

Theoretical Analysis of the Type-I $F_A(\text{Na})$ and Type-II $F_A(\text{Li})$ Centers in KCl in a Point-Ion Model*

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Energy levels for the type-I and type-II F_A centers in KCl:Na and KCl:Li, respectively, are estimated variationally using Gaussian-localized trial wave functions for the excess electron, and a point-ion model for the defect lattice. The ion-size correction of Bartram, Stoneham, and Gash is used, and the ions are taken to be unpolarizable with Coulomb interaction plus Tosi's single-exponential form of Born-Mayer repulsion as devised for perfect KCl, NaCl, and LiCl lattices. The energies of quasistationary and ground states are estimated by self-consistent minimization with respect to trial-wave-function parameters and ionic displacements, using the method of lattice statics as modified for the case of an excess-electron defect with nonharmonic lattice distortion. Absorption is treated as a Franck-Condon transition, assuming C_{4v} symmetry, giving estimates of the F_{A1} energies in reasonable agreement with experiment, but with F_{A1} - F_{A2} splittings about three times too large. Energies for the relaxed excited state (RES) in vacancy and saddle-point configurations are also estimated. For the $F_A(\text{Li})$ center, the vacancy RES, which is not manifested experimentally, is found to have higher energy than the saddle-point RES, as expected. However, the $F_A(\text{Na})$ center is also found to stabilize (though just barely) in the saddle-point configuration in this treatment, contrary to experimental fact. The model and approximations used here do not properly describe the saddle-point emission of the $F_A(\text{Li})$ center, but do adequately estimate the reorientation energies of both $F_A(\text{Na})$ and $F_A(\text{Li})$ centers. The role of the impurity alkali ion (Na^+ and Li^+ , respectively) in lowering the even- and odd-parity activation energies of the F center is analyzed in detail, and it is found to contribute about equally through its effects on the lattice energy and on the point-ion potential for the excess electron. Qualitative conclusions are drawn about the usefulness of this sort of calculation in analyzing this kind of defect.

I. INTRODUCTION

The type-I or type-II F_A center¹ in KCl is basically an F center adjacent to a substitutional impurity Na^+ or Li^+ ion, respectively. Perhaps the most striking single feature² of these centers occurs in the type-II $F_A(\text{Li})$ center where, following absorption of a photon by the center, the lattice relaxes from a vacancy configuration to a saddle-point configuration (Fig. 1), from which emission occurs, followed by lattice relaxation to a vacancy-configuration ground state. This implies that the relaxed excited state (RES) in the saddle-point configuration has lower energy than the RES in the vacancy configuration. Details of the absorption and emission processes,³ as well as reorientation and dissociation activation energies⁴ for both $F_A(\text{Na})$ and $F_A(\text{Li})$ centers, and the behavior of the Li^+ impurity ion in the $F_A(\text{Li})$ center's ground state,^{5,6} have all been studied experimentally some time ago. The energy levels which relate to the two configurations of Fig. 1 are shown in Figs. 2(a) and 2(b). In the caption of Fig. 2, the F_{A1} - F_{A2} absorption splitting refers to the splitting between the two absorption lines from the ground state, corresponding to the two inequivalent orientations of the (unrelaxed) excited-state wave function.⁷

The absorption processes of both the $F_A(\text{Na})$ and $F_A(\text{Li})$ centers have been studied in three previous

theoretical investigations.^{8-10(a)} Two other investigations^{10(b)} have analyzed $F_A(\text{Na})$ absorption only. Experience with the ordinary F center in KCl has shown¹¹ that moderately good agreement with experiment can be obtained for ordinary F -center absorption from a wide variety of theoretical approaches, and the F_{A1} - F_{A2} splitting phenomenon in F_A centers will also be obtained in any reasonable theoretical approach, since it merely reflects the reduction of the F center's symmetry by the impurity alkali ion. The real question is how accurately does a given approach reproduce the experimental results, and what role do various elements

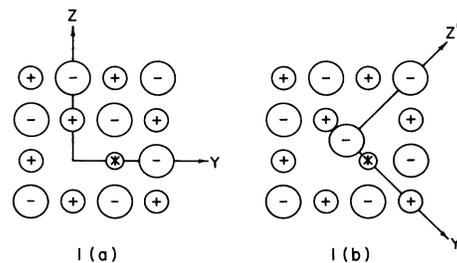


FIG. 1. Vacancy and saddle-point configurations of the lattice for F_A centers in KCl. Ions marked (+) are potassium, (-) are chlorine, and (*) are impurity alkalis (Na^+ or Li^+). (a) Vacancy configuration; (b) saddle-point configuration.

of the model play in the shift and splitting of the F_A absorption line, relative to the F -center absorption. Smith⁸ evaluated the F -center absorption and the F_{A1} and F_{A2} absorption energies of the F_A centers, taking account of the electronic structure of nearest-neighbor ions by using a pseudopotential method, while excluding lattice distortion and ionic polarization. Weber and Dick⁹ evaluated the energy shifts of the ground and excited (F_{A1} and F_{A2}) states of the F_A center relative to the corresponding F -center levels, using the approximate ion-size correction of Bartram *et al.*¹² (hereafter referred to as BSG), without the empirical factor 0.53, and excluding lattice distortion and ionic polarization. Alig^{10(a)} evaluated the energy shifts of F_{A1} and F_{A2} absorptions of the F_A centers relative to the F -center absorption, basically using the BSG ion-size correction without the 0.53 factor, but he also included studies of the effects of nearest-neighbor displacements, ionic polarization,

and corrections to the BSG approximation. In all three of these investigations, type-I Gourary-Adrian wave functions¹³ were used (among others), but only Weber and Dick made them self-consistent with the lattice potential. In all three treatments, and in the present work, dynamical lattice effects are ignored. In Sec. III the results of Refs. 8-10(a), and of the present work, will be compared in detail for the absorption processes of the F_A (Na) and F_A (Li) centers in KCl.

The main purpose of the present work was to investigate the saddle-point states of the type-II F_A center in KCl:Li, following an earlier investigation of such states for the ordinary F center in KCl.^{14,15} The main question was whether a conventional point-ion model of the ionic crystal would exhibit stabilization of the RES in the saddle-point, as opposed to the vacancy, configuration (Fig. 1). This would require an estimate of the RES energy in both configurations. Furthermore, it would be of interest to estimate the reorientation activation energies of the F_A centers in the ground state and compare them with the corresponding F -center process. This would also require energy-level estimates in both configurations. Also, it would be desirable to see how the model would describe the absorption and emission processes of the F_A centers. Finally, it would be interesting to see whether the basic difference between type-I F_A (Na) and type-II F_A (Li) centers emerges from the treatment. This difference, wherein the F_A (Na) center behaves like a perturbed F center, with its RES and emission occurring in the vacancy configuration, while the F_A (Li) center emits in the saddle-point configuration, is expected to be a sensitive test of the theory.¹⁶ It turns out that our treatment fails this test.

It seems obvious that, in an investigation which involves two quite different lattice configurations, the lattice energy will need to be taken into account carefully. Consequently our model and method, which are fully described in Sec. II, deal accurately with the distortions of a discrete-ion lattice, and treat the excess electron self-consistently. While our model and method are relatively simple for their kind, they lead to one of the more extensive computations undertaken to date in defect studies, and the results obtained, which are summarized in Sec. III, cast considerable new light on the theory of radiative and reorientation processes of F_A centers in KCl. In Sec. IV we discuss possible improvements to our procedure and draw some general conclusions.

