supported by the recent results of Dolezalek and Spear[13] where the hole-drift mobility at room temperature is insensitive to hydrostatic pressure up to 5 kbar. However, it is possible that at lower temperatures hopping through localized states may be the transport mechanism. In this model holes do not communicate with the valence band but rather jump from one localized state to the next, with the release time being much larger than the time-of-flight between states. Such a model has been described in detail by Pai[4] and has been used with some success in explaining similar field-dependent mobilities for hole transport in PVK, and by Scharfe[7] in vitreous films of As_2Se_3. However, only in amorphous selenium can one observe a continuous transition from a shallow trap-controlled mobility at high temperatures to an anomalous electric-field-dependent mobility at low temperatures. If this anomalous region were due to a hopping-type transport, one would expect to see a significant decrease in the activation energy with decreasing temperature; otherwise, the activation energy associated with the high-temperature region would dominate. In fact, the activation energy at the lowest field where transits can be observed is 0.23 eV, the same value obtained in the – 10 to – 70 °C region. This smooth transition implies that the release rate is being determined by a function of the form

$$\tau_r = f\{[\phi_A - g(E, T)]/kT\} \quad ,$$

where ϕ_A is the high-temperature activation energy (≈ 0.23 eV) and $g(E, T)$ represents the electric field and temperature modulation of the potential barrier.

In summary, for temperatures above – 70 °C, well-defined electric-field-independent mobilities are observed. As a function of temperature, the hole-drift mobility in this region shows a deviation from a simple exponential dependence confirming the results of Grunwald and Blakney.[3] Below – 70 °C, the apparent hole mobility as calculated from well-defined transit times exhibits an anomalous electric-field dependence. It is suggested that this behavior is caused by an electric-field modulation of the localization time of the trapped holes.

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Energy Levels of the F_A Center

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An approximate expression which describes the effects of finite ion size on the F-center energy levels is developed and investigated. It is used in a study of the F_A-center energy levels; the impurity-induced changes in the ion-size correction, ionic displacements, and polarization are treated as perturbations on the F-center energy levels. We find that the splitting of the F-center excited state results mainly from the difference in the ion-size correction for the impurity and host cations, and that the approximate F-center excited-state wave functions used here concentrate too much charge at the impurity site.

I. F_A CENTER

The F_A center[1] in the alkali halides consists of an F center, an electron bound to an anion vacancy, modified by the presence of an impurity alkali ion of smaller size which substitutionally replaces a cation on a nearest-neighbor site to the vacancy. The introduction of this impurity ion reduces the symmetry of the potential acting on the electron trapped at the anion vacancy, the F electron, from O_h to C_{4v}. This reduction in symmetry will split the excited p state of the unperturbed F center into two levels, one of which is doubly degenerate and transforms according to the E representation of the group C_{4v}, and the other of which is nondegenerate and transforms according to the A_1 representation. Transitions between the ground state and these two levels are characterized by the labels F_{A2} and F_{A1}, respectively. The optical absorption associated with these two transitions consists of two bands, one (F_{A2}) of which is centered near the absorption band of the unperturbed F center and is polarized in a plane perpendicular to the vacancy-impurity axis, and the other (F_{A1}) of which occurs at somewhat longer wavelengths and is polarized parallel to the vacancy-impurity axis.

At least three previous theoretical investigations of the energy levels of the F_A center have been reported. In the first,[2] the ground and excited states of the F electron were represented by a linear combination of the atomic orbitals of the cations surrounding the vacancy, and the lowering of the nondegenerate excited state was found to be a function of the difference in the ionization energies of the host and impurity alkali atoms. In the latter two,[3] the ion-size correction is considered as a perturbation on the point-ion approximation due to a pseudopotential[4] centered on the neighboring ions; the energy of the A_1 level was found to be lowered relative to the E level due to differences in the pseudopotential for the host and impurity ions. In this treatment we shall follow more closely this latter approach in that we examine the effects of finite ion size; in addition, we discuss the effects of a difference in the displacement and the electronic polarizability of the impurity relative to the other nearest-neighbor cations. We find that the difference in the ion-size correction between the impurity and host cations makes the dominant contribution to the energy splitting of the F-center excited state. We find, in addition, that the approximate excited-state F-electron wave functions used in this calculation tend to concentrate too much charge at the lattice sites nearest the vacancy center.

