

Theoretical survey of F centers in alkali halides with NaCl structure. I. Absorption and the ground state*

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The absorption energy and ground state are analyzed for the F center in 16 alkali halides, using a point-ion lattice with ion-size correction, and including lattice distortion. F -center localization and point-ion model energies ignoring ion size and lattice distortion depend on nearest-neighbor distances qualitatively as one would expect.

I. INTRODUCTION

The variation of F -center absorption energy with host-crystal composition was first formulated empirically by Mollwo¹ in 1931, and refined by Ivey² in 1947. The relationship for alkali halides of the NaCl structure is

$$\Delta E = \Delta E_I a^{-n}, \quad (1)$$

where a is the nearest-neighbor spacing of ions in the perfect lattice. Mollwo took $n=2$, and Ivey took $n=1.84$, both on the basis of experimental evidence available at the time. In 1967, systematic experimental surveys of F -center absorption were completed by Buchenauer and Fitchen³ and by Hughes *et al.*⁴ In both cases, the results agreed well with Ivey's value of $n=1.84$.

A theoretical survey of F -center absorption and emission processes in NaCl-type alkali halides has most recently been published in 1964 by Wood and Joy.⁵ In 1968 Bartram, Stoneham and Gash,⁶ hereafter referred to as BSG, published a further theoretical survey of the absorption process. Very recently, Harker⁷ has also surveyed the absorption process, as well as hyperfine interactions of the ground state, and orbital g factors and spin-orbit coupling constants of the excited state, for 20 alkali halides (including four cesium halides). The nature of the model employed in each case is of interest. Wood and Joy⁵ took a crystal lattice of classical point ions whose nearest neighbors repel each other by a potential of the form $ba^{-\lambda}$, where a is the nearest-neighbor distance, and b and λ are constants ($\lambda=8$). They allowed for small radial displacements of the ions nearest to the F center, to second order (harmonic approximation), self-consistent with F -center wave functions whose radial dependence was of the form $r^n e^{-\beta r}$ centered on the vacancy, where β is a variational parameter and n is an integer. The F -center electron sees a static lattice of point ions and is orthogonalized to free-ion outer-shell wave functions of the nearest-neighbor ions. The Franck-Condon principle was

used, in which lattice readjustment during electronic transitions is ignored. Most of their results were for $2s$ - $3p$ transitions. They obtained agreement with experiment to within 10% for absorption, and qualitatively correct Stokes shifts.

The principal objective of the BSG paper⁶ was to develop a simple procedure for taking account of the ion-size effect in color centers. Their model lattice consisted of static point ions with nearest-neighbor repulsion of the form $ba^{-\lambda}$, with $\lambda=9$. They allowed for radial displacement of the nearest neighbors to the F center in harmonic approximation self-consistently. In addition, they included a polarization correction due to Gourary and Adrian,⁸ taking account of the imperfect screening of the vacancy by the excess electron, through its effect in polarizing the ten shells of ions nearest to the defect. They used variational, vacancy-centered trial pseudo-wave-functions (hereafter denoted PWF) of Gourary-Adrian⁸ type III for the ground state, and type II for the excited state. The necessity of orthogonalizing the F -center wave function to the occupied ion-core orbitals was taken into account by introducing the optimum pseudopotential for the smoothest PWF (appropriately, for a variational calculation), approximated by neglecting variation of the PWF over the ion cores and neglecting overlap of ion-core orbitals on different ionic sites, a procedure which is closely equivalent to that of Wood and Joy.⁵ This led to a relatively simple form of ion-size term in the Hamiltonian for the PWF, which involved sets of constants A_γ and B_γ , depending only on ion species γ , which were evaluated for free ions by the Hartree-Fock-Slater method using the Herman-Skillman program. When the results were applied to F -center absorption in the alkali halides, it was found that an empirical correction was required, namely, that A_γ be multiplied by a factor α , whose value $\alpha=0.53$ was found by least-squares fit of theory to experiment. The Franck-Condon principle was applied in analyzing the absorption process. The theoretical results agreed well with the experiment in terms of the

Mollwo-Ivey relationship and the systematic deviations from it.

Harker's recent analysis⁷ is very similar to that of BSG, except that he uses more flexible trial wave functions, and ignores lattice distortion. In our view, the use of more flexible PWF's is an important step forward, and the detailed analysis of properties other than the optical absorption energies is also important. We shall not discuss Harker's results further here, except to point out that he obtains reasonably good agreement with experimental absorption energies, except for LiI.

