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Study of the F' Center in Several Alkali Halides*

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The F' band has been produced and measured in the following alkali halides: NaCl, KCl, KBr, KI, RbCl, RbI, CsBr, and CsI. Additively colored samples were optically bleached in the F band at an optimum temperature to produce a maximum F-to-F' conversion. The observed spectra exhibited two distinctive features. In each salt the F' band had a shoulder on the high-energy side of the principal peak, except in NaCl where the band was bell-shaped. CsBr and CsI exhibited a more complex structure. The shoulder in the potassium and rubidium salts is attributed to low-lying d-like states in their conduction-band structure. In all salts there was a small second absorption shoulder on the high-energy tail of the F' band. This absorption is attributed to F' absorption such that the remaining F center is left in an excited $2p$ or $2s$ state. A semicontinuum-model variational calculation using a correlated Hylleraas wave function yields, for reasonable values of the parameters, F' binding energies in fair agreement with the observed optical absorption edges. An absorption-cross-section calculation yields absorption curves in good agreement with experiment if one excludes the aforementioned structure.

I. INTRODUCTION

In the general area of color centers in alkali halides, the F' center has received little attention experimentally or theoretically. To our knowledge, the most recently published experimental work on the shape and origin of the F' band is that of Pick,[1,2] which was done in 1938 and 1940. Several other papers[3–5] exhibit the F' band in KBr and KCl but do not deal explicitly with the F' center optical absorption or investigate other crystals.

The F' center is commonly accepted as being two electrons trapped at a negative ion vacancy.[6–8] This model is supported by Pick's study[2] of the F-to-F' and F'-to-F quantum yields. Pick found that the conversion reaction could be described by $2F \rightleftarrows F'$. He observed that the F' band could be bleached optically at very low temperatures (Pick bleached at 23°K) with a quantum yield of 2, indicating that the F' center had no bound excited state. This conclusion is supported by the photoconductivity work of Domanic,[9] who observed a photocurrent due to F' centers down to a temperature of 20°K, although it is possible that an electron could be released from a bound excited state upon local relaxation of the lattice. The principal reason that the F' band is so broad is presumably that the final state is a continuum state.

F' centers can usually be formed in a salt containing F centers by optically bleaching the sample in the F band at temperatures between liquid-nitrogen temperature and dry-ice temperature. The F' center is weakly bound and is easily thermally ionized, thus requiring low temperatures for stability. The F centers which supply the electrons for forming the F' center have a bound excited state[6–8] from which the electrons must be thermally ionized, requiring a temperature high enough to allow ionization. Thus to form F' centers by optical bleaching it is necessary to pick the optimum temperature such that the F-to-F' conversion will be largest. For some alkali halides it may not be possible to make F' centers from F centers. F' centers give rise to a broad F' absorption band, peaking on the low-energy side of the F band, but overlapping the F band.

Several theoretical investigations have been made on the F' center. Cheban[10] used a continuum model to describe the F' center and calculated the ionization probability of the center for a final state consisting of either a polaron or a conduction-band electron. To get agreement with experiment he found that the final state had to consist of a conduction-band electron. Raveche,[11] using the results of Gourary and Adrian's[12] point-ion calculation for the F center, calculated the F' binding energy in KCl. The semicontinuum model was applied to the F' center by Pincherle,[13] who calculated the F' binding energies in NaCl and KCl. Two recent calculations by La and Bartram[14] and Strozier and Dick[15] have been made using the point-ion lattice model, corrected by the polarization approximations due to Krumhansl and Schwartz.[16]

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[14] S. Y. La and R. H. Bartram, Phys. Rev. **144**, 670 (1966).

[15] J. A. Strozier and B. G. Dick (unpublished).

[16] J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953).

II. SEMICONTINUUM MODEL

In this section we will discuss the semicontinuum model as it is applied to either the F or F' center. Atomic units will be used throughout, except when noted otherwise. The semicontinuum-model potential is shown in Fig. 1. The three basic parameters of the semicontinuum model are the well depth, well radius, and the average dielectric constant outside the well, given by V_0, R, and K_{eff}, respectively. The other parameters appearing in Fig. 1 which are used to calculate V_0 are V_m, the Madelung energy; χ, the electron affinity; and W, a correction due to polarization effects. V_0 can be written as the sum of three terms as follows:

$$V_0 = -\alpha_m/a + W + \chi\,,$$

where α_m is the Madelung constant and a is the nearest-neighbor distance.

W is calculated using a treatment due to Krumhansl and Schwartz,[16] as expanded in the review by Gourary and Adrian.[17] W is treated by dividing it into ionic and optical parts such that

$$W = W_{\text{opt}} + W_{\text{ion}}\,.$$

W_{opt} is calculated by considering the expression for the electrostatic potential due to the polarization around a cavity of radius R, containing an effective charge q, in an infinite dielectric medium of dielectric constant K. The required potential is

$$\phi(q) = -q(1-1/K)(1/R)\,.$$

The potential $\phi(q)$ is charge-dependent, and the potential energy of an electron in the cavity can be found by integrating $\phi(q)$ over q. If it is assumed that the polarization follows the motion of the trapped electron, we can set $K = k_0$, the optical dielectric constant, and write

$$W_{\text{opt}}(q_i,q_f) = -\left(1-\frac{1}{k_0}\right)\frac{1}{R}\int_{q_i}^{q_f} q\,dq\,, \tag{1}$$

where q_i and q_f are the initial and final effective charges in the cavity, respectively. W_{ion} is found by considering the work done due to the ionic polarization in removing the charges from the well while the ions are held fixed. It is written as

$$W_{\text{ion}} = \left(\frac{1}{k_0}-\frac{1}{k}\right)\int_R^\infty \frac{Z-NP(r)}{r^2}dr\,, \tag{2}$$

where k is the static dielectric constant, N is the number of electrons in the well, Z is the effective charge of the well, and $P(r)$ is the fraction of the one-electron distribution which is inside a sphere of radius r. That is,

$$P(r) = \int_0^r |\psi(r)|^2 d\tau\,,$$

where $\psi(r)$ is the one-electron wave function for the system. W_{ion} is the potential the electron sees at any instant due to the ionic polarization established by its average distribution.