In our treatment of this problem we shall limit our consideration to F-electron wave functions of the form

$$\Phi_{lm}(\vec{r}) = f_l(r)\, Y_{lm}(\theta, \phi) , \tag{1}$$

where $l = 0$ and 1 for the ground and excited states, i.e., we limit ourselves to s-like ground-state wave functions and p-like excited-state wave functions. While we shall regard the Gourary and Adrian[5] (hereafter referred to as GA) type-III wave function to be a good approximation to the unperturbed ground-state wave function of the F electron and the GA type-II wave function to be a good approximation to the excited state, we shall use other approximate forms of $f_l(r)$ as well.

In the point-ion-lattice approximation[5] there can be no splitting of the excited state of the F center because of the impurity ion. Thus the observed splitting must arise from corrections to this approximation, e.g., from differences in the displacement, the electronic polarizability, and the ion-size correction of the impurity ion relative to the remaining nearest-neighbor cations. This ion-size correction includes the repulsive potential arising from the requirement that the F-electron wave function be orthogonal to all the occupied electron orbitals in the crystal and the contribution to the energy of the F electron remaining in the Hartree-Fock potential after the point-ion potential has been removed.[5,6] The contribution of this ion-size correction to the energy E_{lm} of the F-electron state $\Phi_{lm}(\vec{r})$ is shown later in the paper to be

$$E^{\mathrm{IS}}_{lm} = \sum_{\gamma=1}^{N} [A_\gamma + B_\gamma(E_{lm} - U_\gamma)]\, |\Phi_{lm}(\vec{r}_\gamma)|^2 , \tag{2}$$

where the coefficients A_γ and B_γ depend only on the ion at lattice site γ and are identical to those defined by Eqs. (2.23) and (2.24) of Ref. 6, and U_γ is the potential energy of an electron at lattice site γ due to all the other ions in the crystal. The vector $\vec{r}_\gamma$ defines the position of lattice site γ relative to the vacancy site and the sum is to be carried out over all N ions in the crystal.

If an impurity cation is located at the lattice site $\gamma = 1$, the change in the ion-size correction will be

$$\Delta E^{\mathrm{IS}}_{lm} = [(A_1 - A_+) + (B_1 - B_+)(E_{lm} - U_1)]\, |\Phi_{lm}(\vec{r}_1)|^2 \times\left(1 - \sum_{\gamma=1}^{N} B_\gamma |\Phi_{lm}(\vec{r}_\gamma)|^2\right)^{-1} , \tag{3}$$

where A_+ and B_+ refer to the cation in the host crystal and A_1 and B_1 refer, of course, to the impurity. We have used Eq. (3) to calculate the expected shifts of the F_{A1} and F_{A2} transition energies from the F-center transition energy for a number of different approximate forms of the F-electron wave functions; the predicted and the experimental values for these shifts are given in the first part of Table I. Although the use of various approximate forms for the F-electron wave function results in substantial variations in the predicted shifts for the F_A-center transition energies, for all the F_A centers examined and for all the approximate forms of the wave functions used, the F_{A1} transition energy was found to be lower than the F_{A2} transition energy. Furthermore, in nearly all the F_A centers examined where an experimental value

TABLE I. The shifts of the F_{A1} and F_{A2} optical transitions energies from the F-center transition energy due to the change in the ion-size correction are listed for selected F_A centers and selected approximate forms of the F-electron wave functions. The results listed in columns I and II were obtained using GA type-III and type-II wave functions to represent the ground and excited states of the F electron; the wave-function parameters used in obtaining column I were taken from Ref. 5 and those used in obtaining column II were taken from Ref. 6. The results listed in column III were obtained using GA type-I wave functions and the results listed in column IV were obtained from the wave functions defined in Ref. 8. The experimental values listed in column V were taken from Ref. 1. The ratio of the difference between the F_{A1} and F_{A2} transition energies for the Na and Li F_A centers in the same host alkali halide are shown in the last three rows of the table.