From the preceding account, it will be evident that the approaches taken to the problem of F -center transitions by Wood and Joy, BSG, and Harker, have been basically very similar. It has been pointed out, particularly by Wood and Joy, that this approach has several deficiencies, namely, the simplicity of the trial wave functions, the approximations involved in applying the ion-size corrections, the incomplete treatment of lattice distortion and ionic polarization, and the neglect of dynamic lattice effects. In recent years there have been major developments in the computer analysis of electronic states in crystals from first principles, and in the application of the method of lattice statics to the rigorous analysis of defects in point-polarizable-ion models of crystal lattices. The inclusion of dynamic lattice effects in the theory of electronic defects in a consistent way is also now evidently possible, and an important application has been made by Ham⁹ in an attempt to analyze the relaxed excited state of the F center in KCl, which has been shown by Bogan and Fitchen¹⁰ to be a parity mixture induced by the electron-phonon coupling.

In the present work we have removed one of the deficiencies listed above; namely, we have included lattice distortion in a fully self-consistent way, rigorously to second order in small quantities. Apart from this feature, our approach closely parallels that of BSG,⁶ with minor differences which will be specified in the next section. Basically, we use very simple trial PWF's, we neglect ionic polarizability, we apply the BSG-ion-size correction with $\alpha = 0.53$, we use a static lattice, and we apply the Franck-Condon principle. We also investigate the effect of using $\alpha = 1$, in order to show the qualitative effect of the empirical correction. We emphasize that our objective has been to provide comparisons between experimental results and the results which follow from accurate treatment of a well-defined model, rather than to force agreement between theory and experiment by *ad hoc* innovations to the model.

In this paper we analyze the results for absorption and the ground state, and in a subsequent pa-

per we shall deal with emission and the relaxed excited state. For absorption, we consider, in Sec. III, the Mollwo-Ivey relation and systematic deviations from it, and the comparison between theoretical and experimental results.

For the ground state, Sec. IV, we examine the relationship between F -center localization and lattice relaxation, and analyze the dependence of various contributions to the energy on interionic spacing a . Comparison of our PWF with spin resonance results will be the subject of a separate investigation. In Sec. II, we briefly summarize our model and method.

II. MODEL AND METHOD

The model and method of the present work are precisely those used in our previous work on the F_A center,¹¹ Sec. II. Let \vec{r} be the F -center electron's position, and let $\vec{R}_{l\kappa} \equiv \vec{R}_{l\kappa}^{(0)} + \vec{\xi}_{l\kappa}$ be the position of ion κ in unit cell l , where $\vec{\xi}_{l\kappa}$ is its small (harmonic) static displacement from perfect lattice site $\vec{R}_{l\kappa}^{(0)}$. Then we have the Hamiltonian

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V_{PI}(\vec{r}, \underline{\xi}) + V_{IS}^{\phi}(\vec{r}, \underline{\xi}) + V_L(\underline{\xi}) + \frac{1}{2} \underline{\xi} \cdot \underline{A} \cdot \underline{\xi}, \quad (2)$$

where \underline{A} is the force-constant matrix of the perfect lattice, and $\underline{\xi}$ is a column vector containing the three components of $\vec{\xi}_{l\kappa}$ for all the ions of a large lattice with periodic boundary conditions. $V_L(\underline{\xi})$ is the energy to create the vacancy, for given distortion field $\underline{\xi}$, where the ions are point charges with Born-Mayer repulsion given by Tosi,^{12,13} $V_{PI}(\vec{r}, \underline{\xi})$ is the interaction of the F -center electron with the static point-ion charges, and from BSG,⁶ V_{IS} is the ion-size correction, discussed in more detail in Sec. IV D, and $-\hbar^2 \nabla^2 / 2m$ is the electron's kinetic energy. For the ground state, we use a Gaussian-localized spherically symmetric trial PWF, normalized

$$\phi(\vec{r}, \lambda) = (2\lambda^2/\pi)^{3/4} e^{-\lambda^2 r^2}, \quad (3)$$

where λ is the variational parameter. The ground-state energy is evaluated as the sum of two terms

$$E_0 = \langle \phi | H | \phi \rangle = E_0^{(0)} + E_d, \quad (4)$$

where $E_0^{(0)}$ is the expectation value of H neglecting lattice distortion (i.e., with $\underline{\xi} = 0$), minimized with respect to λ , giving a zero-order value $\lambda^{(0)}$. Thus

$$E_0^{(0)} = \langle \phi^{(0)} | \frac{-\hbar^2 \nabla^2}{2m} + V_{PI}(\vec{r}, \underline{0}) + V_{IS}^{\phi^{(0)}}(\vec{r}, \underline{0}) + V_L(\underline{0}) | \phi^{(0)} \rangle, \quad (5)$$