An important element in the rationale of this investigation has been a desire to contribute to the understanding of just how well current models of ionic crystals can describe the properties of defects. We have therefore resisted the temptation

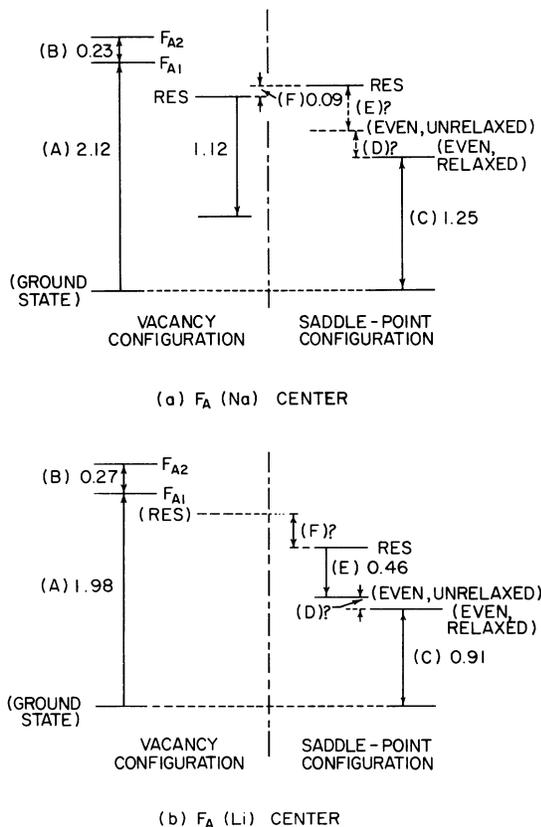


FIG. 2. Experimental energies (in eV), from Ref. 1, for F_A centers in KCl. Energy difference (A) is the F_{A1} absorption, (B) is the F_{A1} - F_{A2} absorption splitting, (C) is the reorientation activation energy, (D) is the even-parity saddle-point relaxation energy, (E) is the saddle-point emission energy, and (F) is the stabilization energy of the RES.

to introduce arbitrary modifications of the model, or to vary our methods or approximations from one energy level to another to improve agreement with experiment, and we have taken care to lay out the calculation and results in such a way that future investigations, directed at systematically improving or modifying the model and method, can yield clear results.

II. MODEL AND METHOD

The model and method are very similar to those described in Secs. 1 and 2 of Brown and Vail,¹⁴ hereafter referred to as BV-I.

A. Ion-Ion Interaction

We begin with a defect lattice of unpolarizable charged point ions interacting through Coulomb forces, and including nearest-neighbor perfect-lattice Born-Mayer repulsion. In BV-I, the Born-Mayer parameters used in the defect were taken from Born and Huang.¹⁷ In the present work, the so-called single-exponential (SE) parameters of Tosi^{18,19} were used, which include correction for finite temperature; that is, perfect-lattice KCl parameters were used in the K^+-Cl^- interaction, and perfect-lattice NaCl or LiCl parameters were used for the interaction of the impurity Na^+ or Li^+ ion with nearest-neighbor Cl^- ions. It is a fundamental question whether perfect-lattice repulsive potentials can be successfully applied in a given defect problem. Tosi has concluded¹⁸ that reasonable results can be obtained for vacancy-migration activation energies in KCl, and since a vacancy, being a charged defect, may be expected to induce more lattice distortion and polarization than an uncharged F or F_A center would, we have felt justified in our present approach. If future investigations indicate that the perfect-lattice repulsive potential is responsible for some major inadequacy of the results, then we believe that it would be best to work with a many-electron description of the ions, rather than to introduce empirical modifications of the Born-Mayer potential.

The harmonic part of the lattice-distortion field is described in terms of the dynamical matrix of Kellermann²⁰ for KCl, incorporating corrections due to Stoneham.^{21(a)}

B. Electron-Lattice Interaction

The electron-lattice interaction is based on the assumption of a static lattice for all states under consideration in the present work. The excess electron of the F_A center sees the Coulomb charges of the point ions, and its wave function can be approximated from a variational estimate of the pseudo-wave-function which satisfies the Schrödinger equation based on the approximate semiempirical pseudopotential of BSG,¹² which includes

an ion-size correction. The BSG pseudopotential is approximate in that it is based on free-ion wave functions and neglects variation of the excess-electron's wave function over the ion cores, and is semiempirical in that an empirically determined parameter $\alpha = 0.53$ is introduced, multiplying the coefficients A_i [Ref. 12, Eqs. (2.21)–(2.23) and Secs. IV B and IV D]. Both Weber and Dick,⁹ and Alig^{10(a)} have found that F_A -center results agree better with experiments in their treatments if $\alpha = 1$ is used rather than $\alpha = 0.53$. However, as BSG have shown, $\alpha = 1$ does *not* give good agreement with experiments for the absorption energies of ordinary F centers. We have chosen to take $\alpha = 0.53$ throughout the present work. Again, if future investigations indicate that a major inadequacy of the model is the incorrect value of α , then we feel that more accurate treatment of the pseudopotential^{10(a),22,23} would be more appropriate than arbitrary readjustments of α to fit special cases.

C. Lattice Distortion and Defect Configuration

Having described our model qualitatively, let us now proceed to its formulation. We wish to estimate the energy of the whole defect system, electron plus lattice, in several states, in both vacancy and saddle-point configurations (Fig. 1). We refer to "relaxed" states as those in which the lattice around the defect has relaxed so as to produce a relative minimum for the system's energy in the presence of the excess electron in a given quantum state. Similarly, an "unrelaxed" state is one in which such energy minimization has not occurred. These unrelaxed states occur as the final states of electromagnetic transitions (photon absorption or emission) in the Franck-Condon approximation, in which it is assumed that the transition occurs in a time very short compared to the relaxation time of the lattice. Ideally, we should work with eigenstates of the excess electron in the presence of the lattice. (Recall that we treat the lattice as static; that is, we assume the validity of the adiabatic approximation.) However, since we include the BSG ion-size correction¹² in our formulation, we must deal with the pseudoeigenstates, and since we do not expect to be able to solve for these exactly, we shall estimate them variationally. For relaxed states this means that the total energy of the defect system must be self-consistently minimized with respect to both the lattice distortion and the excess electron's trial form of pseudo-wave-function.

The technique for estimating defect energies in discrete lattices, the so-called method of lattice statics, or the Kanzaki method,^{24,25} is based on working from a model of the perfect lattice. We express the defect-system's energy as the energy of a perfect lattice, plus corrections. In discussing the resultant distorted defect-lattice configura-

tion, it is important to distinguish between two classes of ions: (a) those which were present in the original perfect lattice before the defect was created, and which are still present and are located near their original sites after the defect has been created; and (b) those which do not satisfy criterion (a). To be precise, the ions in class (a) must be host-lattice ions whose displacements from perfect-lattice sites are within the range of validity of the harmonic approximation. We denote the region of the defect lattice occupied by such ions as region II, and the rest of the lattice as region I. The latter, region I, will be of small extent for a point defect. For the F_A center in KCl, in its ground state [vacancy configuration, Fig. 1(a)], region I consists of the vacancy site plus the substitutional impurity alkali ion. In the saddle-point configuration [Fig. 1(b)] in our model it turns out that region I contains not only the saddle-point ion, the two vacant anion sites, and the alkali impurity, but also the K^+ ion nearest to the saddle point, which is pushed away from its original site by the saddle-point Cl^- ion by a relatively large, nonharmonic amount.

D. Evaluation of the Energy

Let us now write down an expression for the energy of an electronic defect in a crystal. It will be equal to the expectation value of the pseudopotential Hamiltonian with respect to the pseudoeigenfunction. In detail, it is

$$E = U^{(0)} + \frac{1}{2} \underline{\xi} \cdot \underline{A} \cdot \underline{\xi} + V_L(\underline{\xi}, \underline{\mu}) + \langle \phi | T + V_{PI} + V_{IS} | \phi \rangle, \quad (1)$$

where $U^{(0)}$ is the energy of the perfect undistorted lattice; $\frac{1}{2} \underline{\xi} \cdot \underline{A} \cdot \underline{\xi}$ is the energy to create a distortion field $\underline{\xi}$ in region II of the perfect lattice, leaving the ions in region I undisplaced, where \underline{A} is the perfect-lattice force-constant matrix, and where $\underline{\xi}$ is a column matrix whose elements are the components of displacement of all the ions in a given state of the system (including the zero displacements of ions in region I), and $\underline{\xi}$ is the transpose of $\underline{\xi}$; $V_L(\underline{\xi}, \underline{\mu})$ is the energy to create the lattice defect from the perfect lattice in distorted configuration $\underline{\xi}$, where $\underline{\mu}$ stands for the values of the generalized coordinates of ions in the defect region I in a given state of the system; T is the excess-electron's kinetic-energy operator; $V_{PI} \equiv V_{PI}(\vec{r}; \xi, \mu)$ is the Coulomb potential energy of the electron in the presence of the defect lattice of charged point ions; $V_{IS} \equiv V_{IS}(\vec{r}; \underline{\xi}, \underline{\mu})$ is the BSG ion-size correction¹² to the electron-lattice interaction; and ϕ is the electron's pseudo-wave-function. In the BSG approximation,¹²