	I		II		III		IV		V	
F_A center	F_{A1}	F_{A2}	F_{A1}	F_{A2}	F_{A1}	F_{A2}	F_{A1}	F_{A2}	F_{A1}	F_{A2}
KCl:NA	−0.40 eV	0.06 eV	−0.42 eV	0.07 eV	−0.30 eV	0.06 eV	−0.40 eV	0.05 eV	−0.19 eV	0.04 eV
KCl:Li	−0.50	0.08	−0.52	0.08	−0.38	0.08	−0.49	0.06	−0.33	−0.06
KBr:Na			−0.36	0.06			−0.33	0.04	−0.16	0.01
KBr:Li			−0.45	0.08			−0.41	0.06	−0.24	−0.06
RbCl:K			−0.07	0.00						
RbCl:Na			−0.43	0.06					−0.20	0.04
RbCl:Li			−0.52	0.08					−0.33	−0.10
RbBr:K	−0.06	0.00	−0.06	0.00	−0.05	0.00			−0.19	−0.01
RbBr:Na	−0.38	0.05	−0.38	0.06	−0.29	0.05				
RbBr:Li	−0.46	0.07	−0.46	0.07	−0.35	0.07			−0.29	−0.08
KCl	0.79		0.81		0.78		0.82		0.85	
KBr			0, 80				0.79		0.95	
RbCl			0.82						1.04	

of the separation between the transition energies was available, the separation predicted with any of the approximate forms of the F-center wave function was larger than the experimentally observed separation; the only exception was the RbBr:K F_A center. Therefore, we conclude that an important source of the observed shifts of the F_{A1} and F_{A2} transition energies from the F-center transition energy is the change in the ion-size correction resulting from the substitution of an impurity cation in a nearest-neighbor site.

There may however be additional contributions to the splitting of the excited state due to differences in the displacement of the impurity relative to the remaining nearest-neighbor cations. Such a relative displacement of the impurity ion will produce a Stark splitting in the excited p state of the F center; the resulting shifts in the F_{A1} and F_{A2} transition energies from the F-center transition are shown for KCl in Fig. 1. We have considered the lattice distortion about the vacancy center in terms of a model[5] in which the six cations nearest the vacancy center are permitted to undergo radial displacements from their respective lattice sites while the remaining ions in the crystal remain fixed on their respective lattice sites. The application of this model to the F center is discussed in the Appendix; the generalization to the F_A center is straightforward. Typical displacements calculated[7] for both the F and the F_A center are shown in Table II. Use of other approximate forms[5, 6, 8] of $f_0(r)$ and parameters appropriate to other alkali halides lead to similar displacements. The general trend of the calculated displacements of the cations neighboring an F center is outward; this result is consistent with other[9, 10] detailed studies of the lattice distortion in the vicinity of the F center and with measurements of the volume expansion[11] associated with the introduction of F centers into the alkali halides. For the F_A center the calculations indicate that the nearest-neighbor host cations move to a position nearer to the vacancy center than that which they occupied in the unperturbed F center and that the impurity ion moves outward relative to these host cations. These results are consistent with our intuition, since the impurity ion is smaller, and with ENDOR measurements[12] on the KCl:Li and KBr:Li F_A centers.

One may expect further contributions to the shifts of the F_{A1} and F_{A2} transition energies due to the difference in the electronic polarizabilities of the impurity and host cations. We have calculated these shifts using a procedure analogous to that used in Ref. 5 to treat polarization effects in the F center. When polarizabilities[13] and other parameters appropriate to the KCl:Na and KCl:Li F_A centers were used together with selected approximate forms of the F-electron function, the magnitude of the splitting of the F-center excited-state energy level was found to be about 10% of the