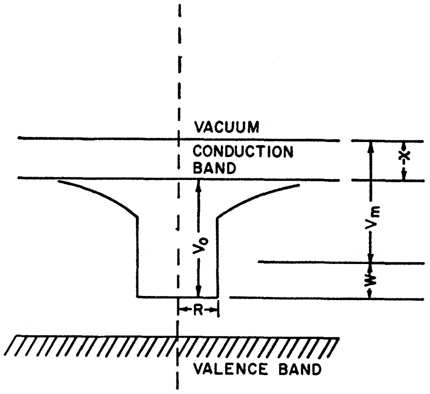

FIG. 1. Potential well for semicontinuum model.

The effective dielectric constant outside the well is found by using a continuum approximation. If we assume a perfect dielectric which contains some sort of trap of effective charge Z, the potential energy of the trap is

$$\phi(r) = -\frac{Z}{kr} - \left(\frac{1}{k_0}-\frac{1}{k}\right)\int_r^\infty \frac{NP(r)}{r^2}dr\,, \tag{3}$$

where N is the number of electrons in the trap. The effective dielectric constant is then obtained by writing

$$\phi(r) = -1/K_{\text{eff}}r\,. \tag{4}$$

In applying the above model to the present problem, the Franck-Condon principle is employed, and the only potential term allowed to change in an optical transition is $W_{\text{opt}}(q_i,q_f)$.

III. F AND F' CENTER HAMILTONIANS

Fowler[18] discusses the F-center Hamiltonian for the semicontinuum model and gives the following approximate expressions. Inside the well (for $r<R$)

$$H = -\tfrac{1}{2}\nabla^2 + V_0$$

and outside the well (for $r>R$)

$$H = -(1/2m^*)\nabla^2 - 1/K_{\text{eff}}r\,,$$

where the effective-mass approximation has been made outside the well to account for the periodic nature of the lattice.

The above Hamiltonian is generalized to apply to the F' center. We now have two electrons in two regions of space; hence the Hamiltonian will have four parts.

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[17] B. S. Gourary and F. J. Adrian, Solid State Phys. **10**, 127 (1960).

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

These are written as

$$H=\sum_{i=1}^{2}\left(-\tfrac{1}{2}\nabla_i^2\right)+2V_0+1/K^*r_{12},\quad r_i<R,\quad r_j<R$$

$$=-\tfrac{1}{2}\nabla_i^2-(1/2m^*)\nabla_j^2+V_0-1/K_{\text{eff}}r_j+1/K^*r_{12},\quad r_i<R,\quad r_j>R \qquad (5)$$

$$=\sum_{i=1}^{2}\left[-(1/2m^*)\nabla_i^2-1/K_{\text{eff}}r_i\right]+1/K^*r_{12},\quad r_i>R,\quad r_j>R,$$

where i, $j=1$, 2; $i\neq j$ and r_{12} is the interelectronic distance. K^* is the dielectric constant for the Coulomb correlation potential and will be discussed later.

IV. F AND F' CENTER WAVE FUNCTIONS

The wave functions used for the F center are given by Fowler.[18] These are

$$\psi_{1s}=(\alpha^3/7\pi)^{1/2}(1+\alpha r)e^{-\alpha r}, \qquad (6)$$

$$\psi_{2p}=(\beta^5/\pi)^{1/2}re^{-\beta r}\cos\theta, \qquad (7)$$

where α and β are variational parameters. ψ_{1s} is not a true hydrogenic wave function but is labeled "1s" because it represents the lowest state of the F center and is spherically symmetrical.

The wave function used for the F' center is a correlated Hylleraas wave function and is written as

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{-(\alpha/2)(r_1+r_2)}\left[1+\beta r_{12}-\gamma(r_1-r_2)^2\right], \qquad (8)$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. This wave function is chosen since it has yielded reasonably good results for the H^- ion,[19,20] the atomic analog of the F' center. Because of the weak binding, and possibly diffuse nature, of the second electron added to the F center to form the F' center, it seemed reasonable that the electron correlation should be explicitly included in the wave function. Since $\psi(\mathbf{r}_1,\mathbf{r}_2)$ is symmetric with respect to interchange of space coordinates, it corresponds to a singlet state. At any instant of time the motion of the electrons will be correlated, while over an extended period of time each electron will have s-like symmetry about the origin.

When calculating W_{opt} [Eq. (1)] for either the initial or final state of a transition, we use the value of W_{opt} appropriate to the region over which the initial or final electronic wave function is being integrated. When calculating W_{ion} [Eq. (2)], the electronic wave function for the initial state [Eq. (8)] is always used.

V. VARIATIONAL CALCULATION

The variational principle says that the quantity

$$\int\psi^*H\psi d\tau\bigg/\int\psi^*\psi d\tau,$$

where the integrals are taken over all space, will be an upper bound to the ground-state energy of our system. These integrals could all be done in a straightforward, however tedious, manner.

The calculation for the F center is done using Eqs. (6) and (7). Fowler's results[18] are obtained when his parameters are used.