$$V_{IS}(\vec{r}; \underline{\xi}, \underline{\mu}) = \sum_{\gamma} [A_{\gamma} + B_{\gamma}(\bar{V} - U_{\gamma})] \delta(\vec{r} - \vec{R}_{\gamma}), \quad (2)$$

where γ labels ions of the defect lattice; \vec{R}_{γ} is the position vector of ion γ , whence part of the dependence of V_{IS} on $\underline{\xi}$ and $\underline{\mu}$; A_{γ} and B_{γ} are numerical parameters which depend only on the ionic species at \vec{R}_{γ} , and are given in Table I of BSG, and in the present work all A_{γ} 's from BSG are multiplied by 0.53, as just discussed; \bar{V} is the expectation value of $(V_{PI} + V_{IS})$ in the electronic state which maximizes \bar{V} (minimizes the expectation value of T ; the "smoothest" wave function); and U_{γ} is taken equal to $\sum_{\gamma' \neq \gamma} V_{PI}$ [Ref. 12, Eq. (2.20)], whence further dependence on $\underline{\xi}$ and $\underline{\mu}$.

In Eq. (1) we now set $U^{(0)} = 0$, and approximate ϕ by a trial wave function which depends on variational parameters, collectively denoted $\underline{\lambda}$. We then have

$$\phi \equiv \phi(\vec{r}; \underline{\lambda}) \quad (3)$$

and

$$E \equiv E(\underline{\xi}, \underline{\mu}, \underline{\lambda}), \quad (4)$$

and we seek to minimize E , Eq. (4), with respect to variations of the components of $\underline{\xi}$, $\underline{\mu}$, and $\underline{\lambda}$ for a relaxed state, or with respect to the components of $\underline{\lambda}$ only for an unrelaxed state, for which $\underline{\xi}$ and $\underline{\mu}$ will be given. Full details of how this self-consistent minimization is accomplished have been given by Stoneham and Bartram,^{21(b)} and by Vail.²⁶

In outline, the procedure for a relaxed state is as follows: (a) Minimize $E(\underline{0}, \underline{\mu}, \underline{\lambda})$ with respect to the components of $\underline{\mu}$ and $\underline{\lambda}$, thus obtaining a zeroth-order solution $\underline{\mu}^{(0)}$, $\underline{\lambda}^{(0)}$, neglecting harmonic distortions ($\underline{\xi} = \underline{0}$); (b) expand $E(\underline{\xi}, \underline{\mu}, \underline{\lambda})$ to quadratic terms in $\underline{\xi}$, $(\underline{\mu} - \underline{\mu}^{(0)})$, and $(\underline{\lambda} - \underline{\lambda}^{(0)})$, and minimize with respect to these three sets of variables, obtaining coupled linear equations; (c) decouple the linear equations, Fourier transform the resulting system of linear inhomogeneous equations in the components of $\underline{\xi}$, and using the known dynamical matrix of the perfect host lattice, solve for the Fourier transform of $\underline{\xi}$ by the perturbative-iteration procedure; (d) substitute the resulting solution for $\underline{\xi}$, and use the minimization equations, to obtain a value for $E(\underline{\xi}, \underline{\mu}, \underline{\lambda})$ which will now be self-consistently minimized, and accurate to second-order small quantities.

For an unrelaxed state, such as the final state of a photon absorption process, the values of $\underline{\xi}$ and $\underline{\mu}$ are known; namely, they are the values associated with the initial, relaxed state of the process, and so one only needs to minimize E with respect to $\underline{\lambda}$, keeping $\underline{\xi}$ and $\underline{\mu}$ fixed at their initial state values.

E. Trial Wave Functions and Lattice Configurations

The analytical and numerical work implicit in the above procedure for evaluating the energy is considerable. We have therefore chosen trial wave functions and defect configurations which are rel-

atively simple. Because V_{PI} in Eq. (1) is a sum of Coulomb terms, which become generating functions for Legendre polynomials, it is convenient to have trial wave functions which are expressed in terms of Legendre polynomials in evaluating $\langle \phi | V_{PI} | \phi \rangle$. We have chosen to use Gaussian localization for all our trial wave functions; Brown and Vail (Ref. 14, Fig 3) have shown that this is qualitatively very similar to the type-II and -III Gou-rary-Adrian wave functions.¹³

With specific reference to the energy levels shown in Fig. 2, and the coordinate systems shown in Fig. 1, we have used the following trial wave functions:

vacancy ground state:

$$\phi_1 \sim e^{-\alpha_1^2 r^2}; \quad (5)$$

F_{A1} absorption:

$$\phi_2 \sim r e^{-\alpha_2^2 r^2} \cos \theta_y = y e^{-\alpha_2^2 r^2}; \quad (6)$$

F_{A2} absorption:

$$\phi_3 \sim r e^{-\alpha_3^2 r^2} \cos \theta_z = z e^{-\alpha_3^2 r^2}; \quad (7)$$

vacancy RES:

$$\phi_4 \sim r e^{-\alpha_4^2 r^2} \cos \theta_y = y e^{-\alpha_4^2 r^2}; \quad (8)$$

s. p. RES:

$$\phi_5 \sim r' e^{-\alpha_5^2 r'^2} \cos \theta_{z'} = z' e^{-\alpha_5^2 r'^2}; \quad (9)$$

s. p. even, unrelaxed:

$$\phi_6 \sim r'^2 e^{-\alpha_6^2 r'^2} \cos^2 \theta_{z'} = z'^2 e^{-\alpha_6^2 r'^2}; \quad (10)$$

s. p. even, relaxed:

$$\phi_7 \sim r'^2 e^{-\alpha_7^2 r'^2} \cos^2 \theta_{z'} = z'^2 e^{-\alpha_7^2 r'^2}. \quad (11)$$

For the "s. p. even" states, even refers to parity, and s. p. means saddle point. We see from Eq. (5) that the vacancy ground-state wave function is taken to be spherically symmetric, i. e., a zeroth-order Legendre polynomial. All the excited states (F_{A1} and F_{A2} absorption, and vacancy and saddle-point RES's) are taken to be first-order Legendre polynomials, but with various orientations and origins. Thus θ_y is the polar angle in a spherical-polar-coordinate system whose polar axis is the y axis of Fig. 1(a), and r is the corresponding radial variable with origin at the vacancy site. Similarly for θ_z , but $\theta_{z'}$ is the polar angle relative to the z' axis of Fig. 1(b) as polar axis, and r' is the corresponding radial variable, with origin at the saddle point. The even-parity saddle-point unrelaxed and relaxed states, Eqs. (10) and (11), both have angular dependence of the form $\frac{1}{2}P_0 + P_2(\cos \theta_{z'})$, where P_0 and P_2 are zeroth- and second-order Legendre polynomials, respectively. Note that the numerical values of the Gaussian localization parameters α_j , ($j = 1, 2, \dots, 7$), found from the variational calculation, will be different in each case. These

values are given in Sec. III. Note also that α_j is the only variational parameter in each trial wave function ϕ_j , playing the role of λ in the general formulation of Sec. IID.

