duction band.

The authors feel that the study of low-tempera-
ture luminescence and conductivity is demonstrated
to be a useful tool for studying irradiation-induced
defects in KBr. Further work at high dosages is
clearly required.

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Distortion and Polarization near Color Centers*

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A general method is presented for calculating the static polarization and distortion near a
defect. It assumes that the lattice responds to the average, but consistently chosen, charge
distribution of the electrons associated with the defect, and uses the shell model to describe
the lattice dynamic and dielectric properties of the host. The lattice is discrete, without
continuum approximations; there are no artificial restrictions on the range of the distortion,
and asymmetric distortions, as from the Jahn-Teller (JT) effect, are included. The varia-
tion of the electronic wave function as the lattice distorts may be included consistently even
in cases where there is mixing of nearby levels. The method is illustrated by a calculation
for the $2p$ excited state of the F center in KBr. It proves necessary to include the ion-size
terms in the interaction of the defect electron with the lattice. The results are sensitive to
the detailed model chosen for the lattice dynamics. However, certain features, such as the
outward motion of the nearest neighbors, the JT distortion, usually tetragonal, and the sub-
stantial energy lowering, typically 0.5 eV, are common to these models.

I. INTRODUCTION

One of the central problems in color-center the-
ory is the question of the polarization and distortion
of the host lattice, and the dependence of these on
the electronic state. Accurate calculations of tran-
sition energies and, more particularly, the Stokes
shift and bandwidths are very sensitive to the model

used. We shall show that these questions can be
dealt with systematically in the Hartree limit, in
which the lattice responds to the average, but con-
sistently calculated, charge distribution of the de-
fect electron, and using a model such as the shell
model to describe the lattice dynamics of the host.
The method can be used for many centers, including
the F center and the V_k center, and can be extended

to predict the interaction between defects. We will illustrate the method with calculations for the excited state of the F center in alkali halides.

Previously, two classes of approach have been particularly important. On the one hand there are continuum models which work in terms of the macroscopic dielectric constants. Although such models can be suggestive, they are not adequate. Their usual justification comes from effective-mass theory, and this is well outside its usual range of validity for centers such as the F center. Further, in most alkali halides the macroscopic dielectric constants are mainly determined by the anions, whereas the F-center electron mainly interacts with its nearest-neighbor cations. Also, lattice distortion can only be treated by taking over results from discrete models, such as the Mott-Littleton radius. In addition, it is not clear how one should treat asymmetric distortions, such as those from Jahn-Teller (JT) instabilities. At the other extreme from continuum models there are the "point-polarizable-ion" models, where polarization is included by using the ionic polarizabilities. This permits a better solution of the relaxation problem, but again there are difficulties. In particular, this model of the lattice does not give an adequate picture of the lattice dynamics or the dielectric properties. This is shown by the failure of the Szigeti relations,[1] which relate the elastic and dielectric properties. Further, the usual procedure allows only a small number of atoms to move, and this may be unduly restrictive.

In the present paper the method described removes a number of the difficulties. It is an atomic model and does not make a continuum approximation for either the polarization or the strain. Cases involving the JT effect can be treated; this is necessary in our discussion of the $2p$ excited state of the F center. Further, the lattice relaxation and polarization can be calculated using the well-known "shell model." This model has been extremely successful in lattice dynamics, and ensures that the Szigeti relations are satisfied; the shell model is undoubtedly a great improvement on the point-polarizable-ion models. In addition, the present approach does not restrict the distortion to a small number of atoms near the defect, and it can be extended to cases where the center has a net charge.

The actual calculation can be divided rather roughly into two parts. The first is the calculation of the wave function of the defect electron for the undistorted unpolarized host lattice. Such calculations are usually based on variational methods, and may be technically difficult. However, they are essential in any color-center calculation and, as they have been discussed in detail elsewhere,[2-5] they will not be treated in detail here. At the pres-

ent time, the best calculations are based on Hartree-Fock methods or on developments of the point-ion models to include ion-size effects and other corrections. The second part, the calculation of the distortion and polarization explicitly, is done by an extension of the method of lattice statics.[6,7] In its simplest form it is recognized that the lattice defect introduces extra terms in the total energy. These depend on the displacements and dipole moments, and the appropriate derivatives of this energy are forces and fields. The method solves the equations of equilibrium under these forces, using a Fourier transform to separate the coupled equations into independent equations, one for each normal lattice mode. This transform corresponds exactly to that used in conventional lattice dynamics and, as a result, the dynamical matrix of the host lattice is a key quantity. As the lattice distorts, the variational parameters describing the defect-electron wave function should change. This change can be calculated without repeated iteration of the variational calculation. This is most readily done by use of a "variation-perturbation" method which can be built in to the solution of the equilibrium equations.