The calculation for the F' center is done by integrating over either of two sets of coordinates, depending on which is more convenient. For integrals over all space, the Hylleraas coordinates, $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$, are used. The volume element is then $d\tau=\pi^2u(s^2-t^2)\times dudsdt$, where $-u\leq t\leq u$, $0\leq u\leq s<\infty$. For integrals over a portion of space the coordinates r_1, r_2, θ_{12} are used. The volume element is then

$$d\tau=8\pi^2\sin\theta_{12}d\theta_{12}r_1^2r_2^2dr_1dr_2,$$

where $0\leq r_1<\infty$, $0\leq r_2\leq\infty$, and $0\leq\theta_{12}\leq\pi$. Integrals involving factors of r_{12} and r_{12}^{-1} are expanded in terms of Legendre polynomials.[19]

Four main integrals are done in applying the variational principle to the F' Hamiltonian given by Eq. (5). The square-well potential is written as

$$V_{\text{sq. well}}=2V_0\langle\psi|\psi\rangle_{\text{in,in}}+2(V_0+W_{\text{opt}})\langle\psi|\psi\rangle_{\text{in,out}},$$

where

$$V_0=-\alpha_m/a+W_{\text{ion}}+\chi,\quad W_{\text{opt}}=(1-1/k_0)(1/2R),$$

and where

$$\langle\psi|\psi\rangle_{\text{in,out}}$$

means that r_1 is integrated over the inside of the well, and r_2 is integrated over the outside of the well and so forth. Here the fact that

$$\langle\psi|\psi\rangle_{\text{in,in}}+2\langle\psi|\psi\rangle_{\text{in,out}}+\langle\psi|\psi\rangle_{\text{out,out}}=\langle\psi|\psi\rangle_{\text{all space}}$$

is used to simplify the integrations.

The Coulomb potential is written as

$$V_{\text{Coul}}=-\frac{2}{K_{\text{eff}}}\langle\psi|\frac{1}{r_1}|\psi\rangle_{\text{out,all}},$$

where K_{eff} is evaluated from Eq. (4) by letting $N=2$ in Eq. (3). In the present calculation we chose to evaluate K_{eff} at $r=R$ since it is found that the electrons spend most of their time in the region of the well. The subscript "all" means that r_2 is integrated from zero to infinity.

The Coulomb correlation potential is written as

$$V_{\text{corr}}=\langle\psi|r_{12}^{-1}|\psi\rangle_{\text{in,in}}+\frac{2}{k_0}\langle\psi|r_{12}^{-1}|\psi\rangle_{\text{in,out}}+\frac{1}{k_0}\langle\psi|r_{12}^{-1}|\psi\rangle_{\text{out,out}},$$

where 1 or k_0 is substituted for K^* as indicated. This

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[19] R. E. Williamson, Astrophys. J. **96**, 438 (1942).

[20] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), 35th ed., p. 88.

integration is done by considering one electron to be moving in the charge cloud of the other and applying Gauss's law.

The kinetic-energy terms are written as

$$T=\langle\psi|\sum_{i=1}^{2}-\tfrac{1}{2}V_i^2|\psi\rangle_{\text{all,all}},\qquad r_i<R$$

$$=\langle\psi|\sum_{i=1}^{2}-\tfrac{1}{2}V_i^2(1/m^*)|\psi\rangle_{\text{all,all}},\quad r_i>R.$$

This integral is done by using Green's theorem to convert the ∇_1^2 operators to $|\nabla_i|^2$ operators. Because of the discontinuity due to the effective-mass approximation, surface terms are also introduced. The standard three-dimension Green's theorem is integrated over all space to obtain the desired relation. T is then written as the sum of four volume and four surface integrals.

Finally, the total energy is written as

$$E(\alpha,\beta,\gamma)=N^{-1}(V_{\text{sq. well}}+V_{\text{Coul}}+V_{\text{corr}}+T),$$

where N is the normalization constant. A computer program is used to minimize this expression.

VI. CALCULATED ABSORPTION CURVE

The optical absorption curve for the F' center is calculated by assuming the initial state ψ_i of the center to be the ground state. The final state ψ_f is then assumed to consist of one bound s-like electron and one free plane-wave electron. The initial state is then given by Eq. (8), and the final state is written as

$$\psi_f(\mathbf{r}_1,\mathbf{r}_2)=(2L^3)^{-1/2}[\phi_{1s}(\mathbf{r}_1)e^{ik_ez_2}+\phi_{1s}(\mathbf{r}_2)e^{ik_ez_1}].$$

This final state is used for calculating the entire F' band, so we are assuming the conduction band is parabolic, even several eV above its minimum.

By applying standard time-dependent perturbation theory,[21] the following formula for the absorption cross section may be derived. In cgs units we find

$$\sigma_{\text{vac}}=\frac{2e^2}{3mc^2k_p}|\langle\psi_i|\sum_{i=1}^{2}\nabla_i|\psi_f\rangle|^2k_eL^3,\tag{9}$$

where k_p and k_e are the magnitudes of the incident photon and emitted electron wave vectors, respectively; L^3 comes from the free-electron density of states; and m, c, and e are the usual physical constants. k_e and k_p are related by $\hbar ck_p=W+\hbar^2k_e^2/2m^*$, where W is the electron affinity of the F center left behind. Equation (9) must be corrected for effects of the dielectric medium in which the F' center is placed. Two corrections must be distinguished. The first is the local field correction,[22] and the second is the correction due to renormalization of the incident photon flux.[22] Combined, these corrections are

$$\sigma_{\text{diel}}=[(n^2+2)^2/9n]\sigma_{\text{vac}},$$

where n is the index of refraction of the dielectric.

The matrix element in Eq. (9) may be done in a straightforward, but tedious, fashion if the usual expansion of the plane wave is done.[19] Here parity considerations yield that the outgoing plane wave will have only a p-wave component.

VII. CALCULATIONS

The selection of physical parameters for the model and the calculation technique will now be discussed. For all salts the band effective mass is taken to be $0.6m_e$. This was thought to be reasonable, as argued by Fowler.[18] Data[23] on KBr gave a band effective mass of $0.55m_e$. For comparison purposes a band effective mass of $1.0m_e$ is also used. [Recent cyclotron resonance data[24] give conduction-band effective masses of 0.50 (KCl), 0.43 (KBr), 0.40 (KI), and 0.52 (RbCl).] The well radius is chosen to be 90% of the nearest-neighbor distance. Since about 50–60% of the total electron distribution is in the well, and the effective positive charge on the vacancy is more than compensated for, the nearest-neighbor cations are probably not displaced outward. The values of χ are taken from Eby *et al.*[25] and Mott and Gurney.[26] Values due to Eby *et al.* are roughly adjusted by adding 0.2 eV to each value to correct for the fact that they were found from photoelectric data taken at 300°K and optical absorption data taken at 80°K.