Qualitatively, we note that, from Eq. (6), it is assumed that F_{A1} absorption occurs to a final state oriented along the y axis, which in our model contains the impurity alkali ion. Experimentally it is known⁵ that in the $F_A(\text{Li})$ center the Li^+ ion does not reside on the y axis, but tunnels between four equivalent off-axis sites, presenting only a time-averaged picture of C_{4v} symmetry. Because such behavior cannot be fully represented in a static model of the lattice, as ours is, we consider only vacancy configurations with C_{4v} symmetry for the ground, F_{A1} , and vacancy relaxed excited states. For simplicity, we have used vacancy-configuration wave functions which are centered at the origin in Fig. 1(a), even though the environment there is asymmetrical owing to the impurity. It would be more accurate to include the position of the center of these wave functions, Eqs. (5)–(8), as variational parameters. It turns out that, using Tosi's SE repulsive potential (see Sec. IIA), the equilibrium position of the impurity alkali ion is displaced along the y axis from the perfect lattice site (0, 1, 0) by a distance y_0 , which is nonharmonic, in all the vacancy-configuration states. Thus y_0 plays the role of $\underline{\mu}$, and y_0 and α must be simultaneously minimized for both the ground-state and the vacancy RES, in zeroth order (see Sec. IID). The F_{A2} absorption state, Eq. (7), is taken to be oriented along the z axis in Fig. 1(a); it could equivalently be taken oriented along the x axis in our C_{4v} -symmetric model. Since it turns out that the F_{A1} state lies lower than F_{A2} on absorption, we have examined the same state, Eq (8), oriented along the y axis, *with* lattice relaxation, to estimate where the RES energy level would come if the RES did occur in the vacancy configuration. In view of the complexity of the RES problem for the ordinary F center in pure KCl,^{27–29} and the fact that the present model does not adequately describe that state,^{14,21(b)} we cannot claim that the results reported in the Sec. III for the vacancy RES of the F_A -centers are conclusive [in fact, the $F_A(\text{Na})$ result disagrees with experiment], but only that they arise from consistent treatment of the present model.

Note that the two kinds of saddle-point states considered, of odd and even parity, Eqs. (9) and (10)–(11), respectively, both have wave functions with double-lobed charge densities, fitting into the two-well potential of the two vacant anion sites which are separated by the saddle-point Cl^- ion. In order to maintain some symmetry in the lattice-distortion field for these states, displacements of the impurity alkali ion were considered only along the y' axis of Fig. 1(b). However, an investigation

TABLE I. Theoretical values of wave-function localizations α_j , in units of perfect-KCl-lattice spacing, and energy levels E_j , in eV, for the F_A (Na) and F_A (Li) centers in KCl, from trial wave functions ϕ_j given in Eqs. (5)–(11).

j	F_A (Na) center		F_A (Li) center	
	α_j	E_j	α_j	E_j
1	1.08	1.01	1.07	0.87
2	1.16	3.09	1.14	2.72
3	1.36	3.88	1.34	3.48
4	0.96	2.84	0.93	2.69
5	0.806	2.76	0.790	2.27
6	0.983	[2.47]
7	0.928	2.43	0.911	1.90

will be described in the Sec. III, in which we examined the possibility that the saddle-point Cl^- ion produces energy minimization by taking up a position on the x' axis, where (x', y', z') is an orthogonal coordinate system. The results of this investigation were tentatively negative for the F_A centers. Thus, for the relaxed saddle-point states, Eqs. (9) and (11), only lattice distortions which maintained reflection symmetry with respect to x' - y' and y' - z' planes were considered. Furthermore, trial wave functions with their centers displayed from the origin of Fig. 1(b) were not used. It then followed that the displacements along the y' axis of the saddle-point Cl^- ion from the strict saddle-point position, and of its adjacent K^+ and impurity alkali (Na^+ or Li^+) neighbors on the y' axis, denoted y_1, y_2 , and y_3 , respectively, and collectively denoted $\underline{\mu}$ in Sec. IID, needed to be determined self-consistently with the appropriate α_j from Eq. (9) or (11), in the zeroth-order energy minimization. The failure of the saddle-point emission trial wave function ϕ_6 , Eq. (10), to yield a Franck-Condon emission energy for the F_A (Li) center led us to try other forms of trial wave functions for this state, without success, as reported in the following.

III. RESULTS

Our model of the crystal lattice, theoretical methods and approximations, and simplifying assumptions about the trial wave functions and lattice configurations, have been fully described in Sec. II. We shall now present the results: wave-function localization parameters α_j , Eqs. (5)–(11), distortion fields $(\xi, \underline{\mu})$, and energy levels.

We begin by presenting, in Table I, the localization parameters α_j and the corresponding estimated energies E_j for the states described in Eqs. (5)–(11), $j = 1, 2, \dots, 7$. In this table, E_6 for the F_A (Li) center is indicated in square brackets because the result is unphysical, as will be discussed. Table II presents a comparison between our theoretical results of Table I and the experimental results

of Fig. 2. There are basically three points at which quantitative comparison between theory and experiment can be made from Table II, namely, (A) F_{A1} absorption, (B) F_{A1} - F_{A2} splitting, and (C) reorientation activation energy. Let us discuss these in order in subsections IIIA–IIIC, and then in subsections IIID–IIIF we shall discuss relaxed excited states, further details of the energy estimates, and the distortion fields.

A. F_{A1} Absorption

Agreement here [energy difference (A), Table II] is within 7%. This is encouraging but not particularly surprising, for two reasons. First, it is well known¹¹ that reasonable agreement with experiment can be obtained for ordinary F -center absorption from a variety of models, and second, in the BSG ion-size correction, the empirical parameter 0.53 which we have used was chosen¹² to give agreement with F -center absorption.

B. F_{A1} - F_{A2} Splitting

The discrepancy here [energy difference (B), Table II] is serious, the splitting being a factor of about 3 too large. The theoretical F_{A2} absorption energies, (A)+(B)=2.87 eV for F_A (Na) and 2.61 eV for F_A (Li), are within about 20% of the experimental values, as expected. It is possible to make a reasonable comparison between our results for absorption and those of the previous theoretical investigations^{8–10(a)} which we have briefly described in Sec. I. The results are collected in Table III, where F_{A1} and F_{A2} absorption energies are given relative to F -center absorption in KCl. In relation to the present work (denoted OV in Table III), we have used the results of BV- I^{14} for F -center absorption, namely, 2.28 eV, since that calculation was carried out with the same model, method, and type of wave function as are used here. In terms of numerical agreement with the experimental F_{A1} - F_{A2} splitting, the present work and that of Smith⁹ are about equal, namely, three times too large, whereas Weber and Dick⁹ and

TABLE II. Comparison of experimental energy differences in eV, as indicated on Fig. 2, and theoretical estimates derived from Table I, for F_A (Na) and F_A (Li) centers in KCl.

Energy difference	F_A (Na) center		F_A (Li) center	
	expt.	theor.	expt.	theor.
(A)	2.12	2.08	1.98	1.85
(B)	0.23	0.79	0.27	0.76
(C)	1.25	1.43	0.91	1.03
(D)
(E)	0.46	...
(F)	+0.09	-0.08	...	-0.42

TABLE III. Theoretical and experimental values of the shifts of F_{A1} and F_{A2} absorption lines of F_A centers relative to F -center absorption in KCl, and the absorption-line splitting (energies, in eV).

	$F_A(\text{Na})$ center			$F_A(\text{Li})$ center		
	F_{A1}	F_{A2}	split.	F_{A1}	F_{A2}	split.
Smith ^a	-0.38	+0.16	0.54	-0.54	+0.24	0.78
WD ^b	-0.34	+0.05	0.39	-0.46	+0.07	0.53
Alig ^c	-0.30	+0.06	0.36	-0.38	+0.08	0.46
OV ^d	-0.20	+0.59	0.79	-0.43	+0.33	0.76
Expt. ^a	-0.19	+0.04	0.23	-0.33	-0.06	0.27

^aReference 1, Table 3-2, p. 193.

^bReference 9, Table 9, columns I.

^cReference 10(a), Table I, columns III.

^dPresent work, Table II, and Ref. 14, Table 3.