The method is capable of treating the general problem of the static distortion and polarization near a defect. Since this is a static model, the energies are to be interpreted as thermodynamic internal energies. Also, considerable caution must be used in calculating observable properties when the wave functions and energies are very sensitive to the displacements. In particular, the Condon approximation in its usual form may not be valid. In this article, we illustrate the method by discussing the JT effect in the $2p$ state of the F center. The essential theory will be developed to discuss general cases in terms of the shell model, and explicit calculations will be given for this case and for the simpler rigid-ion model. More detailed discussions of both this system and others will appear later.

II. METHOD OF LATTICE STATICS

The displacements of the atoms in the crystal lattice will be written $\underline{x}$. In the point-ion model there are three Cartesian displacements per ion; in the shell model there are six: three for the core and three for the shell. The electronic dipole moment of a given ion can be written in terms of the shell charge and the relative displacements of the core and shell.

The energy of the distorted perfect lattice E_L with respect to the undistorted energy E_{L0} is quadratic in the displacements:

$$E_L - E_{L0} = \tfrac{1}{2}\underline{x}\cdot\underline{\underline{A}}\cdot\underline{x} , \tag{2.1}$$

where $\underline{\underline{A}}$ gives the complete harmonic response of

the lattice. When the defect is introduced there is an extra term

$$W(\lambda, \underline{x}) = T(\lambda) + V(\lambda, \underline{x}) - V_L(\underline{x}), \qquad (2.2)$$

where λ is a variational parameter in the defect-electron wave function. T is the defect-electron kinetic energy, which depends only implicitly on the lattice configuration, and V is the defect-electron–lattice interaction. V_L accounts for the change in lattice energy when, for example, an anion is removed in forming an F center. Any local changes in force constant are included in V_L, and may depend implicitly on the defect-electron wave function. We emphasize, however, that such changes should be introduced using a proper microscopic model, rather than from a phenomenology with arbitrary parameters.

The extra term $W(\lambda, x)$ can be expanded in the form

$$W(\lambda, \underline{x}) = W_0(\lambda_0, 0) - \underline{F}_0(\lambda_0) \cdot \underline{x}$$
$$+ \text{(higher-order terms)}. \qquad (2.3)$$

Usually F_0 and the higher-order terms are of short range; their components which refer to ions far from the defect are generally small. This is not true when the defect has a net charge, since the Coulomb forces are long ranged. However, this case is still tractable, as we mention later. It is often possible to expand the higher-order terms in the form

$$\text{higher-order terms} = \underline{x} \cdot \underline{\underline{F}}' \cdot \underline{x} + (\lambda - \lambda_0)\underline{\Lambda} \cdot \underline{x}$$
$$+ \tfrac{1}{2}\Lambda'(\lambda - \lambda_0)^2 + \cdots. \qquad (2.3')$$

This form assumes that the variational parameter λ does not change much from its value λ_0 when there is no distortion. The expansion (2.3') allows us to use a perturbation-variation method later on, with a considerable simplification. However, such an expansion in $(\lambda - \lambda_0)$ is not necessary. If the higher-order terms are strongly dependent on $(\lambda - \lambda_0)$, then the problem becomes more complex, but is still soluble. Similarly, we can incorporate anharmonic corrections, but only if these involve just a small number of coordinates x. Cases where (2.3a) is not valid include "off-center" defects in alkali halides, some models of the F-center excited state which involve large changes in the defect-electron wave function, and, possibly, the V_k center. For simplicity, we shall retain the expansion in $(\lambda - \lambda_0)$ in this section.