Two techniques are used to calculate the polarization corrections. The first calculates the corrections given by Eqs. (2) and (3) self-consistently. In Eq. (3), as stated before, the lower limit of the integral is set equal to R. The second routine varies the value of the integral appearing in Eqs. (2) and (3) to force agreement between the F' binding energy and experiment. The wave functions produced by this routine are used to calculate the optical absorption curve. This latter method also eliminates uncertainties in our knowledge of χ.

VIII. EXPERIMENTAL PROCEDURE

All spectral data were taken on a Cary model 14R recording spectrophotometer equipped with a liquid-nitrogen cryostat. The spectrophotometer was modified such that the sample could be examined with dispersed radiation from 1.7 to 2.5 μ. This was necessary since normally the sample would be exposed to the undispersed radiation of the source which would produce undesirable optical bleaching of the F' band. No

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[21] J. L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Mass., 1965).

[22] D. L. Dexter, Solid State Phys. **6**, 353 (1958).

[23] M. Mikkor, K. Kanazawa, and F. C. Brown, Phys. Rev. Letters **15**, 489 (1965).

[24] J. W. Hodby, J. A. Borders, F. C. Brown, and S. Foner, Phys. Rev. Letters **19**, 952 (1967).

[25] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[26] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940).

bleaching of the F' band could be detected during measurements of the F' spectra.

All alkali halides used were from commercial suppliers. All samples prepared were additively colored using the method of van Doorn.[27] Colored samples were cut to proper size, about 8×10×2 mm, quenched from their coloring temperature in the dark, and then loaded into the cryostat under a safe light.

The absorption spectra of the samples were first measured at liquid-nitrogen temperature (LNT), and then the sample was optically bleached in the spectrophotometer at a variety of temperatures until the maximum F-to-F' conversion was found. The sample was then cooled in the dark to LNT, and the F' band measured. The F' band shapes were found by carefully subtracting, from the curves measured after bleaching, scaled-down curves obtained before bleaching. In making this subtraction only the F, K, and F' bands were considered. Aggregate bands, such as the M band, could not be detected after bleaching. Any L bands present were very small and hence were neglected. The number of F' centers formed was obtained by applying

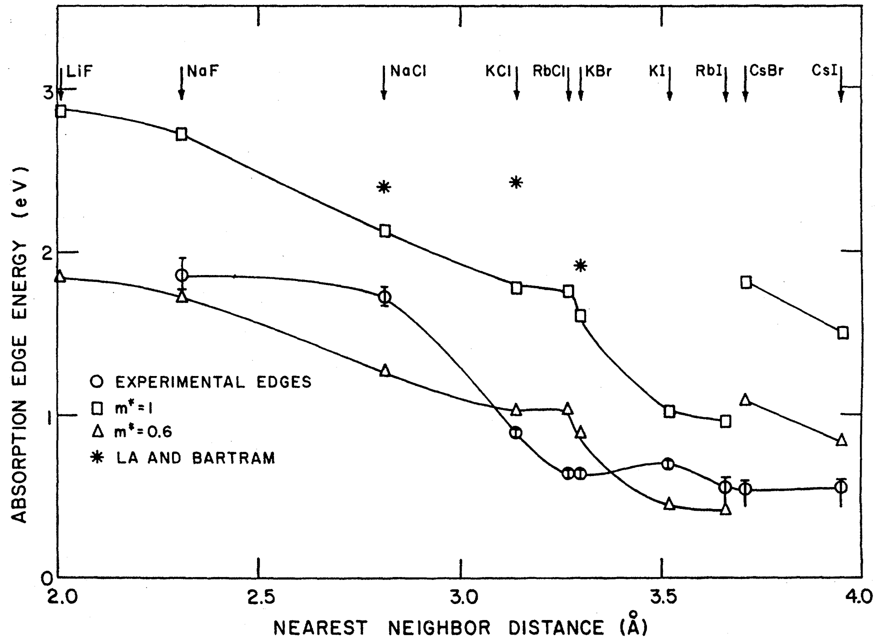

FIG. 2. Calculated and experimental F' absorption edges. The asterisk points are from Ref. 14.

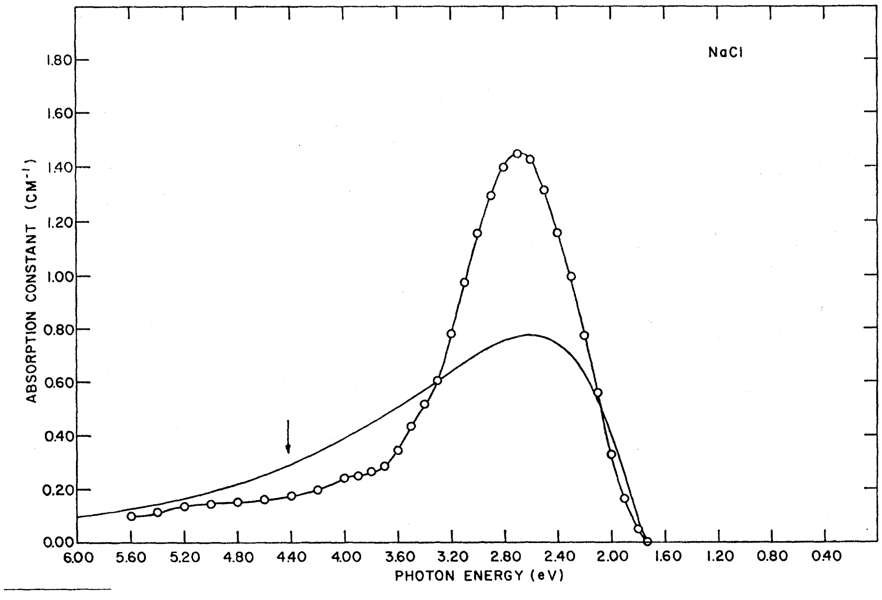

FIG. 3. F'-center absorption in NaCl, 10^{16} (F' centers)/cm^3. The circles are measured points, while the other curve is calculated, after adjusting the potential-well depth to make the ionization energy agree with experiment. The arrow indicates the energy at which the F center can be left in the $2p$ state.