Alig,^{10(a)} with type-I Gourary-Adrian wave functions and neglecting lattice distortion, obtain results about two times too large. The details of our results for F_{A1} - F_{A2} splitting are given in Table IV. Here, the lattice energy does not contribute, because it is constant throughout both F_{A1} and F_{A2} absorption processes. Thus the splitting depends on the difference in expectation values of T , V_{PI} , and V_{IS} in the two unrelaxed excited states ϕ_2 and ϕ_3 , Eqs. (6) and (7). From Table IV we observed that, in our treatment, the kinetic-energy and point-ion contributions to the splitting cancel almost exactly, and the overly large resultant splitting can be said to arise almost entirely from the ion-size correction, V_{IS} . Since Smith's treatment of the ion-size effect is the most accurate of the four theoretical investigations quoted in Table III, and since the present work treats lattice distortion most accurately and at the same time, we feel, does not treat the ion-size correction any worse than Weber and Dick or Alig, it is clear that to obtain more accurate theoretical results than those presented in Table III it will be necessary to treat all aspects of the model and calculations with considerable care. We shall elaborate this point in Sec IV.

C. Reorientation Activation Energy

Agreement with experiment here [energy difference (C), Table II] is within about 15%, the theoretical result being 0.18 eV too high for $F_A(\text{Na})$ and 0.12 eV too high for $F_A(\text{Li})$. This agreement is gratifying, if somewhat surprising at first sight. It is comparable in accuracy to the best results¹⁸ obtained with somewhat similar models for the activation energy for anion-vacancy diffusion in KCl. The magnitude of disagreement with experiment, ~ 0.1 eV, is considerably smaller than that obtained in Ref. 15 (hereafter denoted BV-II), for F -center step diffusion, namely, ~ 0.5 eV discrep-

ancy. In a sense, our defects are more complicated than those of Tosi, in that they contain an off-center impurity. On the other hand, since the F_A center is a neutral defect, it may be that ionic polarization effects, neglected in the present work, are less important than in the case of the charged anion vacancy, where polarization is only approximately incorporated by the Mott-Littleton method.³⁰ Regarding the results of BV-II,¹⁵ we must remark that ordinary F -center step diffusion in both even- and odd-parity states involves electronic energies which in the saddle-point configuration may be well into the conduction band, so that the simple characterization of the states used in BV-II may not be very appropriate. By contrast, it is reasonable to assume³¹ that the saddle-point states in the $F_A(\text{Li})$ center, and perhaps even in the $F_A(\text{Na})$ center, are well below the conduction band, so that the simple, localized type of state investigated here may be fairly realistic.

Furthermore, it appears that the strict saddle-point configuration which we have used may be more appropriate for the F_A centers than for the F center. This emerges from the following investigation. Consider the question whether the configuration shown in Fig. 1(b), in which the saddle-point ion lies in the y' - z' plane, is stable with respect to displacements in the x' direction, perpendicular to the y' - z' plane. The results are shown in Fig. 3, where the zeroth-order estimate $E^{(0)}$ of the defect's energy is plotted against displacement x' of the saddle-point ion along the x' axis for the $F_A(\text{Na})$, $F_A(\text{Li})$, and ordinary F center in KCl. In the zeroth-order estimate we neglect region-II distortion (i. e., $\xi = 0$), but for a given value of x' , we minimize the system's energy with respect to the odd-parity wave-function's localization parameter α_5 , Eq. (9), and with respect to displacements along the y' axis of the two nearest cations [K^+ and Na^+ or Li^+ for $F_A(\text{Na})$ and $F_A(\text{Li})$, and two K^+ ions for the F center]. In the case of the F_A centers in KCl, Figs. 3(a) and 3(b), it appears that there is a flat minimum within a tenth of a nearest-neighbor distance. Since we do not consider our energy estimates to be meaningful to an accuracy of better than about 0.1 eV, and since

TABLE IV. Contributions to the F_{A2} - F_{A1} absorption splitting (eV), with wave functions ϕ given in Eqs. (6) and (7), with localization parameters α given in Table I.

	$F_A(\text{Na})$ center			$F_A(\text{Li})$ center		
	F_{A2}	F_{A1}	$F_{A2}-F_{A1}$	F_{A2}	F_{A1}	$F_{A2}-F_{A1}$
$\langle \phi T \phi \rangle$	3.55	2.60	0.95	3.44	2.50	0.94
$\langle \phi V_{PI} \phi \rangle$	-6.91	-5.96	-0.95	-6.52	-5.59	-0.93
$\langle \phi V_{IS} \phi \rangle$	1.09	0.30	0.79	1.04	0.29	0.75
Totals	0.79	0.76

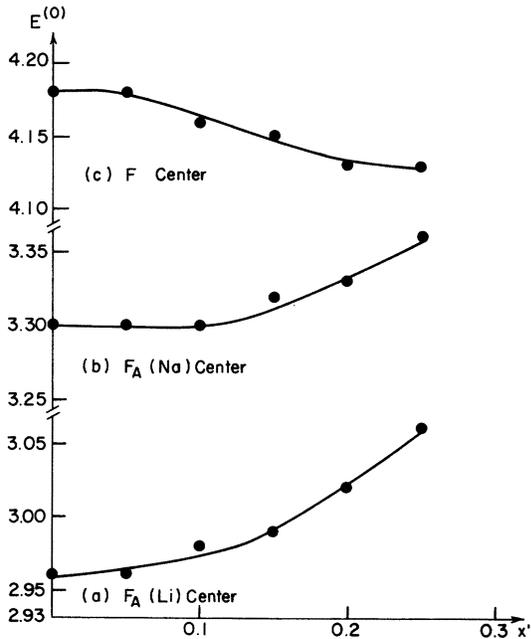


FIG. 3. Zeroth-order odd-parity energy (eV) of F and F_A centers in KCl in the saddle-point configuration, as a function of displacement x' of the Cl^- ion from the saddle point (x' in units of perfect KCl nearest-neighbor distance). (a) $F_A(\text{Li})$ center; (b) $F_A(\text{Na})$ center; (c) F center.

the configuration with $x' = 0$ is analytically much easier to calculate energies for, because of symmetry, we have carried through the calculation only for this case. In Fig. 3(c) for the F center, the curve appears to be monotonic decreasing with increasing x' . This is interesting because, if there is a relative minimum for $x' \neq 0$, it might be expected to occur in the vicinity of $x' \sim 0.5$. We have not pursued this calculation to such large values of x' because, even in zeroth order, it becomes very complicated, since one must begin to consider the displacements and Born-Mayer repulsion of the two nearest Cl^- ions as well as of the two nearest cations, and these displacements must all be allowed to have both y' and x' components. Furthermore, the trial-wave-function center should then not be restricted to the origin of Fig. 1(b), and finally, the lattice-statics calculation becomes very complicated owing to the low symmetry of the defect. In summary, we do not consider the question of the saddle-point configuration to be settled, but the results of Fig. 3 strongly suggest that for the $F_A(\text{Na})$ and $F_A(\text{Li})$ centers in KCl a value $x' \leq 0.1$ is the stable configuration, with energy negligibly lower than that for $x' = 0$, whereas for the ordinary F center, the stable configuration involves $x' > 0.2$, with energy at least 0.1 eV lower than that for $x' = 0$. This would go some way toward explaining the discrep-

ancies, $\sim +0.5$ eV, between the theoretical estimates of BV-II^{15} and the experimental value of the activation energy for F -center step diffusion, since the theoretical estimates were made with $x' = 0$. The different behaviors displayed between Figs. 3(a) and 3(b) and Fig. 3(c) are qualitatively understandable, since the saddle-point Cl^- ion is much less tightly squeezed by the small Na^+ or Li^+ ion in the F_A center than it is by the corresponding larger K^+ ion in the ordinary F center.

D. Relaxed Excited States and Emission

As we mentioned in the Introduction, the stabilization in, and emission from, a RES in the saddle-point configuration is perhaps the most striking feature of the $F_A(\text{Li})$ center. Our calculation predicts [row (F), Table II] a stabilization energy of 0.42 eV. Our reservations about our treatment of the RES in the vacancy configuration have been expressed in Sec. II E, but the magnitude of the stabilization energy in the present model renders the result qualitatively convincing.

The $F_A(\text{Na})$ center is found experimentally (Ref. 1, Table 3-6) to have its RES stabilized in the vacancy configuration by only about 0.09 eV relative to the saddle-point RES, whereas our theoretical results show the opposite ordering of these levels, $E_5 - E_6 = -0.08$ eV, from Table I. This is perhaps the most direct evidence that our model and approximations are not generally accurate to better than a few tenths of an eV when dealing with the RES, for our theoretical results show the $F_A(\text{Na})$ center weakly stabilized in the saddle-point configuration, while experimentally it is found to be weakly stabilized in the vacancy configuration.