A. Linear Theory

The linear terms $W_0 - \underline{F}_0 \cdot \underline{x}$ are treated separately from the higher-order terms. Thus, we start by considering the equations for static equilibrium of the lattice:

$$\frac{\partial}{\partial x}\left[W_0(\lambda_0, 0) - \underline{F}_0(\lambda_0) \cdot \underline{x} + \tfrac{1}{2}\underline{x} \cdot \underline{\underline{A}} \cdot \underline{x}\right] = 0. \qquad (2.4)$$

This represents a set of coupled equations, since the various components of x are connected by $\underline{\underline{A}}$. Formally, the solutions of (2.4) can be written as

$$\underline{x} = \underline{\underline{A}}^{-1} \cdot \underline{F}_0$$

and give the linear response of the host to the presence of the defect. In practice, however, inversion of $\underline{\underline{A}}$ is usually intractable. Instead, we separate the equations by the Fourier transform used in lattice dynamics. This also simplifies the treatment of any long-range Coulomb interactions in $\underline{\underline{A}}$ or in $\underline{F}_0$; it is these terms which make the direct inversion of $\underline{\underline{A}}$ particularly difficult. The separated equations for each wave vector $\vec{k}$ have the form

$$-\underline{G}(\vec{k}) + \underline{\underline{D}}(\vec{k}) \cdot \underline{Q}(\vec{k}) = 0. \qquad (2.5)$$

Q is the Fourier transform of the displacements:

$$\underline{Q}(\vec{k}) = \sum_l \underline{x}(l)e^{-i\vec{k}\cdot\vec{r}_l},$$
$$\underline{x}(l) = (1/N)\sum_{\vec{k}} \underline{Q}(\vec{k})e^{i\vec{k}\cdot\vec{r}_l}, \qquad (2.6)$$

in which l labels the ion at $\vec{r}_l$ and $\underline{G}(\vec{k})$ is the transform of the forces $\underline{F}_0$:

$$\underline{G}(\vec{k}) = \sum_l \underline{F}_0(l)e^{i\vec{k}\cdot\vec{r}_l},$$
$$\underline{F}_0(l) = (1/N)\sum_{\vec{k}} \underline{G}(\vec{k})e^{i\vec{k}\cdot\vec{r}_l}. \qquad (2.7)$$

$\underline{\underline{D}}(\vec{k})$ is the dynamical matrix of lattice dynamics, and it is through $\underline{\underline{D}}$ that the connection with models such as the shell model is made,

$$\underline{\underline{D}}(\vec{k}) = \sum_{l-l'} e^{+i\vec{k}\cdot(\vec{r}_l - \vec{r}_{l'})}\underline{\underline{A}}_{ll'}. \qquad (2.8)$$

In the shell model for alkali halides $\underline{\underline{D}}$ is a 12×12 matrix. The eigenfrequencies of the perfect lattice can be found from[8]

$$\det\left|\left|\underline{\underline{D}}(\vec{k}) - \underline{\underline{m}}\omega^2(\vec{k})\right|\right| = 0. \qquad (2.9)$$

in which $\underline{\underline{m}}$ is the (diagonal) mass matrix. The uncoupled equations can be solved by matrix multiplication

$$\underline{Q}(\vec{k}) = +\underline{\underline{D}}^{-1}(\vec{k}) \cdot \underline{G}(\vec{k}) \qquad (2.10)$$

followed by Fourier-transforming Q to give x, using (2.6). The final result gives the linear response of the lattice to the forces $\underline{F}_0$ and can be written as

$$\underline{x} = \underline{\underline{a}} \cdot \underline{F}_0. \qquad (2.11)$$

Since (2.11) is linear one can simply superimpose the displacements from various separate contributions to $\underline{F}_0$. We emphasize that $\underline{F}_0$ may have any point symmetry at the defect, and need not have full rotational symmetry, for example.

The actual matrix multiplication giving (2.10),

and transformation giving (2.11), may be performed in two ways. If the distortions near the defect are wanted, as in calculations of transition energies, they are carried out numerically at, say, 1000 points in the Brillouin zone. This corresponds to treating a superlattice of defects with one defect per 1000 sites. Greater accuracy can, of course, be achieved by treating a larger number of $\vec{k}$. If the long-range distortion is needed, as in estimates of the change in volume per defect, then only the wave vectors with $|\vec{k}|$ small are important, and the manipulation can be carried out analytically by expansion in $|\vec{k}|$. In this regime, results of continuum elasticity and dielectric theory are regained, although, of course, the cubic anisotropy of the lattice is retained. The treatment of long-range Coulomb interactions is made much easier by working in reciprocal space, as the Coulomb contributions to $\underline{D}$ and $\underline{G}$ can be calculated once and for all, and used in calculations for a variety of different defects.