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[27] C. Z. van Doorn, Rev. Sci. Instr. 32, 755 (1961).

Smakula's equation[7] and using the oscillator strengths as given by Schulman and Compton.[7] For the salts not listed there the oscillator strength was taken to be 0.8.

IX. RESULTS AND DISCUSSION

The calculated and experimental F' absorption edges are shown in Fig. 2. The calculated values are the F' binding energies and were found by determining the polarization corrections in a self-consistent manner. The experimental edges were found by a detailed replotting of the raw data to expand the region of interest. The error bars represent our best judgment concerning the accuracy of the measurements. Even on an expanded energy scale the edges were not well defined. Lines are drawn between data points for aid in reading and are not intended to indicate any analytical relationship. A smooth dependence is not to be expected since the energies are very sensitive to the dielectric constants and electron affinities for the various salts, and these parameters, at best, are simply monotonic functions of the nearest-neighbor distance.

The calculated and experimental absorption curves are shown in Figs. 3–9. The solid line represents the calculated absorption and the circles are the experimental data. The theoretical absorption curves are calculated using the wave functions from the variational problem for $m^* = 1.0m_e$, where the sum of χ and the

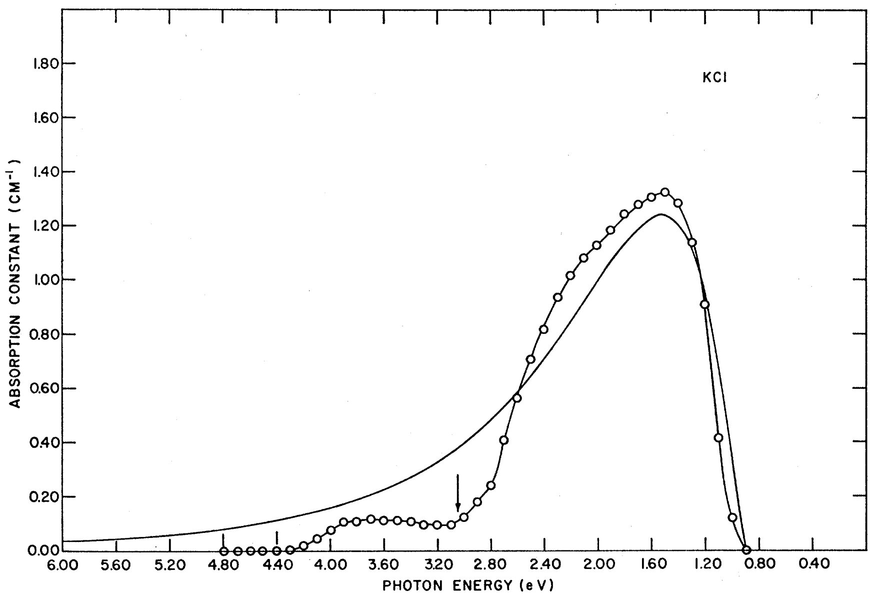

FIG. 4. F'-center absorption in KCl. See caption for Fig. 3.

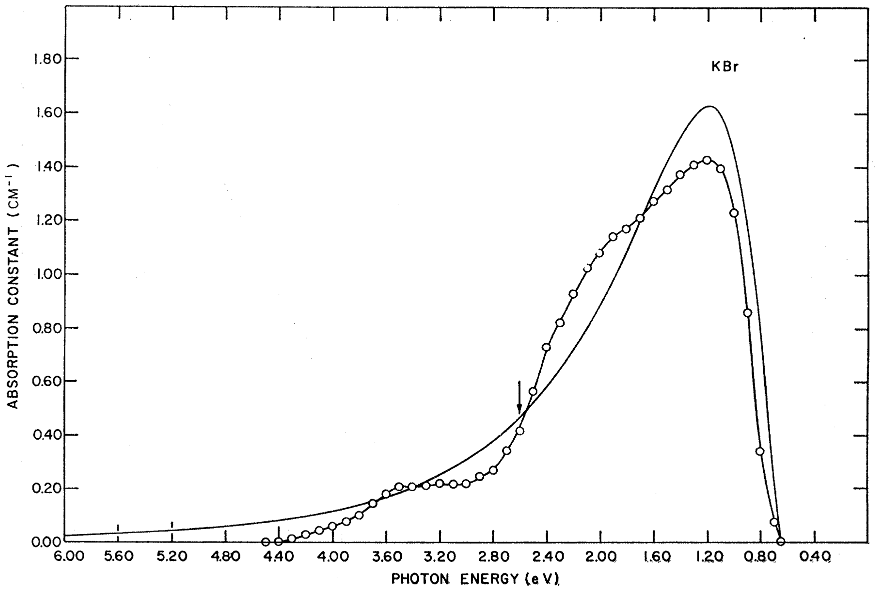

FIG. 5. F'-center absorption in KBr. See caption for Fig. 3.