The present model fails to describe the emission process of the $F_A(\text{Li})$ center in the saddle-point configuration, as seen by comparison of rows 5 and 6 of Table I. The result there implies that the unrelaxed even-parity state ($j=6$), a linear combination of s and d ($l=0, 2$) wave functions, has higher energy than the p -type ($l=1$) RES ($j=5$). Thus spontaneous dipole emission would not occur from the RES, contrary to the experimental fact. In seeking to understand why our model failed at this point, we examined the details of our even-parity saddle-point wave function, Eq. (10). We observed that, with only the one variational parameter α_6 , the wave function could not simultaneously adjust the position and sharpness of its two charge-density lobes to the two-well potential of the two vacant anion sites [Fig. 1(b)], with lattice-distortion field (ξ, μ) determined by the RES of Eq. (9). We therefore applied two other types of trial wave functions in place of ϕ_6 , Eq. (10), in an attempt to describe the emission process; namely,

$$\phi'_6 \sim (b^2 + \frac{3}{2}r'^2 \cos^2\theta_{r'}) e^{-\alpha^2 r'^2}, \quad (12)$$

TABLE V. Wave-function parameters and energies (eV) for the saddle-point emission state of the $F_A(\text{Li})$ center in KCl (even parity, unrelaxed), Eqs. (10), (12), and (13).

	ϕ_6	ϕ_6'	ϕ_6''
α	0.983	0.979	0.931
$b; \beta$...	0.182	0.362
E_6	2.47	2.45	2.40

$$\phi_6'' \sim (1 - e^{-\beta^2 r'^2}) \cos^2 \theta_{r'} e^{-\alpha^2 r'^2}. \quad (13)$$

Although these two trial wave functions each have two variational parameters, (α, b) for ϕ_6' and (α, β) for ϕ_6'' , they were only slightly more flexible than ϕ_6 , and only marginally lower in energy, but still qualitatively unsatisfactory, lying higher in energy than the saddle-point RES, as shown in Table V. We have given preliminary consideration to some other forms of trial wave functions, but those which are not simply linear combinations of low-order even-parity Legendre polynomials, and whose radial r' dependence is analytically complicated, lead to computations which are prohibitive in terms of both computer time and investigator's time. Furthermore, we believe that aspects of our treatment other than the trial wave function may be equally likely to be responsible for the failure to describe the emission process. This point will be further discussed in Sec. IV.

E. Detailed Energetics

Brown and Vail¹⁵ found it illuminating to express the contributions to F -center activation energies (energy differences between saddle-point and vacancy configurations) in relation to specific elements of the model and method. Thus, consider a relaxed-state energy to be written in the form

$$E = \bar{T} + \bar{V}_{\text{PI}} + \bar{V}_{\text{IS}} + V_L(\underline{0}, \underline{\mu}^{(0)}) + E_d, \quad (14)$$

where

$$\bar{T}(\underline{\lambda}^{(0)}) = \langle \phi(\underline{\lambda}^{(0)}) | T | \phi(\underline{\lambda}^{(0)}) \rangle, \quad (15)$$

$$\bar{V}_{\text{PI}}(\underline{\lambda}^{(0)}, \underline{\mu}^{(0)}) = \langle \phi(\underline{\lambda}^{(0)}) | V_{\text{PI}}(\underline{0}, \underline{\mu}^{(0)}) | \phi(\underline{\lambda}^{(0)}) \rangle, \quad (16)$$

$$\bar{V}_{\text{IS}}(\underline{\lambda}^{(0)}, \underline{\mu}^{(0)}) = \langle \phi(\underline{\lambda}^{(0)}) | V_{\text{IS}}(\underline{0}, \underline{\mu}^{(0)}) | \phi(\underline{\lambda}^{(0)}) \rangle, \quad (17)$$

are the zeroth-order estimates of the excess-electron's kinetic energy, point-ion potential energy, and ion-size correction, respectively; $V_L(\underline{0}, \underline{\mu}^{(0)})$ is the zeroth-order estimate of the lattice-defect energy, and E_d is the total contribution to the energy associated with region-II relaxation ξ . Note that E_d includes both region-II harmonic distortion energy $\frac{1}{2} \underline{\xi} \cdot \underline{A} \cdot \underline{\xi}$, and contributions from T , V_{PI} , V_{IS} , and V_L arising from the readjustment of $\underline{\lambda}$ and $\underline{\mu}$ from their zeroth-order values ($\underline{\lambda}^{(0)}$, $\underline{\mu}^{(0)}$) as they follow variations of ξ in self-consistently minimizing the energy. These contributions to the four relaxed states of the $F_A(\text{Na})$ and $F_A(\text{Li})$ centers in KCl, and to the reorientation and saddle-point stabilization energies, are given in Table VI. The results are interesting in themselves, and in comparison to the results for the ordinary F center in KCl, Ref. 15, Table 1.

Let us first compare the theoretical *even-parity* reorientation energies 1.43 eV for $F_A(\text{Na})$ and 1.03 eV for $F_A(\text{Li})$ with the calculated F -center even-parity step-diffusion energy of 2.23 eV. In all cases the contributions in the column labeled diff. are comparable and small from \bar{T} , \bar{V}_{IS} , and E_d , with the contributions from E_d just about canceling those from \bar{T} and \bar{V}_{IS} . The contributions from V_{PI} are large in all cases, but about 0.35 eV less for $F_A(\text{Na})$, and 0.6 eV less for $F_A(\text{Li})$, than for the F center. Regarding $V_L(\underline{0}, \underline{\mu}^{(0)})$, it makes a negligible contribution for the F center, but for the F_A centers gives a strongly negative contribution which is about another 0.5 eV lower for $F_A(\text{Na})$, and 0.6 eV lower for $F_A(\text{Li})$, than for the F center. Thus we see that the lowering of the even-parity F -center step-diffusion activation energy induced by an adjacent impurity Na^* or Li^* ion is about half due

TABLE VI. Contributions (eV) to energy differences between saddle-point (s.p.) and vacancy (vac.) configurations for even- and odd-parity relaxed states of the F_A center in KCl [see Eqs. (14)–(17)].

	$F_A(\text{Na})$ center						$F_A(\text{Li})$ center					
	s.p.	vac.	diff.	s.p.	vac.	diff.	s.p.	vac.	diff.	s.p.	vac.	diff.
$\bar{T}(\lambda^{(0)})$	+1.56	+1.44	+0.12	+1.31	+2.68	-1.37	+1.57	+1.43	+0.14	+1.33	+2.64	-1.31
$\bar{V}_{\text{PI}}(\lambda^{(0)}, \mu^{(0)})$	-5.28	-7.11	+1.83	-4.67	-6.28	+1.61	-5.37	-6.95	+1.58	-4.76	-6.11	+1.35
$\bar{V}_{\text{IS}}(\lambda^{(0)}, \mu^{(0)})$	+0.23	+0.08	+0.15	+0.34	+0.31	+0.03	+0.22	+0.08	+0.14	+0.33	+0.30	+0.03
$V_L(0, \mu^{(0)})$	+6.22	+6.64	-0.42	+6.23	+6.62	-0.39	+5.82	+6.39	-0.57	+5.85	+6.41	-0.56
E_d	-0.29	-0.04	-0.25	-0.45	-0.49	+0.04	-0.34	-0.08	-0.26	-0.48	-0.55	+0.07
Totals, theor.	+2.44	+1.01	+1.43	+2.76	+2.84	-0.08	+1.90	+0.87	+1.03	+2.27	+2.69	-0.42
Experiment	+1.25	+0.09	+0.91	<0

to a lower relative zeroth-order region-I lattice energy between saddle-point and vacancy configurations, and half due to a smaller rise in point-ion potential energy \bar{V}_{PI} in going from vacancy to saddle-point configuration.