The method we have described is essentially a Green's-function method at zero frequency. It differs from such approaches in emphasis, rather than principle. Most Green's-function methods ignore changes in the mean displacements of the lattice modes, at least in the harmonic approximation; our discussion concentrates on just these changes in mean displacement. Further, we have used a proper microscopic model throughout, and do not introduce phenomenological parameters like force-constant changes.

B. Higher-Order Terms

The higher-order terms are evaluated by a calculation in real space, using the displacements $\underline{x}(l)$ rather than the $\underline{Q}(\vec{k})$. We shall exploit the fact that few displacements $\underline{x}$ are large. The variational condition which determines the defect-electron wave function is, for given $\underline{x}$,

$$\partial W(\lambda, \underline{x})/\partial \lambda = 0 . \tag{2.12}$$

Here, we are using an adiabatic approximation. It is through (2.12) that we recognize that the defect-electron wave function changes as the lattice distorts. We also assume that we need consider only one variational parameter; generalization to several parameters is straightforward but tedious. If we may use the expression (2.3') for the higher-order terms the variational condition becomes

$$\lambda = \lambda_0 - \underline{A} \cdot \underline{x}/\Lambda' . \tag{2.12'}$$

When this equation is substituted into (2.3) and (2.3a) we find that

$$W = W_0 - \underline{F}_0 \cdot \underline{x} + \underline{x} \cdot \underline{\underline{F}}' \cdot \underline{x} - \tfrac{1}{2}(\underline{x} \cdot \underline{A})^2/\Lambda' .$$

Thus, the forces are linear in $\underline{x}$:

$$-\frac{\partial W}{\partial \underline{x}} = \underline{F}_0 + \underline{\underline{\beta}} \cdot \underline{x} . \tag{2.13}$$

The higher-order terms have led us to replace $F_0(\lambda_0)$ by $F(\lambda_0, \underline{x})$; with the simple expansion (2.3') the corrections to $\underline{F}_0(\lambda_0)$ are simply linear in $\underline{x}$. The final values of the displacements can be found by solving

$$\underline{F} = \underline{F}(\lambda_0, \underline{x}) \equiv \underline{F}_0 + \underline{\underline{\beta}} \cdot \underline{x}$$

simultaneously with (2.11)

$$\underline{x} = \underline{\underline{\alpha}} \cdot \underline{F}_0 .$$

If we use (2.13), the final distortions are

$$\underline{x} = (\underline{\underline{1}} - \underline{\underline{\alpha}} \cdot \underline{\underline{\beta}})^{-1} \cdot \underline{\underline{\alpha}} \cdot \underline{F}_0 , \tag{2.14}$$

and the new value of the variational parameter is

$$\lambda = \lambda_0 - \underline{A} \cdot (\underline{\underline{1}} - \underline{\underline{\alpha}} \cdot \underline{\underline{\beta}})^{-1} \cdot \underline{\underline{\alpha}} \cdot \underline{F}_0/\Lambda' . \tag{2.15}$$

Similarly, the change in electronic and elastic energy can be obtained from Eqs. (2.3), (2.3'), (2.14), and (2.15).

In practice these second-order terms can be rendered fairly simple for two reasons. First, only a very few of the x will change by large amounts. In the F center the nearest-neighbor radial displacements are usually the only ones which will alter appreciably. Then the β matrix may be of low rank. Second, in both (2.11) and (2.13) the $\underline{x}$ which are the Cartesian displacements of the ions may be written in terms of symmetry-adapted coordinates. In the F center, for example, these symmetry-adapted coordinates would usually be the normal modes of the complex consisting of the nearest neighbors of the vacancy. Later, we discuss the case in which only the totally symmetric displacements of the nearest neighbors need to be taken beyond the linear theory.