where $\phi^{(0)} \equiv \phi(\vec{r}, \lambda^{(0)})$, with $\lambda^{(0)}$ determined from

$$\frac{\partial E_0^{(0)}}{\partial \lambda^{(0)}} = 0. \quad (6)$$

In Eq. (5) we denote the separate terms as follows:

$$E_0^{(0)} = \bar{T} + \bar{V}_{PI} + \bar{V}_{IS} + V_L(0), \quad (7)$$

i.e., a sum of kinetic, point-ion, ion-size, and lattice defect energies, all neglecting lattice distortion. We emphasize that the minimization, Eq. (6), is complicated by the fact that V_{IS}^ϕ is a functional in ϕ through the quantity \bar{V} [see Sec. IV D, Eq. (22) and (23)]; that is, we have a self-consistent-field problem. Once we have evaluated $E_0^{(0)}$ and $\lambda^{(0)}$, we apply a perturbation-iteration procedure to the Kanzaki method^{14, 15} to determine ξ and a corrected value of $\lambda \neq \lambda^{(0)}$ self-consistently. This yields the term denoted E_d in Eq. (4): the contributions due to lattice relaxation ξ , plus corrections to \bar{T} , \bar{V}_{PI} , and \bar{V}_{IS} arising from readjustment of λ from $\lambda^{(0)}$ to its final self-consistent value. For the final state of the absorption process, i.e., the unrelaxed excited state, the trial PWF is taken to be of the form $\phi'(\vec{r}, \lambda) \sim r \cos \theta \exp(-\lambda^2 r^2)$, and the energy $E_1 = \langle \phi' | H | \phi' \rangle$ is minimized only with respect to λ , while ξ is held fixed in the distorted configuration which has been determined for the ground state.

It will be seen that our results do not fully agree with those previously obtained by Brown and Vail¹⁶ for KCl and NaCl, ostensibly using an identical

procedure. The reason is that the present calculation has been increased in accuracy in two respects, namely, in the self-consistent variational treatment of \bar{V} in V_{IS} [see Eqs. (22) and (23)], and in a certain sum over ions which occurs in the perturbation-iteration solution for ξ .

III. RESULTS: ABSORPTION

A. Mollwo-Ivey relation

In Table I we show our theoretical results for F -center absorption energies in sixteen crystals, for values $\alpha = 0.53$ and $\alpha = 1$ of the BSG empirical parameter, giving the experimental results and the theoretical results of BSG, and of Wood and Joy for comparison, and also the values of interionic spacing a and ionic radii ratios R . In order to survey the results we first consider a Mollwo-Ivey plot, Eq. (1), for the five sets of absorption energies given in Table I. These plots are taken of the form

$$\ln(\Delta E_i) = \ln(\Delta E_j) - n \ln(a_i), \quad (8)$$

$$i = 1, 2, \dots, 16,$$

and $\ln(\Delta E_j)$ and n are determined by a least-squares fit to the data. The results are shown in Table II, including the coefficient of correlation r ,

TABLE I. F -center absorption energies (Ry), present work denoted OV, where α is BSG empirical factor (Ref. 6). Also nearest-neighbor spacing a (units Bohr radii a_0), and ratio R of negative-to-positive ion radii.

Crystal	Absorption energies						
	OV $\alpha = 0.53$	OV $\alpha = 1$	Expt. ^a	BSG ^b $\alpha = 0.53$	Wood and Joy ^c	a^d	R^e
LiF	0.404	0.630	0.378	0.386	0.337	3.80	1.96
LiCl	0.253	...	0.243	0.242	0.237	4.86	2.66
LiBr	0.218	0.144	0.199	0.208	0.215	5.20	2.88
LiI	0.192	0.253	0.240	0.184	...	5.68	3.22
NaF	0.310	0.399	0.274	0.278	0.256	4.39	1.36
NaCl	0.211	0.202	0.204	0.201	0.200	5.33	1.85
NaBr	0.188	0.120	0.173	0.176	0.183	5.65	2.00
NaI	0.167	0.175	0.153 ^g	0.160	...	6.11	2.23
KF	0.225	0.440	0.206	0.202	0.206	5.05	1.00
KCl	0.173	0.256	0.172	0.161	0.176	5.95	1.36
KBr	0.156	0.176	0.153	0.146	0.166	6.24	1.47
KI	0.141	0.188	0.138	0.135	...	6.69	1.65
RbF	0.145	0.369	0.179	0.169	...	5.32	0.90
RbCl	0.147	0.256	0.149	0.140	...	6.23	1.22
RbBr	0.137	0.183	0.136	0.128	...	6.52	1.32
RbI	0.126	0.187	0.126	0.121	...	6.95	1.48

^aReference 6, Table III, from Ref. 4.