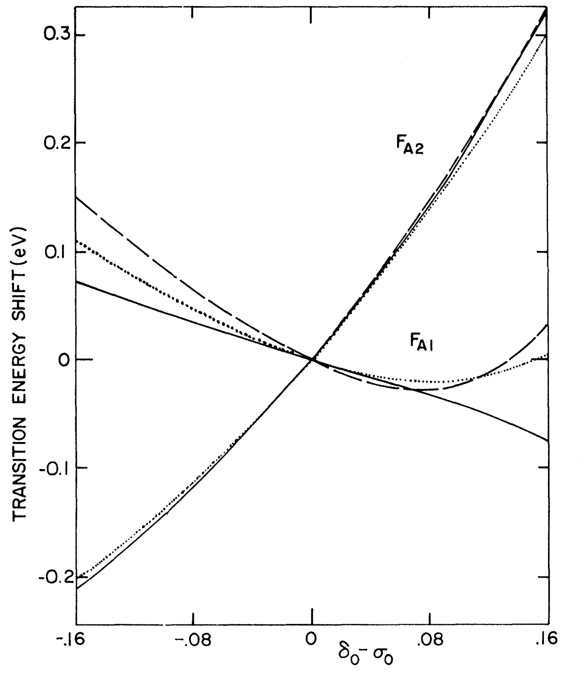

FIG. 1. Calculated shifts in the optical absorption energies of the F_{A1} and F_{A2} transition from the F-center absorption energy due to the Stark splitting associated with a radial displacement $\delta_0 - \sigma_0$ of the impurity ion relative to the other nearest-neighbor cations ($\delta_0 - \sigma_0$ is positive for an inward displacement and has the units of the lattice constant) are shown for selected approximate forms of the F-electron wave functions in KCl. The approximate forms of the wave functions used are (a) GA type I, solid line; (b) GA type-III and type-II ground and excited state, dashed line; and (c) those given in Ref. 8, dotted line.

splitting observed in the F_A center, and the F_{A1} transition energy was shifted to a higher energy than the F_{A2} transition.

TABLE II. The calculated equilibrium radial displacements of the cations nearest the vacancy, denoted by σ_0(F), are shown in the first column for selected unperturbed F centers, and the calculated equilibrium radial displacements of the impurity ion, denoted by $\delta_0(F_A)$, and of the remaining cations nearest the vacancy, denoted by $\sigma_0(F_A)$, for the F_A center are shown in the second and third columns. These displacements are given in units of the lattice constant and inward displacements are taken to be positive. The relative displacement of the impurity ion is shown in the fourth column. These calculations were done using the GA type-III wave function with parameters from Ref. 6.

	$\sigma_0(F)$	$\delta_0(F_A)$	$\sigma_0(F_A)$	$\delta_0-\sigma_0$
KCl:Na	−0.022	−0.061	−0.018	−0.043
KCl:Li	−0.022	−0.104	−0.016	−0.088
KBr:Li	−0.021	−0.112	−0.015	−0.097
RbBr:Li	−0.018	−0.125	−0.011	−0.114

Figure 2 illustrates the contribution of each of these sources to the energy levels of the F_A centers in KCl. Also shown are the results of an attempt to estimate the error introduced in these energies due to the approximations made in obtaining Eq. (2); this error will be discussed in more detail in Sec. II. One notes from Fig. 2 that the F_{A2} transition in the KCl:Li F_A center is lowered to an energy nearly equal to the F-center transition energy. This downward energy shift is primarily due to the outward relative displacement of the impurity ion; also this downward shift brings the predicted E_{A2} transition energy into better agreement with the experimental transition energies shown in Table I. However, one also notes that the separation of the E and A_1 excited-state levels is considerably larger than the experimental separation and that this large separation is clearly due to the ion-size correction. Since it is evident

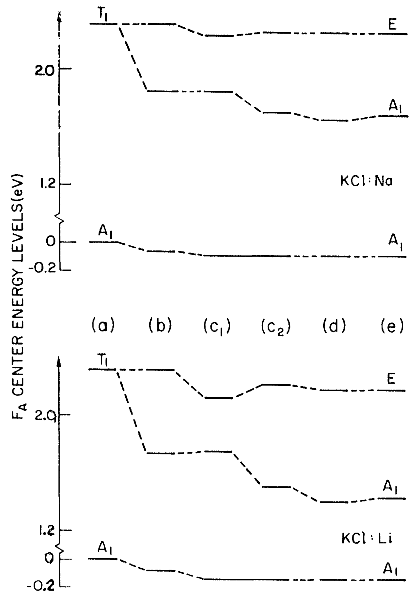

FIG. 2. Changes in the F-center energy levels due to the presence of an impurity ion in a nearest-neighbor position for the KCl:Na and KCl:Li F_A centers. The energy levels of the unperturbed F-center are shown in (a) and the changes are due to (b) the change in the ion-size correction, (c_1) the Stark splitting and (c_2) changes in the ion-size correction associated with the displacement of the impurity ion relative to the other nearest-neighbor cations, (d) the errors arising from the assumption that the F-electron wave function is constant throughout the ion core, and (e) polarization effects. The calculations were done using GA type-III and -II wave functions to represent the ground and excited states of the F electron. Each energy level is labeled with the representation of the symmetry group according to which the level transforms.