We have assumed that the displacements are never very large. If they are appreciable, the displacements should be treated by considering the crystal as a region I, near the defect, and as region II in which the higher-order terms are negligible. In region I, direct solution of the equilibrium equations (2.4) gives the $\underline{x}$, and those in region II can then be obtained by the methods discussed earlier. However, any calculation to order $\underline{x}^3$ will suffer loss of accuracy because the anharmonic response of the perfect lattice is not so well known as the harmonic properties given by the dynamical matrix $\underline{\underline{D}}$. We emphasize that use of model potentials, such as the Born-Mayer form, does not solve the problem of anharmonicity in region I, but merely introduces extra, sometimes plausible, approximations. Later, we will also find that the harmonic properties of the lattice, described by $\underline{D}$, are often not known in sufficient detail to permit accurate prediction of defect properties.

III. LATTICE DYNAMICS

The dynamical matrix $\underline{\underline{D}}$ discussed in Sec. II determines the dynamics of the perfect host lattice. We discuss two models for D: Kellermann's "rigid-ion" model[9] and the "shell model."[10,11]

The rigid-ion model ignores the polarization of the lattice ions, and treats them as point ions interacting by long-range Coulomb and short-range repulsive forces. The parameters in the dynamical matrix can be expressed in terms of the ionic charge Z and elastic constant (usually the compressibility $3/[c_{11}+2c_{12}]$) and the equilibrium lattice parameter a. The matrix is 6×6 for alkali halides, and has the form

$$\underline{\underline{D}}_{RI} = \begin{pmatrix} C_{11}+R_{11} & C_{12}+R_{12} \\ C_{12}+R_{12} & C_{11}+R_{11} \end{pmatrix} , \qquad (3.1)$$

where we assume nearest-neighbor repulsive forces only. Each term in (3.1) represents a 3×3 matrix which we may write in terms of Kellermann's[9] coefficients,[12] with units $e^2/2a^3$,

$$C_{II}(\alpha,\beta) = - \begin{bmatrix} I & I \\ \alpha & \beta \end{bmatrix} ,$$

$$C_{IJ}(\alpha,\beta) = + \begin{bmatrix} I & J \\ \alpha & \beta \end{bmatrix} , \qquad (3.2)$$

$$R_{11}(\alpha,\alpha) = + (A+2B) ,$$

$$R_{12}(\alpha,\alpha) = - \{A\cos(2\pi a k_\alpha) + B[\cos(2\pi a k_\beta) + \cos(2\pi a k_\gamma)]\} .$$

Other elements are zero.

The shell model takes into account the polarization of the ions. The outer electrons of each ion are treated as a shell which can move relative to the core, giving a dipole moment. The shell mass is assumed negligible. Arbitrary short-range forces connect the shells to their cores and the shells to neighboring shell. We usually shall assume nearest-neighbor forces only. The repulsive interaction is assumed to occur entirely between the shells of the ions; we ignore the shell–other-core and core-core interactions.

The parameters in the dynamical matrix can be expressed in terms of those needed for the rigid-ion model $(Z, c_{11},$ and $a)$ together with the shell charges $(Y_+ \, |e| \, , Y_- |e| \,)$ and the shell-core force constants (k_+, k_-). These extra parameters Y_+, $Y_-, k_+, k_-,$ can be fitted from the residual ray frequency $\omega_{T\,0}$, the dielectric constants ϵ_0 and ϵ_∞, and the ionic polarizabilities α_+, α_-. The equations used in such a fit are given in the Appendix. Alternatively, the parameters can be obtained from lattice dispersion data. The results do not always agree well, and there are no simple criteria for deciding between the various fits. This uncertainty is made worse by the fact that the fits to lattice dynamic data are not unique.

If we write $Z_+ = X_+ + Y_+ = Z$ and $Z_- = X_- + Y_- = -Z$ for the various ionic, core, and shell charges, the dynamical matrix has the form

$$\underline{\underline{D}}_s = \begin{pmatrix} (C_{11}X_+^2 + k_+) & (C_{12}X_+ X_-) & (C_{11}X_+ Y_+ - k_+) & (C_{12}X_+ Y_-) \\ (C_{12}X_+ X_-) & (C_{11}X_-^2 + k_-) & (C_{12}X_- Y_+) & (C_{11}X_- Y_- - k_-) \\ (C_{11}X_+ Y_+ - k_+) & (C_{12}X_- Y_+) & (C_{11}Y_+^2 + k_+ + R_{11}) & (C_{12}Y_+ Y_- + R_{12}) \\ C_{12}X_+ Y_- & (C_{11}X_- Y_- - k_-) & (C_{12}Y_+ Y_- + R_{12}) & (C_{11}Y_-^2 + k_- + R_{11}) \end{pmatrix} . \qquad (3.3)$$

The k matrices are $\vec{k}_\pm = k_\pm \vec{1}$, where $\vec{1}$ is a 3×3 unit matrix.