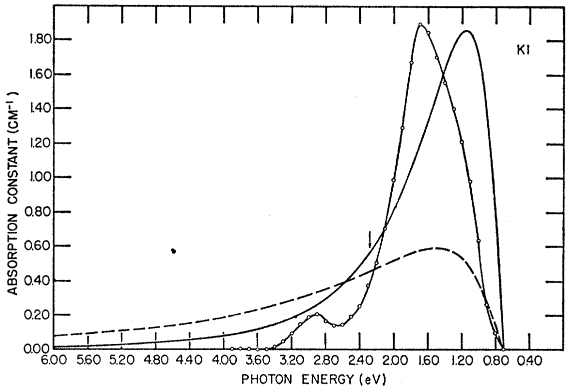

Fig. 6. F'-center absorption in KI. See caption for Fig. 3. The dashed curve is the calculated spectrum using $m^*=0.45m_e$ instead of $1.0m_e$.

ionic polarization is adjusted to yield the correct binding energy. Here we identify the binding energy as the experimental optical absorption edge. The theoretical curves are plotted using the experimental edges as starting points, and hence the curves coincide at this point. The curves are "fit" only at this one point. The theoretical curves are calculated for $N=10^{16}$ (F' centers)/cm^3, and the experimental curves are normalized so that a direct comparison can be made. The agreement is seen to be satisfactory.

One systematic feature is quite apparent, and this is the weak second absorption shoulder to the high-energy side of the F' band in each of the salts. One mechanism which can be proposed for this absorption is that it corresponds to a final state of the ionized F' center consisting of a free electron and an F center in the first excited ($2s$ or $2p$) state. The $2p$ excited-state energy was calculated for the F center for each salt, and the absorption edge energies corresponding to this mechanism are shown by the arrows in Figs. 3–9.

It must be noted that our calculated optical ionization energies should *not* agree with those observed because we have neglected phonon broadening. The calculated ionization energies should be higher than those observed. We also believe that the calculations of La and Bartram[14] should be compared with optical ionization energies, rather than with F' band peaks. The peaks result from the product of a matrix element that decreases with increasing photon energy and a density of states which increases.

The one-electron radial distribution functions are plotted in Fig. 10. These were calculated from the wave functions which resulted from the calculation to yield the correct experimental F' binding energies. The tick marks indicate the potential-well radius for each salt and show what percent of the total electron distribution is in the well. The radial distribution function for Fowler's F-center calculation[18] for NaCl is also shown. By comparison with the F center our F' center is surprisingly compact and not as diffuse as we would have expected. Two features of these calculations should be noted for a valid comparison to be made. First, our calculation was done using an effective mass of $m^*=1.0m_e$, whereas Fowler used an effective mass of $m^*=0.6m_e$. This is important since, as Fowler states, and as we also found, making m^* smaller has the effect of pushing out the wave function. Thus, for comparison, our wave function should be more diffuse than indicated. Also our well for NaCl has about the same radius as Fowler's (2.53 versus 2.65 Å); however, it is about 3 eV deeper than his (−9.62 versus −6.8 eV). The fact that the electron distributions are so similar results, presumably, from the cancellation between the

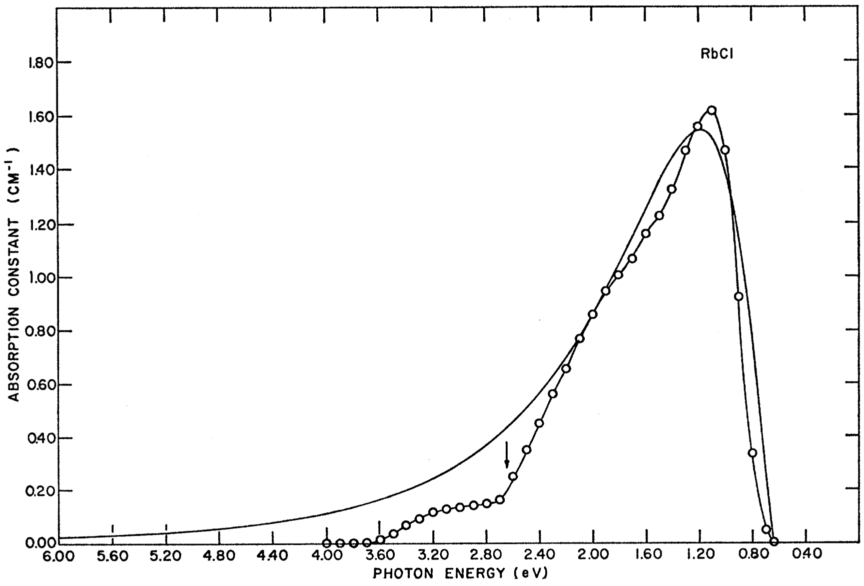

Fig. 7. F'-center absorption in RbCl. See caption for Fig. 3.

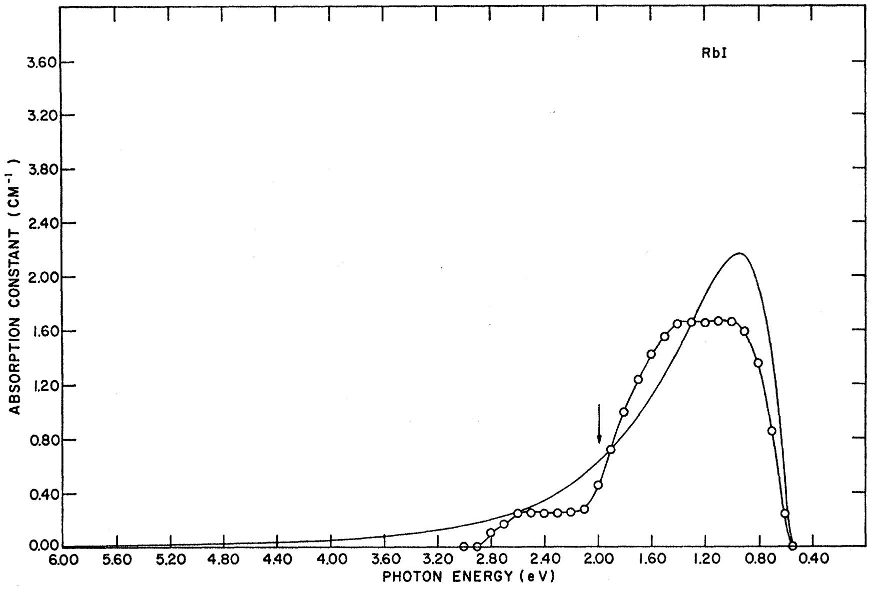

Fig. 8. F'-center absorption in RbI. See caption for Fig. 3.

increased attractive polarization potential and the electron-electron repulsion potential in our model.