from Eq. (3) that the calculated separation between the transition energies of the F_A center depends on the magnitude of the F-electron excited-state wave function at a nearest-neighbor site, one concludes from Table II that the approximate forms of the excited-state F-electron wave function which we have chosen for our calculation concentrate too much charge at the nearest-neighbor sites. That the electron wave function is indeed the source of the overestimate of the calculated splittings is evidenced by the good agreement between the experimental ratio of the energy-level splittings for the Na and Li F_A center in the same host alkali halide and the calculated ratio. These ratios are listed in the latter part of Table I. It has been observed previously[5, 14] that the F-electron ground-state wave functions obtained in the point-ion approximation tend to concentrate too much charge at the nearest-neighbor sites.

Although the discussion of this article has been limited to the F_A center, which is known to exist in the alkali halides, it is interesting to speculate regarding the existence of other similar defect-impurity centers. One such center, consisting of an F center modified by the presence of an alkali ion of larger size in a nearest-neighbor site, has been identified[15] in KCl containing Rb impurities. The optical absorption[16] associated with this center shows a slight shift to lower energies from the F-center absorption and does not exhibit the two absorption bands characteristic of the F_A center. While the transition energies calculated for this center using Eq. (3) are not inconsistent with the experimental observations described above, transition energies significantly greater than the F-center transition were calculated for similar centers in other materials. Another such center might be defined by the presence of an anion impurity in a next-nearest-neighbor position to the F center. For these centers the predicted transition energy shifts due to the ion-size correction are comparable to those expected from a Stark splitting of the F-center excited state; both are of order 0.05 eV. In view of the recent identification[17] of the F center in the alkaline-earth fluorides, it is not unreasonable to expect that an analog of the F_A center may exist in these materials. We have calculated the shifts in the transition energies from the F-center transition energy due to the change in the ion-size correction for several such centers. As an example of our results the predicted transition energies of the CaF_2:Mg center are 1.8 and 3.5 eV for transitions polarized parallel and perpendicular to the vacancy-impurity axis.

In Fig. 2 we have ignored the difference in the ion-ion repulsion energy between an F_A center and an F center together with a distant alkali ion impurity. While this energy difference will not be important in a discussion of the transition energies of the F_A center since it alters all the energy levels by an equal amount, it will be important in a discussion of the relative total ground-state energies of the F_A center and the F center plus a distant alkali impurity. We estimate[18] the ion-ion repulsive energy difference between an impurity ion in a nearest-neighbor site to an F center and one in a distant-neighbor site to an F center to be 0.08 eV for a typical F_A center (KCl:Na). From this result and the results shown in Fig. 2, there seems to be little difference between the total ground-state energies of these two systems.

II. ION-SIZE CORRECTION

We have arrived at the approximate form of the ion-size correction given in Eq. (2) by a development similar to that given in Ref. 6. We insist, however, that when a variational or perturbation technique is to be used to obtain the energies and wave functions of the F electron, the Phillips-Kleinman[4] form of the repulsive potential, denoted by V_R^{PK}, should be used. This repulsive potential results from orthogonalizing the smooth envelop function of the F electron to the filled ion-core states and it can be combined with the Hartree-Fock potential to form what is known as a pseudopotential, denoted V_P. The solutions $\psi(\vec{r})$ of the resulting eigenvalue problem,