To improve accuracy it is helpful to change from the four vector displacements per unit cell (two core displacements and two shell displacements) to a combination of these. We replace the shell displacements $\underline{x}_{s\pm}$ by relative shell-core displacements $\underline{d}_\pm = \underline{x}_{s\pm} - \underline{x}_{c\pm}$. These relative displacements are proportional to the dipole moment of the ion. If the dynamical matrix (3.3) is written schematically as

$$\begin{pmatrix} D_{cc} & D_{sc} \\ D_{cs} & D_{ss} \end{pmatrix} , \qquad (3.4)$$

then the equilibrium equation is

$$\begin{pmatrix} D_{cc} & D_{sc} \\ D_{cs} & D_{ss} \end{pmatrix} \begin{pmatrix} Q_c \\ Q_s \end{pmatrix} = \begin{pmatrix} G_c \\ G_s \end{pmatrix} . \qquad (3.5)$$

Writing $q_s = Q_s - Q_c$ the revised form is

$$\begin{pmatrix} (D_{cc} + D_{cs}) & D_{cs} \\ (D_{sc} + D_{ss}) & D_{ss} \end{pmatrix} \begin{pmatrix} Q_c \\ q_s \end{pmatrix} = \begin{pmatrix} G_c \\ G_s \end{pmatrix} . \qquad (3.6)$$

In more detail, if $Z_+ = -Z_- = 1$, (3.3) is transformed into

$$
\begin{pmatrix} G_{+c} \\ G_{-c} \\ G_{+s} \\ G_{-s} \end{pmatrix} = \begin{pmatrix} C_{11}X_+ & -C_{12}X_+ & (C_{11}X_+ Y_+ - k_1) & C_{12}X_+ Y_- \\ C_{12}X_- & -C_{11}X_- & (C_{12}X_- Y_+) & (C_{11}X_- Y_- - k_2) \\ (C_{11}Y_+ + R_{11}) & (-C_{12}Y_+ + R_{12}) & (C_{11}Y_+^2 + k_1 + R_{11}) & (C_{12}Y_+ Y_- + R_{12}) \\ (C_{12}Y_- + R_{21}) & (-C_{11}Y_- + R_{22}) & (C_{12}Y_+ Y_- + R_{12}) & (C_{11}Y_-^2 + k_2 + R_{22}) \end{pmatrix} \begin{pmatrix} Q_{+c} \\ Q_{-c} \\ q_+ \\ q_- \end{pmatrix}, \tag{3.7}
$$

and this is the most convenient equilibrium equation to solve.

For future use we will need to know the response of the lattice to various external forces. It is convenient to calculate the response to unit symmetrized forces, rather than the inverse of the dynamical matrix at many points in the Brillouin zone. Thus, for a defect like the F center, we find the displacements of near neighbors to the defect when various unit forces are applied. The results are components of the $\underset{=}{\alpha}$ matrix of Sec. II. We have calculated the response to the following symmetric forces: (i) totally symmetric (A_{1g}) forces on the nearest neighbors, (ii) tetragonal symmetry (E_g) forces on the nearest neighbors, (iii) trigonal symmetry (T_{2g}) forces on the nearest neighbors, and (iv) totally symmetric (A_{1g}) forces on the second neighbors. In each case the responses to forces on the cores and on the shells were calculated separately. The displacements were found at a number of sites near the defect.

These response functions do not depend on the defect; they are simply properties of the lattice dynamics of the host. Thus, the same response functions can be used in treating a variety of defects. The various response functions have also been calculated for several models of the lattice dynamics. These are the rigid-ion model, the shell model derived from neutron data, and the shell model derived from dielectric, infrared, and elastic data.

In our numerical calculations we have used the Kellermann mesh of 999 points in the Brillouin zone.[9] It is trivial, in principle, to use a finer mesh, although this is at the expense of greater computer time. There is no simple way of deciding the number of points needed for given accuracy, but we believe that the results to be described are not very sensitive to the mesh.

