienssen[59] on the U band in KBr crystals with low OH^- concentrations show that the U center displays a long high-energy tail. This is so similar to the K band that the authors commented on the point. Earlier measurements of W. Martienssen[60] on U centers in KCl, KBr, and RbCl also show these tails as do U-center spectra measured by Ueta and co-workers.[61] As in the case of the F-center K band, both KCl and RbCl show a definite band with a peak toward the high-energy side of the U band.[62]

A more complicated situation exists for the M center because crystal field and exchange effects split the various transitions.[48,49,63] There appear to be three main transitions associated with the M_1, M_2, and M_2' bands. Presumably these differ in energy because of the details of the center. In addition there are high-energy tails on the M_2 and M_2' bands that appear to correspond to transitions of the M center. These tails are often referred to as the M_3 and M_3' bands,[48] but in high-resolution measurements on KBr and KCN, Susman[49] has found structures which he denotes as M_5, M_6, M_7, etc. bands. It is tempting to speculate that the high-energy tails may be K-band-like transitions to bound states below the conduction band. However, the higher M bands have been observed by orienting the centers and measuring the difference between absorption for different orientations of linearly polarized light. According to the present point of view, the more highly excited states would not be strongly affected by the anisotropic center so that the tail of a K-band-like absorption may not be dichroic and, hence, not observable by these techniques.

The conjectures on the U band are strengthened by photoconductivity measurements.[61,64] As in the case of

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[55] M. Ishiguro and E. Sugioka, Phys. Rev. **110**, 1070 (1958).

[56] F. Lüty, reported at the International Symposium on Color Centers in Alkali Halides, Corvallis, Oregon, 1959 (unpublished); Z. Physik **165**, 17 (1961).

[57] K. Kojima, N. Nishimaki, and T. Kojima, J. Phys. Soc. Japan **16**, 576 (1961); **16**, 2033 (1961).

[58] F. Lüty, reported at the International Symposium on Color Centers in Alkali Halides, Stuttgart, Germany, 1962 (unpublished).

[59] T. Timusk and W. Martienssen, Z. Physik **176**, 305 (1963).

[60] W. Martienssen, Z. Physik **131**, 488, 1952 (unpublished).

[61] M. Ueta, M. Hirai, and M. Ikezawa, J. Phys. Soc. Japan **16**, 538 (1961); T. Goto, T. Ishii, and M. Ueta, *ibid.* **18**, 1422 (1963).

[62] It is interesting to note that in the case of KCl the difference between the maxima of the U_a and U_b bands reported by Goto *et al.*, Ref. 61, is roughly the same as the difference between the K and the L_1 bands.

[63] C. Z. van Doorn and Y. Haven, Phys. Rev. **100**, 753 (1955); Phillips Res. Rept. **11**, 479 (1956); C. Z. van Doorn, *ibid.* **12**, 309 (1957).

[64] G. Glaser, Ann. Physik **27**, 217 (1936).

the F band, there is no appreciable photoconductivity in the main U band, but photoconductivity increases rapidly toward higher energies in the short-wavelength tail. The photoconductivity resulting from excitation in the M band has been measured by various workers.[65] However, M centers are produced along with large numbers of F centers which complicates the interpretation of the results. The measurements of Barth[66] suggest that in the M_1 band the quantum efficiency for photoconductivity is approximately $\frac{1}{10}$ that of the F band at room temperature. Unfortunately, the overlapping of various bands makes estimates for the photoconductive quantum efficiency for excitation in the other M bands difficult. Further experiments on this point would be very enlightening.

Several other experiments yield indirect evidence supporting the present point of view. Fischer and Hilsch[67] and Baldini[68] have observed structure in the so called "step" on the high-energy side of the exciton absorption in RbI. They interpret this as components of a Wannier exciton series.[69] Hopfield and Worlock[70] have studied the two-quantum absorption spectra of both KI and CsI and find that the spectrum is also best understood in terms of the Wannier model. Similar findings are also reported for the rare gas solids which are isoelectronic with the alkali halides. Baldini[71] finds that in thin films of solid rare gases the absorption shows strong bands corresponding to perturbed atomic transitions followed by a series of absorptions that can be interpreted in terms of Wannier excitons. Baldini and Knox[72] also report that mixed crystals of the rare gases show impurity absorption spectra in which absorption appears to occur into effective-mass states. Baldini and Teegarden[73] have found similar effective-mass series of lines in RbCl-RbI. Thus, it would appear that in both the exciton spectra and the absorption of many defects in insulators one should expect to find transitions to atomic-like states or states determined by the defect followed by transitions to excited states that may be described rather well in terms of an effective-mass approximation.

Since the present picture suggests that K-band-like absorptions are to be expected in many cases, a more descriptive nomenclature would be to denote this type of high-energy absorption as a K band for the center involved. That is, the K band would be the K_F, the U-band tail the K_U, and so forth.

The present considerations suggest several possible experiments. A detailed study of the K band of oriented F_A centers would be most useful in testing the prediction that dichroism should decrease in the high-energy tail of the band. Investigations of the L-band absorptions of the F_A center would also be of interest. If the L bands arise from transitions to localized states, the bands for the F_A center should be dichroic; whereas, if they are transitions to diffuse states insensitive to the local anisotropy of the center, they should show little if any dichroism.

Photoconductivity studies of the various M bands and further work on the U center might be profitable. The anology between the U and F centers suggests that L-type bands might also be associated with the U center. Another possibility suggested by this anology is that of a U center with a nearest-neighbor impurity or a "U_A center."[74] Further work on absorptions underlying the K band would also be useful both to justify the tentative explanation of some of the apparently contradictory experiments and to elucidate the character of the assumed absorption bands.

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[65] See W. D. Compton and H. Rabin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 16.

[66] N. Barth, Z. Physik **149**, 370 (1957).

[67] F. Fischer and R. Hilsch, Nachr. Akad. Wiss. Goettingen, II. Math. Physik. Kl. **8**, 241 (1959).

[68] G. Baldini (private communication).

[69] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1964).

[70] J. J. Hopfield and J. M. Worlock, Phys. Rev. **137**, A1455 (1965).

[71] G. Baldini, Phys. Rev. **128**, 1562 (1962).

[72] G. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963); G. Baldini, Phys. Rev. **137**, A508 (1965).

[73] G. Baldini and K. Teegarden (to be published).

[74] Some evidence for such a center exists from infrared studies. See G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960).