^bReference 6, Table III.

^cReference 5, Tables II, III, and IV.

^dFrom Ref. 13.

^eC. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1966), p. 105.

^fSelf-consistency of \bar{V} Eqs. (22) and (23), could not be achieved.

^gFrom Ref. 3.

TABLE II. Mollwo-Ivey parameters, Eq. (1), and coefficient of correlation r , for the data of Table I.

	OV		Expt.	BSG $\alpha = 0.53$	Wood and Joy
	$\alpha = 1$	$\alpha = 0.53$			
ΔE_I	7.39	4.88	3.76	4.54	2.13
n	1.99	1.89	1.75	1.88	1.41
r	-0.707	-0.952	-0.955	-0.984	-0.988

measuring the closeness of fit ($|r| = 1$ is a perfect fit). Two simple qualitative facts emerge: (i) the theoretical results of Wood and Joy agree well with the experimental absorption energies, but have a Mollwo-Ivey exponent n which is somewhat smaller than the experimental value, with a closeness of fit somewhat better than experiment; and (ii) that the present calculations, when $\alpha = 1$ is used, give absorption energies which are mostly higher than the experimental values, and a Mollwo-Ivey plot whose exponent n is somewhat larger and whose closeness of fit is much poorer, than those for the experimental data. Henceforth we shall concentrate on comparisons among the results of experiment, BSG, and the present work with $\alpha = 0.53$.

B. Deviations from the Mollwo-Ivey relation

The systematic deviation from the Mollwo-Ivey relation for *F*-centers in crystals with small values of R has been discussed by Buchenauer and Fitchen (Ref. 3, Sec. IV C, Fig. 6), and BSG have similarly analyzed their own results (Ref. 6, Fig. 2). Both of these works include CsF, whereas the present work does not. CsF provides the largest deviation from the Mollwo-Ivey plot. Nevertheless, we have analyzed our results, as well as those of BSG and experiment, in terms of a curve of the form introduced by BSG [Ref. 6, Eq. (4.22)]:

$$\Delta E_i = \Delta E_{Ii} [A - B \exp(-CR_i)], \quad i = 1, 2, \dots, 16, \quad (9)$$

where A , B , and C are constants, R_i are given in Table I, and ΔE_{Ii} are the values of the transition energies which would occur if they satisfied the appropriate Mollwo-Ivey relationship exactly. The

TABLE III. Mollwo-Ivey parameters, Eq. (1), and coefficient of correlation r , from data of Table I, omitting the worst point in each case.

	OV		BSG $\alpha = 0.53$
	$\alpha = 0.53$	Expt.	
ΔE_I	5.37	3.79	4.72
n	1.94	1.77	1.90
r	-0.996	-0.989	-0.992

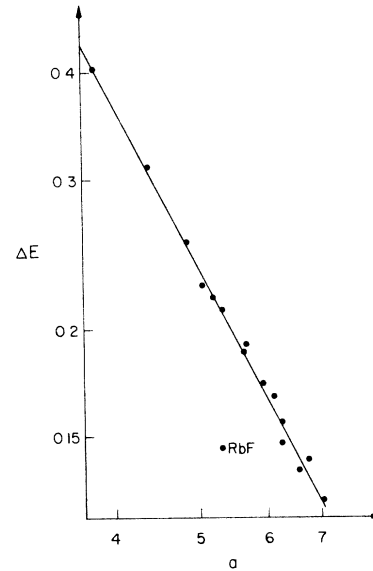


FIG. 1. Mollwo-Ivey plot of calculated transition energy ΔE (Ry) vs nearest-neighbor spacing a (Bohr radii) on log-log scale. Straight line is least-squares fit omitting RbF (see Table III).

actual Mollwo-Ivey plots reveal that in each case, one point lies well off the curve, namely, LiI in the experimental results, and RbF in the theoretical results (BSG and the present work). Accordingly, we have redetermined the Mollwo-Ivey parameters in Table III, omitting the worst point in each case. The Mollwo-Ivey plot for our data, using the results of Tables I and III, is shown in Fig. 1.