The calculated *odd-parity* F -center step-diffusion activation energy, Ref. 15, Table 1, is +0.51 eV, and for the F_A centers, we see from Table II of the present work that it is approximately zero for F_A (Na) and -0.42 eV for F_A (Li), the negative sign indicating stabilization of the saddle-point RES relative to the vacancy RES. For both the F center and the F_A centers, the odd-parity-state's kinetic energy drops considerably in going from vacancy to saddle-point configurations, by about 1.5, 1.37, and 1.3 eV for F , F_A (Na), and F_A (Li), respectively. The ion-size and E_d contributions to the energy differences are both small in all cases. The point-ion contribution is large in all cases (though smaller than for the even-parity case), being about 0.45 eV smaller for F_A (Na), and 0.7 eV smaller for F_A (Li), than for the F center. The contribution from V_L , as in the even-parity case, is small for the F center, but strongly negative for the F_A centers, about 0.5 and 0.6 eV lower for F_A (Na) and F_A (Li), respectively, than for the F center. Thus for the odd-parity case as for the even-parity case, the Na^+ or Li^+ substitutional impurity lowers the activation energy, driving it negative in odd parity [spuriously so for F_A (Na)], with the lowering effect being about equally shared between point-ion and zeroth-order region-I lattice-energy effects. In these odd-parity cases, the contribution from the harmonic distortion energy E_d is not negligible, contrary to the even-parity case, but tends to reduce the effect of the impurity.

The fact that for both even- and odd-parity cases about half the lowering in energy of the saddle point relative to that of the vacancy, induced by the Na^+ or Li^+ impurity, is due to the effect of the impurity on the point-ion potential through region-I distortion in zeroth order, illustrates the importance of lattice relaxation in these processes. If

one had ignored region-I distortion, the point-ion potential would have been unchanged, and one would have attributed the effect entirely to the change in lattice energy induced by Na^+ or Li^+ substitution.

F. Lattice Relaxation

Some details of the lattice-distortion fields associated with the various states of this defect are of interest, both in themselves and for comparison with other work.^{10(a),14} In Table VII we compare our results with those of Alig^{10(a)} for the radial component of displacement of nearest-neighbor ions in the ground states of F and F_A centers in KCl. The displacements of second, third, and fourth neighbors are also available, but are all less than 0.03 times the perfect-lattice nearest-neighbor distance. For the F center in KCl, the only substantial difference in treatment between Alig^{10(a)} and BV-I¹⁴ was the inclusion of self-consistent lattice relaxation in the latter work. The result, Table VII, is essentially a change in sign of the small nearest-neighbor relaxation, from outward for Alig to inward for BV-I. Alig used Gourary-Adrian type-III wave functions,^{12,13} not self-consistent with the lattice, and in the F_A centers treated the K^+ ions at $(0, \bar{1}, 0)$ in Fig. 1(a) and the four K^+ ions at $(\pm 1, 0, 0)$ and $(0, 0, \pm 1)$ all equivalently. In our treatment, only C_{4v} symmetry about the y axis has been assumed, and lattice distortion and electronic wave function, Eq. (5), have been treated self-consistently. The qualitative result in Table VII is that the impurity alkali ion shifts somewhat farther along the y axis in our treatment than in Alig's, the K^+ ion at $(0, \bar{1}, 0)$ shifts outward by about the same amount as do the four K^+ ions in the x - z plane, as Alig assumed, but these four ions are found to also shift slightly in the positive y direction in the present treatment.

The distortion field of the F_{A1} RES in the vacancy configuration has also been evaluated. However, since this state is not observed experimentally in F_A (Li), and is not properly stabilized by our model in F_A (Na), and because of our reservations about our present treatment of it (Sec. II E), we do not

TABLE VII. Radial component of nearest-neighbor ion displacements in the ground state of F and F_A centers in KCl, in units of the perfect KCl nearest-neighbor distance, with positive direction outward from the vacancy.

Center Ion	F		F_A (Na)		F_A (Li)		
	(0, 1, 0)	(0, $\bar{1}$, 0)	(0, $\bar{1}$, 0)	(1, 0, 0)	(0, 1, 0)	(0, $\bar{1}$, 0)	(1, 0, 0)
Alig ^a	+0.022	0.061	0.018	0.018	0.104	0.016	0.016
BV-I ^b ; OV	-0.025	0.072	0.025	0.022 ^c	0.119	0.027	0.026 ^c

^aReference 10(a), Table II.

^bFor the F center, Ref. 14, Table II.

^cThe *three Cartesian components* of displacement [see Fig. 1(a)] for the ion at $(1, 0, 0)$ are $(+0.022, +0.004, 0)$ in F_A (Na) and $(+0.026, +0.012, 0)$ in F_A (Li); i. e., there is a nonzero y component.

present or discuss the details here.

Let us now turn to the distortion field of the relaxed saddle-point states. We have remarked that the ions at $(0, \pm \frac{1}{2}\sqrt{2}, 0)$ in the (x', y', z') coordinate system of Fig. 1(b), namely, the Na^+ or Li^+ impurity and a K^+ ion, respectively, are found to be displaced by nonharmonic amounts from perfect-lattice sites, and that, because of the lowering of the symmetry by the impurity, the saddle-point ion itself is displaced from the origin. Toward the end of Sec. III C we discussed our assumption of symmetry with respect to the $y'-z'$ plane. Thus, in our treatment, the saddle-point states involve a lattice defect containing the lattice sites $(0, 0, \pm \frac{1}{2}\sqrt{2})$ which are anion vacancies, $(0, \pm \frac{1}{2}\sqrt{2}, 0)$ which are a Na^+ or Li^+ impurity and a K^+ ion, respectively, and the Cl^- ion near the saddle point, $(0, 0, 0)$. The displacements of the latter three ions, and of all the nearest neighbors to the four-site lattice defect, are obtainable, given the defect's assumed symmetry, from Table VIII for both odd- and even-parity relaxed saddle-point states. This covers all the ions shown in Fig. 1(b), plus the ions in the two nearest planes parallel to the $y'-z'$ plane which are immediately adjacent to the four defect sites. The main qualitative result is that the impurity Na^+ or Li^+ ion at $(0, \frac{1}{2}\sqrt{2}, 0)$ shifts from the perfect-lattice site a distance along the y' axis of about 0.15 times the perfect-lattice nearest-neighbor distance, and the saddle-point Cl^- ion at $(0, 0, 0)$ follows it about the same distance in $F_A(\text{Li})$, and about half that distance in $F_A(\text{Na})$, in shifting away from the strict saddle-point position. The K^+ ion on the other side of the saddle point, at $(0, -\frac{1}{2}\sqrt{2}, 0)$, is squeezed outward by the Cl^- ion by about 0.07 and 0.09 nearest-neighbor distances in $F_A(\text{Li})$ and $F_A(\text{Na})$, respectively, in spite of the Cl^- ion's displacement.

IV. DISCUSSION AND CONCLUSIONS

In Sec. II we described a simple model for the problem of an impurity-associated electronic point defect in an alkali halide, and fully described the theoretical method and approximations to be applied to this model. Because the method is variational, we have used a consistent level of approximation for all energy estimates in applying it to the F_A centers in KCl. The results, reported in Sec. III, were only partially in agreement with experiment, the main discrepancies being in the splitting of the absorption line and in the failure to describe the saddle-point emission process for the $F_A(\text{Li})$ center and the RES of the $F_A(\text{Na})$ center (Secs. III B and III D). The F_{A1} absorption line, the saddle-point stabilization of the RES of the $F_A(\text{Li})$ center, and the even-parity reorientation energies, all were in satisfactory agreement with experiment (Secs. III A, III C, and III D). The results clearly indicate that greater accuracy of treatment and sophistication of model are called for if accurate and complete energy estimates are to be obtained for the states of such defects. The model and method are such that several improvements could be incorporated and systematically investigated. We list and discuss these now.

First, we remark that the accuracy of the calculation could be improved, with the given model, in two principal respects. One is to allow for lower symmetry in the relaxed states, by taking account of the possibility of Jahn-Teller distortions and, in the case of the vacancy-configuration ground state, relaxing the requirement of C_{4v} symmetry. A certain amount of additional analytical and computational work is required for each reduction of symmetry in applying the lattice-statics method,

TABLE VIII. Theoretical estimates of the Cartesian components of displacements (x', y', z') in units of the perfect KCl nearest-neighbor distance, for ions neighboring the F_A center in KCl in even- and odd-parity relaxed states in the saddle-point configuration [see Fig. 1(b)].