IV. EVALUATION OF DEFECT TERMS

In this section we calculate the various contributions to the change in energy due to the defect, $V(\lambda, x)$. To be specific, we discuss the F center in alkali halides. Our calculations will be described in two stages. First, we discuss the contributions to $\underline{F}_0$, which enter in the linear theory. Second, we discuss the various higher-order terms. In both stages we will treat both the point-ion model for the defect-electron–host-lattice interaction[13] and in a model which allows for the detailed elec-

tronic structure of the ions.[4] For ease of comparison we shall include the ion structure terms in calculating the wave function in all versions. We then drop the terms in the ionic structure in calculating the *forces* in some cases. Thus, we shall always start from the same undistorted, unpolarized crystal results. We emphasize that we use a detailed microscopic model for the defect and do not, as in some Green's-function approaches, merely represent the defect by a combination of mass and force constant changes from a perfect lattice.

A. Calculation of the First-Order Terms

The first-order term is linear in the displacements and contains $\underline{F}_0 \equiv -\partial V(\lambda_0, \underline{x})/\partial \underline{x}$. There are three contributions to $\underline{F}_0$ from any given shell of ions. First, there is a point-ion contribution because an anion has been replaced by a spread out electronic charge distribution. In this term the defect electron is assumed to interact with a lattice of point ions. Second, there is a "repulsive" contribution, because the removal of the anion eliminated some of the short-range interactions between the ions. Finally, there are "ion-size" terms, which appear because the detailed structure of the ions of the host lattice must be considered in treating their interaction with the defect electron; these terms are corrections to the point-ion interaction.

In the $2p$ excited state of an F center, there are forces which lead to a JT effect, with either tetragonal (E) or trigonal (T_2) distortions in addition to the totally symmetric (A_1) distortions. Initially, we will only consider the forces on the nearest neighbors to the F center. The extension to more distant neighbors is straightforward. The neighbors are labeled as follows:

$$
\begin{aligned}
1 &\equiv (a, 0, 0), & 4 &\equiv (-a, 0, 0), \\
2 &\equiv (0, a, 0), & 5 &\equiv (0, -a, 0), \\
3 &\equiv (0, 0, a), & 6 &\equiv (0, 0, -a).
\end{aligned} \tag{4.1}
$$

It is convenient to introduce symmetrized forces, partly because of the simplifications which result, and partly because symmetry of the center is kept explicit. The forces F_A, F_E, and F_T act on all the neighbors of the F center, and the forces on each of the neighbors are given below:

neighbor 1, $(F_A + F_E, \quad F_T, \quad F_T)$;

2, $(F_T, \quad F_A - \tfrac{1}{2}F_E, \quad F_T)$;

$$3, \quad (F_T, \; E_T, \; F_A - \tfrac{1}{2} F_E);$$

$$4, \quad -(F_A + F_E, \; F_T, \; F_T);$$

$$5, \quad -(F_T, \; F_A - \tfrac{1}{2} F_E, \; F_T); \qquad (4.2)$$

$$6, \quad -(F_T, \; F_T, \; F_A - \tfrac{1}{2} F_E).$$

The corresponding displacements are Q_A, Q_E, and Q_T.

We have arbitrarily singled out the [100] tetragonal distortion and the [111] trigonal distortion. The total Hamiltonian, of course, has full cubic symmetry. By choosing a direction of distortion we are, in essence, placing the system on one specific energy surface of those which are degenerate for zero distortion.

The magnitudes of F_A, F_E, and F_T can be found by evaluating the change in energy for some appropriate displacement of neighbors. We must, of course, ignore the terms which would arise if the electron were a point change at the vacancy center, since these are already built into the dynamical matrix $\underline{\underline{D}}$, and into $\underline{\underline{A}}$. When a center has a net charge, the long-range Coulomb forces can be calculated by a modification of the Ewald method.[14]