In order to display the deviations of our results from the Mollwo-Ivey relation, we plot $\Delta E_i / \Delta E_{Ii}$ vs $\ln R_i$ in Fig. 2, as BSG did, using Table III. From our Fig. 2 compared to BSG's Fig. 2, we observe several qualitative differences. First, ignoring the four host crystals with the smallest values of R (and also CsF in BSG), the scatter is somewhat less in our results than for BSG and experiment. Second, the theoretical points for the iodides of K, Na, and Li lie systematically above the rest, unlike the experimental points. Third, the theoretical deviations of RbF, RbCl, and RbBr are significantly larger than those from experiment. The latter two comments, relating to the heaviest cation with light anions, and the heaviest anion with light cations, suggest inaccuracy in the ion-size correction. The most extreme deviations, for LiI experimentally, with which theory and the Mollwo-Ivey relation disagree, and for RbF theoretically, disagreeing with experiment and Mollwo-Ivey, also point to the ion-size correction as defective.

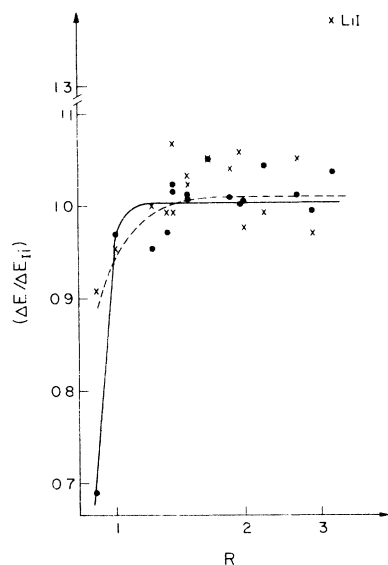


FIG. 2. Deviations from Mollwo-Ivey plots ΔE_I (Table III) for experimental (x) and calculated (solid circle) transition energies ΔE as functions of anion-to-cation radii ratio R , compared to curves fitted to Eq. (9) (see Table III) with C minimizing $|\tau|$. Note break in vertical axis.

C. Deviations from experiment

In Fig. 3 we show the deviation of theoretical results from experiment as a function of lattice spacing a . We observe that, apart from LiI and the four fluorides, there is a small linear downward trend with a for the remaining halide series. The plotted lines are least-squares fits. This trend probably arises from the ion-size correction,

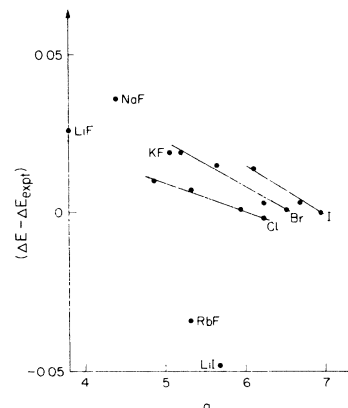


FIG. 3. Deviation of calculated results from experiment $\Delta E - \Delta E_{\text{expt}}$ (Ry) vs nearest-neighbor spacing a (Bohr radii) with straight-line least-squares fits to chloride, bromide, and iodide (omitting LiI) series.

whose parameter $\alpha = 0.53$ was derived by BSG without fully self-consistent lattice relaxation. The split-up into halide series will be seen to be characteristic of the ion-size correction.

IV. GROUND STATE

In Table IV our results are presented for the ground-state energy and the various terms contributing to it [Eq. (4), (5), and (7)], as well as the localization parameter λ for the trial PWF, Eq. (3), and the x component of displacement $u_x(1, 0, 0)$ of a nearest-neighbor ion at 100. The data of Table IV were obtained with the BSG parameter $\alpha = 0.53$. Since the results for $\alpha = 1$ fail to agree with the experimental absorption energies, we shall not dis-

TABLE IV. F -center ground-state energies E_0 calculated with $\alpha = 0.53$, showing various contributions [see Eqs. (4), (5), and (7)]; also localization parameter λ (units a^{-1}) and nearest-neighbor displacement u_x (units a), with positive displacement outward.