Ion	$F_A(\text{Na})$ center		$F_A(\text{Li})$ center	
	Odd parity	Even parity	Odd parity	Even parity
$(0, \frac{1}{2}\sqrt{2}, 0)$	(0, 0.160, 0)	(0, 0.161, 0)	(0, 0.142, 0)	(0, 0.151, 0)
$(0, -\frac{1}{2}\sqrt{2}, 0)$	(0, -0.094, 0)	(0, -0.101, 0)	(0, -0.068, 0)	(0, -0.069, 0)
$(0, 0, 0)$	(0, 0.076, 0)	(0, 0.072, 0)	(0, 0.134, 0)	(0, 0.140, 0)
$(1, 0, \frac{1}{2}\sqrt{2})$	(0.017, 0.006, -0.053)	(0.021, 0.007, -0.032)	(0.035, 0.004, -0.041)	(0.040, 0.005, -0.019)
$(1, \frac{1}{2}\sqrt{2}, 0)$	(0.050, 0.056, 0)	(0.044, 0.050, 0)	(0.063, 0.040, 0)	(0.063, 0.033, 0)
$(1, -\frac{1}{2}\sqrt{2}, 0)$	(0.026, -0.032, 0)	(0.021, -0.025, 0)	(0.021, -0.019, 0)	(0.015, -0.009, 0)
$(0, \frac{1}{2}\sqrt{2}, \sqrt{2})$	(0, 0.056, 0.020)	(0, 0.035, 0.030)	(0, 0.058, 0.023)	(0, 0.038, 0.034)
$(0, -\frac{1}{2}\sqrt{2}, -\sqrt{2})$	(0, -0.041, -0.031)	(0, -0.019, -0.039)	(0, -0.038, -0.042)	(0, -0.017, -0.052)
$(0, \sqrt{2}, \frac{1}{2}\sqrt{2})$	(0, 0.040, -0.013)	(0, 0.028, -0.011)	(0, 0.023, -0.022)	(0, 0.012, -0.024)
$(0, -\sqrt{2}, -\frac{1}{2}\sqrt{2})$	(0, -0.007, 0.008)	(0, 0.005, 0.008)	(0, 0.013, 0.010)	(0, 0.029, 0.011)
$(0, \frac{3}{2}\sqrt{2}, 0)$	(0, 0.055, 0)	(0, 0.048, 0)	(0, 0.041, 0)	(0, 0.037, 0)
$(0, -\frac{3}{2}\sqrt{2}, 0)$	(0, -0.027, 0)	(0, -0.021, 0)	(0, -0.011, 0)	(0, -0.002, 0)
$(0, 0, \frac{3}{2}\sqrt{2})$	(0, 0.005, -0.025)	(0, 0.004, 0.002)	(0, 0.005, -0.019)	(0, 0.006, 0.009)

but Jahn-Teller distortion has been found to considerably lower the energy in Stoneham and Bartram's analysis of the RES of the F center.^{21(b)} Another way of improving the accuracy would be to allow more flexibility in the trial wave functions, first by allowing their centers to move away from the origins of Figs. 1(a) and 1(b), and second by using different analytical forms. These measures will usually increase the number of variational parameters in λ , Eq. (3), and a different analytical form will usually also increase the amount of analytical and computational work considerably, mostly in evaluating \bar{V}_{PI} , Eq. (16).

Once these improvements in accuracy have been effected, there are several aspects of the model which can and should be improved. First, ionic polarization should be included via the shell model^{32,33} or the deformation-dipole model.³⁴ This can be done straightforwardly, in principle, provided the adiabatic approximation is maintained.^{21(b),35} Stoneham and Bartram^{21(b)} have found indications that excess-electron defect calculations based on the lattice-statics treatment of the shell model may be inconclusive, in that variations of the shell-model parameters, consistent with perfect-lattice data, may give rise to crucial differences in some of the predicted defect results. In such a case, it would seem that one must discard semiclassical models and deal more explicitly with the electronic structure of the lattice, but it is not known how to execute this in full detail. These remarks apply not only to region II of the lattice, but even more to region I, the defect region where, for example, our use of perfect LiCl or NaCl Born-Mayer parameters is particularly questionable. Another major improvement to the model would be a more thorough pseudopotential (or other) treatment of ion-size effects, as we have mentioned. The semi-empirical aspect of the BSG ion-size correction, and its sweeping simplification, need to be systematically removed if one wishes to have a fundamental treatment of these defects. In principle, we feel that both ionic polarization and improved treatment of ion-size effects should be incorporated in the theory, whether or not more accurate treatment of our present model leads to more satisfactory agreement with experiment.

Once the preceding improvements in the approximations and in the static model have been carried out, one can assess whether the neglect of lattice-dynamic effects is important. The failure to date of the model and method to describe the emission processes of F and F_A centers even in a qualita-

tively satisfactory way suggests that lattice-dynamic effects are not negligible, in general. A formulation has been developed³⁶ to incorporate these effects in the lattice-statics treatment of excess-electron defects. At least three aspects of the treatment of the F - and F_A -center problems could be improved by taking them into account, namely, (i) relaxation of the Franck-Condon principle for electronic transitions, (ii) inclusion of nonadiabatic interaction between the defect electron and the polarizable ionic shells, and (iii) parity mixing in the RES. In addition, energy shifts of different states of the defect induced by lattice-dynamic effects may make non-negligible contributions to the activation energies which are presently only qualitatively satisfactory in the theory.

Finally, we should like to comment on the general feasibility of calculations of the sort reported here, and of the improvements proposed above. We feel that the present investigation plus that of Brown and Vail^{14,15} have defined the limitations of the model and method (energy levels to within a few tenths of an eV, emission processes not included), and that they indicate where increased accuracy and improvements in the model are needed, in seeking a comprehensive, numerically accurate theory of excess-electron defects in ionic crystals. The accuracy already attained might be very useful in some projects directed at device development, and it is estimated that the relevant calculations could be carried out by a small group of experienced investigators in a matter of weeks, using an acceptable amount of computer time. The additional complexities which would be introduced into a full defect analysis by lowering lattice symmetry, increasing trial-wave-function flexibility, introducing the shell model, improving the ion-size correction, and including lattice-dynamic effects would require the collaborative, full-time efforts of a small research group. However, we are convinced that such a group could make good progress, and that the goal of developing the theoretical techniques for analyzing a large range of defects in a relatively fundamental way is both attainable and worthy.

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Phonons in Cinnabar

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A mixed-valence-Coulomb-force field has been constructed and used to calculate the phonon frequencies for waves propagating in symmetry directions of α -HgS—cinnabar. The model is similar to the one previously used to describe the lattice dynamics of partially ionic semiconducting compounds with wurtzite and zinc-blende structures. The calculated frequencies and velocities of sound are in agreement with the experimental values.

I. INTRODUCTION

There are two polymorphs of mercury sulphide: α -HgS or cinnabar is red and has a trigonal structure (D_3^4); β -HgS or metacinnabar is black and has a cubic structure (T_2^2). The transition takes place at 344 °C under atmospheric pressure.

Cinnabar appears to be a material of considerable interest, since it is a II-VI semiconducting compound with a highly anisotropic structure. It is strongly piezoelectric and it is the most optically active of all known mineral compounds. The promising acousto-optical properties of cinnabar have been recently pointed out by Sapriel.¹ Crystal

growth of cinnabar is very difficult. It is only recently that a detailed experimental study of phonon frequencies by Raman scattering² was made possible because monocrystals of fairly good quality and size were grown at the Centre National d'Études des Télécommunications (Lannion, France).³

A fairly extensive study of the long-wavelength vibrations and polaritons in cinnabar has been done by Zallen, Lucovsky, Taylor, Pinczuk, and Burstein.⁴

In this paper, we present the results of a calculation of phonon frequencies in α -HgS—cinnabar. The model is based upon the mixed-valence Coulomb-force-field model previously used to cal-