Table I lists the well parameters which yielded the correct experimental F' binding energies. The experimental F' binding energies are also shown. Thermal depths for the F' centers in a few salts as measured by Scaramelli[28] are shown in the last column. Note that the thermal depths are about one-half the optical depths, which is reasonable. Table II lists the well parameters which resulted from the self-consistent solution for the F' binding energies.

Table III lists the temperature at which maximum F-to-F' conversion occurred during optical bleaching of the F band. Also listed are the quantum efficiencies for optical bleaching of the F band and the fraction of the original F band destroyed. The quantum efficiencies were found using Spinolo's[29] data to evaluate the expression given for this quantity by Swank and Brown.[30]

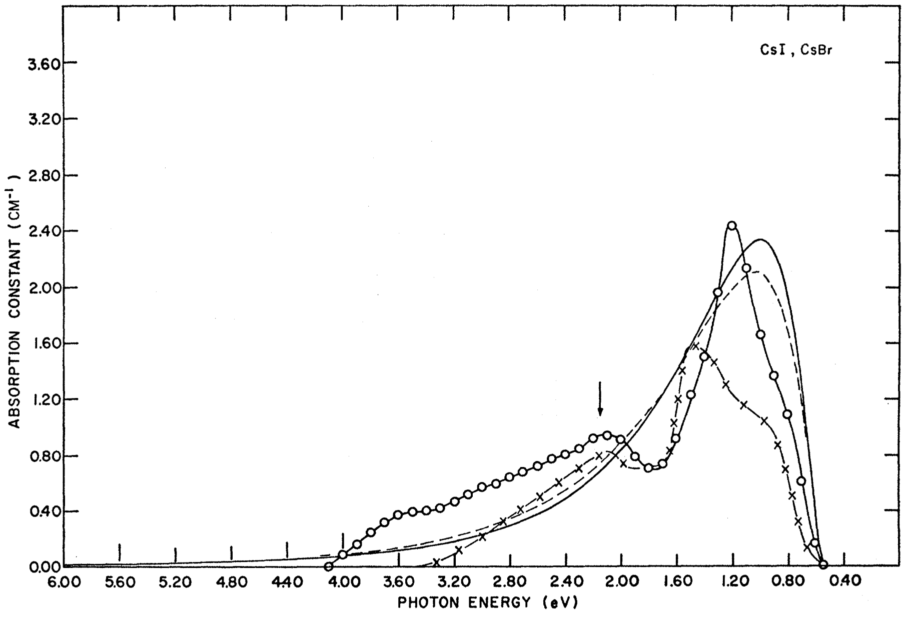

Fig. 9. F'-center absorption in CsBr and CsI. See caption for Fig. 3. Solid curve, calculated CsBr; solid curve with circles, measured CsBr; dashed curve, calculated CsI; dashed curve with crosses, measured CsI.

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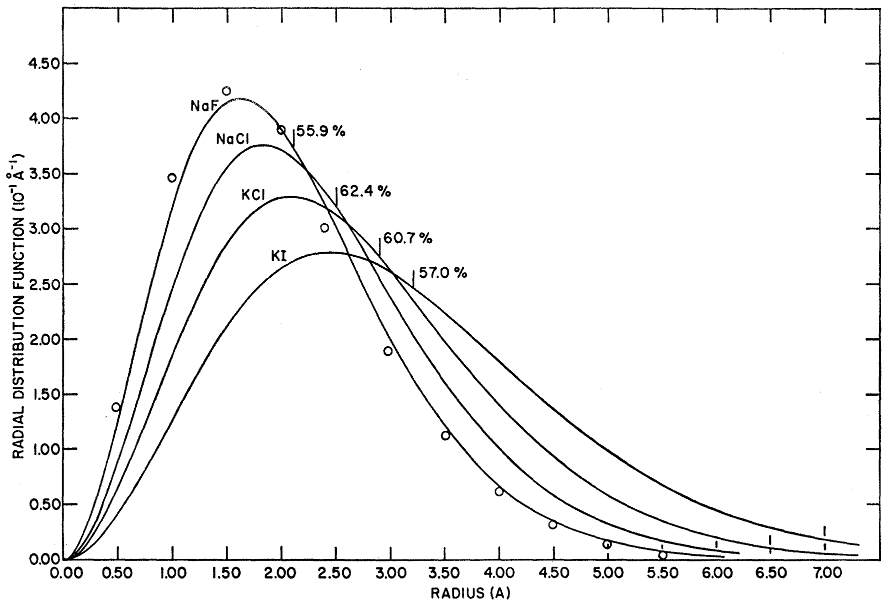

FIG. 10. F'-center radial distribution function. The tick marks indicate the edge of the potential well, and the associated numbers are the fraction of the F'-center electronic charge inside the well. The circles represent Fowler's (Ref. 18) calculated values for F centers in NaCl, using $m^*=0.6m_e$.

TABLE I. Well data for experimental fit of F' binding energy for $m^*=1.0m_e$.