$$(T+V_P)\psi(\vec{r})=E\psi(\vec{r}) \quad , \tag{4}$$

where T is the kinetic energy, are referred to as pseudo-wave-functions. If one uses V_R^{PK} in V_P, any linear combination of the core-state wave functions may be added to $\psi(\vec{r})$ without altering the valence eigenvalue E.[19] One may use this indeterminacy of $\psi(\vec{r})$ to fix the projection of $\psi(\vec{r})$ on the core states in such a way as to yield a more convenient form V_R' of the repulsive potential. If this is done, Eq. (4) can sometimes be solved with greater ease. However, the pseudo-wave-function $\psi'(\vec{r})$ associated with V_R' contains a specific linear combination of core states. This limitation on the pseudo-wave-function presents no difficulty when Eq. (4) is integrated directly, but it can lead to problems when approximate methods of solving Eq. (4) are used. For example, if a variational technique is used to solve Eq. (4) and one wishes to use variational wave functions which are not orthogonal to the core states, then it is necessary[20] that V_R^{PK} be used since only this form yields pseudo-wave-functions which are degenerate with the core states. In other applications it may be more convenient to regard the repulsive potential as a perturbation on the Hartree-Fock potential. In these the approximate solutions to the Hartree-Fock

Hamiltonian (for exact solutions, the repulsive potential is zero) must be regarded as the pseudo-wave-functions. Since the pseudo-wave-function is then known and the core wave functions are assumed to be known, this pseudo-wave-function is associated with a particular, but generally not easily specified, form of the pseudopotential, i.e., it contains a specific linear combination of core wave functions. However, if V_R^{PK} is used in such a perturbation calculation, one need not be concerned with the projection of the pseudo-wave-function on the core states since[21]

$$V_R^{\mathrm{PK}}\psi'(\vec{r}) = V'_R\psi'(\vec{r}) \quad .$$

In order to obtain the ion-size correction to the F-electron energy due to an ion at lattice site γ, we replace the pseudo-wave-function $\psi(\vec{r})$ with $\Phi_{lm}(\vec{r})$ given in Eq. (1) and expand this function in a Taylor's series about the point $\vec{r}_\gamma$. If we retain only the first term in this expansion, i.e., we make the approximation that the variation of $\Phi_{lm}(\vec{r})$ over the volume of the ion cores may be neglected in calculating the magnitude of the ion-size correction, then it can be shown that matrix elements of the electron kinetic energy between $\Phi_{lm}(\vec{r})$ and the core s states are negligible compared to corresponding matrix elements of the electron potential energy.[22] This result immediately leads one to the approximate form of the ion-size correction given in Eq. (2). Expressions similar to Eq. (2) have been obtained in at least two other treatments of the effect of finite ion size on the energy levels of the F electron. In the first[5] of these, which arises in a discussion of the effect of finite ion size on the F center in LiF, the finite-ion-size effects were restricted to the nearest-neighbor cations. In the second,[6] a different form of the pseudopotential was used, and this resulted in the F-electron energy E appearing in Eq. (2) being replaced by the expectation value of the pseudopotential. In application the effect of this difference is expected to be small compared to the errors involved in the approximation.

By retaining further terms in the expansion of $\Phi_{lm}(r_\gamma)$ about r_γ, one can gain some insight into the range of validity of the approximation described above. We did this and carried out calculations for the cations nearest the vacancy center. One finds the error to be proportional to the product of the radial derivative of $f_l(r)$ evaluated at $\vec{r}_\gamma$ and a function of order unity which increases with the size of the cation. Thus we expect that the approximation described above will be least valid when the ratio of radii of the anion and cation is small. In addition, we find that, owing to the presence of the radial derivatives of $f_l(r)$, the estimate of the error is quite sensitive to the choice of $f_l(r)$. Estimates of this error are shown in Fig. 2.

The coefficients A_γ and B_γ used in Eq. (2) are defined in Ref. 6. Numerical values of these coefficients for the alkali, alkaline-earth, and halide ions are also given in Ref. 6. It is suggested there that the coefficient A_γ must be reduced by an empirical factor 0.53 in order to obtain agreement between the theoretically predicted and experimentally observed F-center absorption energies in the alkali halides. We find that inclusion of this reduction factor causes the terms of Eq. (3) to cancel, resulting in calculated shifts of the F_{A1} and F_{A2} transition energies from the F-center transition energy which are smaller in magnitude than those observed and which vary in sign from center to center. In view of this lack of correlation with observation, and since this reduction factor serves only to make the calculated F-band energies correlate with experiment, we have chosen to ignore it in our calculations.