Crystal	\bar{T}	\bar{V}_{IS}	\bar{V}_{PI}	$V_L(0)$	E_d	E_0	λ	$u_x(1, 0, 0)$
LiF	0.247	0.058	-0.835	0.797	-0.0014	0.266	1.108	-0.018
LiCl	0.162	0.0305	-0.665	0.640	-0.0029	0.165	1.157	-0.029
LiBr	0.138	0.022	-0.618	0.604	-0.0024	0.144	1.144	-0.027
LiI	0.125	0.020	-0.576	0.549	-0.0040	0.114	1.193	-0.039
NaF	0.193	0.036	-0.732	0.697	-0.0029	0.191	1.142	-0.030
NaCl	0.137	0.0225	-0.609	0.595	-0.0027	0.143	1.173	-0.029
NaBr	0.120	0.017	-0.572	0.561	-0.0027	0.123	1.168	-0.029
NaI	0.109	0.016	-0.536	0.517	-0.0036	0.102	1.207	-0.036
KF	0.134	-0.016	-0.622	0.616	-0.0165	0.096	1.141	-0.075
KCl	0.107	0.003	-0.542	0.535	-0.0066	0.096	1.174	-0.047
KBr	0.098	0.003	-0.518	0.514	-0.0052	0.092	1.175	-0.042
KI	0.091	0.007	-0.491	0.481	-0.0056	0.082	1.214	-0.045
RbF	0.113	-0.049	-0.580	0.594	-0.0300	0.048	1.132	-0.102
RbCl	0.094	-0.011	-0.513	0.518	-0.0092	0.079	1.155	-0.055
RbBr	0.086	-0.009	-0.491	0.494	-0.0078	0.072	1.163	-0.052
RbI	0.082	-0.001	-0.469	0.468	-0.0066	0.073	1.197	-0.048

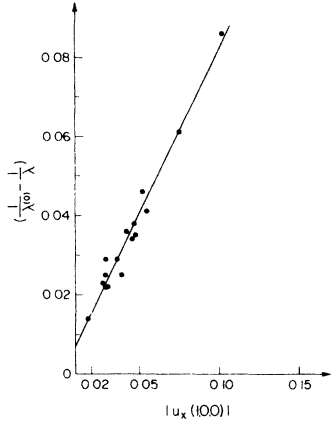


FIG. 4. Change $1/\lambda^{(0)} - 1/\lambda$ of PWF localization (units a) vs nearest-neighbor relaxation $u_x(1, 0, 0)$, with straight-line least-squares fit, Eq. (12).

Discuss this case further, but details of the sort given in Table IV are available from the authors on request.

A. Localization and lattice distortion

It is possible to see from our results how the *F*-center wave function responds to lattice relaxation, because \bar{T} in Table IV is evaluated without lattice distortion (see Sec. II), whereas λ in Table IV is self-consistent with the lattice distortion. If $\lambda^{(0)}$ is the zero-order (lattice unrelaxed) value of λ , then

$$\bar{T} = 3(\lambda^{(0)})^2/a^2, \quad (10)$$

in Rydberg units, with $\lambda^{(0)}$ in units of $1/a$, and a in units of the Bohr radius a_0 . If we compare λ and $\lambda^{(0)}$, both seen as functions of lattice spacing a , then we observe that (i) λ and $\lambda^{(0)}$ are nearly constant ($\lambda^{(0)}$ would be strictly constant in units of a , without the ion-size correction); (ii) they break up into halide series; (iii) the scatter of λ is less than that of $\lambda^{(0)}$; and (iv) $\lambda > \lambda^{(0)}$ or $1/\lambda < 1/\lambda^{(0)}$; i.e., the size of the *F* center decreases with lattice relaxation, which from Table IV is seen to be inward in this model.

Intuitively, we might expect the reduction in *F*-center size to be equal to the inward shift of the nearest neighbors, i.e.,

$$1/\lambda^{(0)} - 1/\lambda = |u_x(1, 0, 0)|, \quad (11)$$

in units of a . In Fig. 4, we plot $1/\lambda^{(0)} - 1/\lambda$ vs $|u_x(100)|$, and we find that a least-squares fit is given by

$$1/\lambda^{(0)} - 1/\lambda = 0.834 |u_x(1, 0, 0)| - 0.001. \quad (12)$$

Thus, we see that the simple intuitive idea is qualitatively correct, but that quantitatively it is in er-

ror by about 17%.

Finally we note that, for KCl, Kersten¹⁷ has deduced from experiment a value +0.010 for $u_x(1, 0, 0)$, opposite in direction to our result.

B. Zero-order point-ion energy

A very simple picture of the *F* center would be to treat the ions as charged points with Born-Mayer repulsion, and neglect lattice relaxation. Then the energy would be

$$E_{\text{PI}}^{(0)} = \bar{T} + \bar{V}_{\text{PI}} + V_L(0). \quad (13)$$

We can estimate these three terms as follows. First, $\bar{T} = 3(\lambda^{(0)})^2/a^2$ Ry, as in Eq. (10). Second, the point-ion potential may be taken as roughly hydrogenic

$$\begin{aligned} \bar{V}_{\text{PI}} &= \langle \phi^{(0)} | \sum_{ik} \frac{-eq_k}{|\vec{r} - \vec{R}_{ik}|} | \phi^{(0)} \rangle \\ &\approx \langle \phi^{(0)} | \frac{-e^2}{r} | \phi^{(0)} \rangle, \end{aligned} \quad (14)$$

which in Rydbergs is

$$\bar{V}_{\text{PI}} = -4(2/\pi)^{1/2} \lambda^{(0)}/a = -3.19(\lambda^{(0)}/a). \quad (15)$$