Salt	R (Å)	V_0 (eV)	K_{eff}	W_{ion} (eV)	F' binding energy (eV) Calc.	Expt.	Thermal depth (eV)[a]
NaF					2.72	1.85±0.1	
NaCl	2.53	−9.62	1.17	−0.80	1.72	1.72±0.05	0.91
KCl	2.83	−7.62	2.11	−0.02	0.904	0.90±0.03	0.537
KBr	2.97	−6.87	2.63	0.24	0.654	0.65±0.03	0.35
KI	3.17	−6.05	2.38	−0.22	0.695	0.70±0.03	
RbCl	2.94	−7.00	2.50	0.28	0.649	0.64±0.03	
RbI	3.29	−5.58	2.45	−0.12	0.553	<0.55	
CsBr	3.34	−6.07	4.94	0.68	0.527	<0.54	
CsI	3.56	−5.60	5.05	0.54	0.544	<0.55	

[a] After Scaramelli. See Ref. 28.

TABLE II. Well data for self-consistent solution of F' binding energy.

Salt	$m^*(m_e)$	R (Å)	V_0 (eV)	K_{eff}	W_{ion}(eV)	Calculated F' binding energy (eV)
LiF	1.0	1.81	−14.89	1.20	−2.49	2.85
	0.6		−14.69	1.24	−2.29	1.84
NaF	1.0	2.08	−12.97	1.12	−2.21	2.72
	0.6		−12.80	1.15	−2.04	1.72
NaCl	1.0	2.53	−10.07	1.50	−1.25	2.13
	0.6		−9.97	1.55	−1.15	1.26
KCl	1.0	2.83	−8.66	1.47	−1.07	1.79
	0.6		−8.59	1.50	−0.99	1.02
KBr	1.0	2.97	−7.99	1.64	−0.88	1.61
	0.6		−7.92	1.68	−0.81	0.88
KI	1.0	3.17	−6.44	1.98	−0.61	1.02
	0.6		−6.36	2.05	−0.53	0.432
RbCl	1.0	2.94	−8.32	1.49	−1.04	1.77
	0.6		−8.24	1.53	−0.97	1.02
RbI	1.0	3.29	−6.07	1.92	−0.62	0.954
	0.6		−6.00	1.98	−0.54	0.402
CsBr	1.0	3.34	−7.52	1.86	−0.77	1.82
	0.6		−7.47	1.89	−0.72	1.09
CsI	1.0	3.56	−6.67	2.16	−0.54	1.50
	0.6		−6.63	2.20	−0.50	0.828

Several more results may be pointed out. NaCl (Fig. 3) shows a symmetrical F' band with a very broad high-energy tail. It is not obvious that a second distinct absorption curve could be present in the high-energy tail; however, the small shoulder at about 4 eV appeared consistently in the raw data for four different runs.

In each of the three potassium salts (Figs. 4–6) the second absorption is very clear. It is difficult to compare

TABLE III. Optical bleaching data.

Salt	Bleaching temperature (°K)	Fraction of F centers destroyed	Quantum efficiency[a]
NaCl	153	0.39	0.99
KCl	183	0.76	0.99
KBr	133	0.58	0.99
KI	143	0.83	0.99
RbCl	133	0.54	0.92
RbI	103	0.25	
CsBr	103	0.80	0.99
CsI	87	0.84	

[a] After data due to Spinolo (Ref. 29).

the calculated and experimental second edges since the shape of the second absorption is not known. In general, the agreement is good enough to indicate that the mechanism given earlier for it is a reasonable one. Compared to NaCl, the F' bands in the potassium halides are not symmetrical. KCl and KBr both show a large shoulder on the high-energy side of the main peak, and the entire peak in KI is skewed to the high-energy side. This difference in peak shape can be attributed to the presence of a low-lying d-like minimum in the conduction band of the potassium salts. Recent band-structure calculations on KCl [31] and KI [32] indicate that for both crystals the s-like states at Γ are lowest, and d-like states at Γ are found only 1–2 eV higher. The low-lying d-like levels would increase the density of final states and produce the observed asymmetry. It might also be possible to have additional absorption in this spectral region by a transition to a localized state, split from the upper conduction band by the F'-center potential. Low-lying d-like states are not present in NaCl.[33,34]

The band effective mass for KI is on the order of $0.4m_e$,[24] one of the smallest for the alkali halides. A calculation for KI using $m^*=0.45m_e$ shifted the calculated peak in the direction of the experimental peak but removed only about one-half of the discrepancy, as shown in Fig. 6. It was also suspected that the large skewing of the experimental peak could be due to an underlying F_A band. Bleaching and examination of the band with polarized light indicated that the absorbing centers were isotropic. Thus, it was concluded that the band was a pure F' band.

RbCl (Fig. 7) is similar to KBr with respect to its lattice parameter and dielectric constants. Thus we might expect their F' bands to be similar. This was found to be the case here. Also, it is probable that RbCl has a second conduction-band minimum just above the bottom of the conduction band, as in the potassium salts.

Several other alkali halides were studied experimentally. F' bands were produced in additively colored RbI, CsBr, and CsI, and F' centers were produced in NaF by x radiation at LNT.[35] Because of hole bands only the F' optical ionization energy could be found in NaF. This was done by subtracting the absorption curves measured before and after optical bleaching of the F' band initially formed by the x radiation. The F' band in RbI (Fig. 8) had a very flat maximum, the result of either impurities or the fact that the conduction band in that salt may not be at all parabolic several tenths of an eV above, its minimum. An upper limit for the ionization energy of the F' center in RbI was obtained, however. CsBr and CsI (Fig. 9) seem to have rather complex F' bands whose ionization energies lie at wavelengths too long to be determined reliably. Therefore only upper limits are reported in Table I. The complex shapes may arise from a complex conduction band in these salts[36] or from the production of other centers when the F band is bleached. Previous experience[37] with these crystals indicates that another band forms in the low-energy tail of the F band of CsBr upon bleaching, but it is too small to account for the structure observed.

X. SUMMARY

The shapes of F' bands have been observed in many alkali halides. A semicontinuum model can be used to calculate the optical ionization energy and the band shape, using reasonable values of the parameters. Extra structure in the experimental curves can plausibly be attributed to d-like portions of the conduction band and to transitions which leave the remaining F' center in an excited state.

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