At the conclusion of our calculations on the F_A center we noted that the excited-state F-electron wave functions used here concentrate too much charge at the nearest-neighbor cation sites. Prompted by this observation we have examined the ion-size correction using the rather arbitrary assumption that the F-electron charge density at all the ion sites in the crystal was reduced by a factor of 2 from that given by $\Phi_{lm}(\vec{r})$. This assumption leads to calculated F-center transition energies which go more or less continuously from good agreement to very poor agreement with experiment as one goes from alkali halides with large ratios of the anion and cation radii to those with small ratios. This is, of course, consistent with our earlier discussion of the validity of the approximate form of the ion-size correction used in this calculation and it also suggests a possible reason for our poor results for the RbBr:K F_A center.

APPENDIX

We shall investigate the effect of the ion-size correction on the lattice distortion in the vicinity of the F center in the context of the model[5] in which the six nearest-neighbor ions move into the vacancy by an amount σR, where R is the lattice constant, and the remaining ions remain fixed at their respective lattice sites. The energy changes accompanying this distortion resulting from changes in the expectation value of the F-electron potential energy, in the ion-ion repulsion and in the electrostatic interaction are discussed in Ref. 5 and will be denoted here by ΔE_1. The total energy change accompanying the distortion will be

$$\Delta E = \Delta E_1 + \Delta E_2 \ . \tag{A1}$$

In the presence of a distortion of the nearest-neighbor ions, the ion-size correction, which is given by Eq. (2) of the text, is changed by an amount

$$\Delta E_2 = 6[A_1 + (E'_{00} - U'_1)B_1]\,|\Phi_{00}(R(1-\sigma))|^2$$
$$+\sum_{\gamma=7}^{N} [A_\gamma + (E'_{00} - U'_\gamma)B_\gamma]\,|\Phi_{00}(\vec{r}_\gamma)|^2$$
$$-\sum_{\gamma=1}^{N} [A_\gamma + (E_{00} - U_\gamma)B_\gamma]\,|\Phi_{00}(\vec{r}_\gamma)|^2 \;, \qquad \text{(A2)}$$

where the subscript $\gamma = 1 - 6$ denotes the six nearest-neighbor ions and the primed quantities are to be evaluated in the distorted system. Since the terms of ΔE_2 are proportional to $|\Phi_{00}(\vec{r})|^2$, and since this wave function decays exponentially in the region outside the space enclosed by the nearest-neighbor ions, we shall make the approximation that only the terms evaluated at nearest-neighbor sites contribute significantly to ΔE_2. The difference in energy between the distorted and the undistorted systems is simply the total energy change ΔE. If we expand the wave function $\Phi_{00}(R(1-\sigma))$ in a Taylor series, the total energy change accompanying the distortion is

$$\Delta E = \Delta E_1 + 6V[-\xi\sigma + (\eta + \Gamma\xi^2)\sigma^2]$$
$$+\Gamma[\Delta E_1 - (U'_1 - U_1)][1 - (1+\Gamma)\xi\sigma], \qquad \text{(A3)}$$

where

$$V = \frac{[A_1 + (E_{00} - U_1)B_1]\,|f_0(R)|^2}{4\pi - 6B_1|f_0(R)|^2} \;, \quad \Gamma = \frac{6B_1|f_0(R)|^2}{4\pi - 6B_1|f_0(R)|^2} \;,$$

$$\xi = 2Rf'_0(R)/f_0(R) \;,$$

$$\eta = R^2[f''_0(R)f_0(R) + f_0^{12}(R)]/f_0^2(R) \;. \qquad \text{(A4)}$$

In these expressions the primes on $f_0(r)$ denote the radial derivatives of $f_0(r)$. For certain composite approximations to the F-electron wave functions, e.g., the GA type-II and -III wave functions, the quantity $f_0''(R)$, and, hence, the quantity η, is not well defined. For the wave functions used in these calculations, the uncertainties in η due to this ambiguity are small compared to the variations introduced by the choice of $f_0(r)$.

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