Third,

$$V_L(0) = c_M e^2/a - 6B(a)e^{-\rho/a}, \quad (16)$$

where c_M is the Madelung constant. Since we do not have simple formulae for the Born-Mayer parameters B and ρ as functions of a , let us neglect this term for our rough approximation. Then in rydbergs

$$V_L(0) \approx \frac{2c_M}{a} = \frac{3.50}{a}. \quad (17)$$

If we now combine Eqs. (10), (15), and (17), and in Eq. (10) use the average value $\lambda_{\text{av}}^{(0)} = 1.12$, we obtain from Eq. (13)

$$E_{\text{PI}}^{(0)} \approx (3.76/a^2) - (0.073/a) \text{ Ry} \quad (18)$$

In Fig. 5 we plot the calculated values of $\bar{T} + \bar{V}_{\text{PI}} + V_L(0)$ from Table IV, vs a , and the right-hand side of Eq. (18) as a dashed line. While there is qualitative agreement between the rigorously calculated data from Table IV and the rough approximation, Eq. (18), a least-squares fit to the data is shown by the solid line in Fig. 6, and is given by

$$E_{\text{PI}}^{(0)} \text{ fitted} = \frac{1.925}{a^2} - \frac{0.273}{a} \text{ Ry}. \quad (19)$$

The numerical coefficients in Eq. (18) and (19) are quite different, but the form of dependence on a predicted by the rough approximation is correct. We should point out that the data of Table IV are based on values of $\lambda^{(0)}$ which are derived from a zero-order Hamiltonian which contains V_{IS} . So,

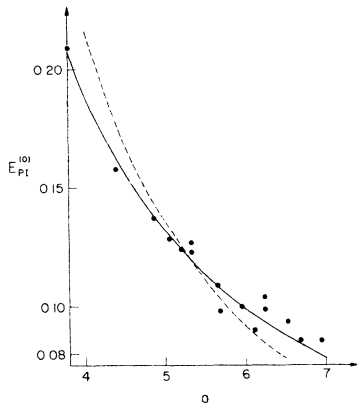


FIG. 5. Zero-order point-ion energy $E_{PI}^{(0)}$, Eq. (13) (Ry) vs lattice spacing a (Bohr radii), with solid line least-squares fit, Eq. (19), and dashed-line rough estimate, Eq. (18).

the data plotted in Fig. 5 are not strictly those that would be calculated from the simple point-ion model.

C. F center as replacement for the anion

One commonly thinks of the F center as a localized negative charge which replaces a negative ion in the lattice. To what extent is this replacement complete? First we note that $V_L(0) + \bar{V}_{PI}$ gives the difference in negative potential between the original anion and an F center in state $\phi^{(0)}$, ignoring lattice relaxation and the ion size contribution to the electron's potential energy. From the data of Table IV we conclude (i) that the difference is very small; (ii) with the exception of three rubidium salts, the F center has more negative potential energy than the anion; and (iii) the difference rises monotonically in halide series, as functions of a . When the ion-size correction \bar{V}_{IS} is added to $V_L(0) + \bar{V}_{PI}$ we see that (i) for the halide series other than the fluorides, the deviations from zero are reduced; and (ii) the halide series are turned downwards, as functions of a .

D. Ion-size correction

The ion-size correction is given explicitly⁶ by

$$\bar{V}_{IS} = \sum_{I\kappa} [A_{I\kappa} + B_{I\kappa}(\bar{V} - U_{I\kappa})] |\phi(\vec{r} = \vec{R}_{I\kappa})|^2, \quad (20)$$

where

$$\bar{V} = \langle \phi | V_{PI} + V_{IS} | \phi \rangle / \langle \phi | \phi \rangle \quad (21)$$

and

$$U_{I\kappa} = \sum_{\substack{I' \neq I \\ \kappa' \neq \kappa}} V_{PI}(I', \kappa'), \quad (22)$$

where $A_{I\kappa}$ and $B_{I\kappa}$ are constants which depend only on the ionic species κ . Let us seek a simple approximation to Eq. (20). For the ground state we have, ignoring lattice distortion, $\phi = \phi^{(0)}$, and let $\lambda^{(0)} \approx \lambda_{av}^{(0)} = 1.12$, as before. Also, write $|\vec{R}_{I\kappa}^{(0)}| \approx |\mathbf{R}_{I\kappa}^{(0)}| = n_{I\kappa} a$, and let us neglect all but the six nearest neighbors, for which $n_{I\kappa} = 1$, and the 12 second neighbors, for which $n_{I\kappa} = \sqrt{2}$. Then

$$|\phi^{(0)}(\vec{R}_{I\kappa}^{(0)})|^2 = (2/\pi)^{3/2} [(1.12)^3/a^3] e^{-2(1.12)^2 n_{I\kappa}^2}. \quad (23)$$

In zeroth order, we neglect the contribution of V_{IS} to \bar{V} , so

$$\bar{V}^{(0)} \approx \langle \phi^{(0)} | V_{PI} | \phi^{(0)} \rangle = \bar{V}_{PI}. \quad (24)$$

If we fit \bar{V}_{PI} to LiF of the form a^{-1} , then we obtain

$$\bar{V}^{(0)} \approx -3.173/a \text{ Ry}. \quad (25)$$

Furthermore, for nearest and second-nearest neighbors

$$U_{(+)}^{(0)} = [(c_M e^2/a) - e^2/a] - 1.495/a \text{ Ry}, \quad (26)$$

$$U_{(-)}^{(0)} = [(-c_M e^2/a) - (e^2/\sqrt{2}a)] - 4.909 \text{ Ry}. \quad (27)$$

If we combine Eqs. (23) and (25)–(27) with the correct values of $n_{I\kappa}$ in Eq. (20), we obtain

$$\begin{aligned} \bar{V}_{IS}^{(0)} = & (0.3484/a^3) [(A_{(+)} + 0.1627A_{(-)}) \\ & + (1/a)(-4.668B_{(+)} + 0.2824B_{(-)})]. \end{aligned} \quad (28)$$

For a given halide series, $A_{(-)}$ and $B_{(-)}$ are fixed constants, and $A_{(+)}$ and $B_{(+)}$ must be regarded as functions of a , monotonic increasing, as it happens, from BSG.⁶ Equation (28) is plotted for the fluorides and iodides, along with the rigorously calculated values for \bar{V}_{IS} from Table IV, in Fig. 6. The agreement is quite good.

If \bar{V}_{IS} is plotted as a function of negative-to-positive ion radii ratio R , the points for different ha-

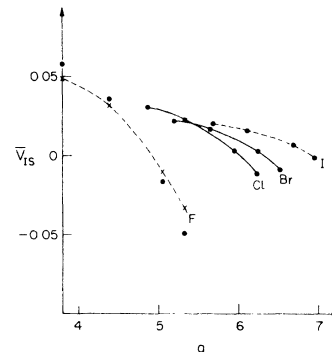


FIG. 6. Ion-size correction \bar{V}_{IS} (Ry) vs lattice spacing a (Bohr radii) showing halide series (solid lines for chlorides and bromides), and zero-order estimate, Eq. (28), as dashed lines for fluorides and iodides.

lides lie on curves which are segments of a single curve, i.e.,

$$\bar{V}_{\text{IS},h} = A - Be^{-CR} - D_h, \quad (29)$$

with different vertical displacements D_h for different halide series h . The fit of the calculated values to Eq. (29) is very good, having a rms deviation of 1.3×10^{-3} . We have been able to show that Eqs. (28) and (29) are consistent, but the latter is much more accurate, though deduced empirically.

V. SUMMARY AND CONCLUSION

The absorption energy and ground-state properties have been evaluated for the F center in 16 alkali halides in the point-ion model with ion-size correction, including lattice distortion. The results for absorption, Fig. 3, agreed well with experiment, and deviated slightly and systematically, except for LiI and the four fluorides. The relationship between F -center localization and nearest-neighbor relaxation Fig. 4, was qualitatively as expected, as were the point-ion results for ground-state energy as a function of lattice spacing

α , without ion-size correction or lattice distortion (Fig. 5). A simple formula, Eq. (28), was derived for the ion-size correction \bar{V}_{IS} as a function of α , which was found to be reasonably accurate for the separate halide series, and a very accurate empirical formula, Eq. (29), was deduced for \bar{V}_{IS} as a function of ionic radii ratio R .

This work is a survey of the results which are provided by rigorous treatment of a rather simple model. Particularly in the detailed comparison with experiment, Sec. III, it demonstrates the need for improvement of the model (ion-size correction, polarizable ions), and increased accuracy (flexibility) in the trial wave function.

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