We now calculate the point-ion terms explicitly. Writing the $2pZ$ wave function of the defect electron

$$|pZ\rangle = (3/4\pi)^{1/2}(z/r)R(r) , \qquad (4.3)$$

then these terms are, in the rigid-ion model,

$$F_A^{PI} = (Z_+ e^2/a^2) \int_a^\infty dr \, r^2 R^2(r) ,$$

$$F_E^{PI} = \tfrac{2}{5}(Z_+ e^2/a^2)[-3 \int_0^a dr \, r^2(r/a)^2 R^2(r)$$
$$+ 2 \int_a^\infty dr \, r^2(a/r)R^2(r)] , \qquad (4.4)$$

$$F_T^{PI} = \tfrac{4}{15}(Z_+ e^2/a^2)[\int_0^a dr \, r^2(r/a)^2 R^2(r)$$
$$+ \int_a^\infty dr \, r^2(a/r)R^2(r)] ,$$

$$F_{AA}^{PI} = \tfrac{1}{2}(Z_- e^2/a^2) \int_{(\sqrt{2})a}^\infty dr \, r^2 R^2(r) ,$$

where we normalize $R(r)$ by

$$\int_0^\infty dr \, r^2 R^2(r) = 1 .$$

$Z_\pm$ is the charge of an ion in the shell of ions concerned, and has opposite signs for anions and cations.

The force F_{AA} is a totally symmetric force on the second neighbors. The breathing mode (A_1) force is outward when positive, and the tetragonal (E) force is outward on two neighbors and inward on four when positive. It is clear that F_E^{PI} is the sum of two terms of opposite sign, and the sign and magnitude of the distortion may prove sensitive to $R(r)$. the radial wave function. The trigonal (T_2) force, when positive, tends to move the nearest-neighbor ions towards the [111] axis.

The point-ion forces act on both the cores and shells of the lattice ions. The separate core and shell forces in this case are found by replacing $Z|e|$ by the core charge $X|e|$ or the shell charge $Y|e|$, as appropriate.

The repulsive forces, which result from the changes in the short-range interionic terms, usually contribute to the totally symmetric A_1 distortion alone. This is not true for off-center substitutional ions, where two short-range forces are appreciable: the polarization forces and the repulsive forces. The polarization terms lead to an asymmetric configuration. We make the usual assumption that these forces act between the shells of neighboring ions, and do not involve the cores directly. It is not necessary to assume any specific radial dependence for this interaction, since the equilibrium condition for the perfect crystal can be used instead. This gives directly a net inward force

$$F_{A,S}^{REP} = -(Z^2 e^2/a^2)\tfrac{1}{6}\alpha , \qquad (4.5)$$

where Z is the ionic charge and α the Madelung constant. For the NaCl structure $(\tfrac{1}{6}\alpha)$ is 0.29127. The important point to note here is that both $F_{A,S}^{REP}$ and its derivative with respect to the totally symmetric mode of displacement of the shells can be written in terms of Kellermann's A and B coefficients:

$$F_{A,S}^{REP} = -(Z^2 e^2/4a^2)B_{Kell} ,$$

$$\frac{\partial}{\partial Q_{AS}} (F_{A,S}^{REP}) = +\frac{Z^2 e^2}{4a^3} A_{Kell} . \qquad (4.6)$$

When second-neighbor repulsive forces occur, similar, but more complicated, relations hold.

We can also write down contributions from van der Waals forces in the same way; again, this gives essentially a shell-shell interaction. However, it is not obvious that we should include this (at least with its $1/r^6$ dependence) while ignoring other factors; indeed, experimentally the lattice dynamics of the alkali halides seems to indicate that short-range forces other than between nearest neighbors are barely significant. We have not included the van der Waals terms in the present calculations.

The ion-size terms are more complicated. They give a term in the potential experienced by the defect electron of the form

$$V_{IS} = \sum_i [A_i + B_i(\overline{V} - U_i)]\delta(\vec{r} - \vec{r}_i) \equiv \sum_i C_i \delta(\vec{r} - \vec{r}_i) . \qquad (4.7)$$

A_i and B_i depend only on the species of ion i, $\overline{V}$ is the potential energy of the defect electron, and

$$U_i = \sum_{j \neq i} V_j^{PI} \qquad (4.8)$$

is the point-ion potential energy of the electron at site j. For convenience later, we define

$$\beta = \sum_i B_i \, |\phi(\vec{r}_i)|^2 , \qquad (4.9)$$

where $\phi(\vec{r})$ is the defect-electron wave function. It is less simple to derive the forces in this case, mainly because of the factor $(\overline{V} - U_i)$. Our results will depend on our division of the interaction (4.7) between the ion cores and the ion shells. We shall assume that the ion-size potential V_{IS} is produced entirely by the shells. The argument here is that the shells correspond to the outermost electrons in each ion, and it is just these electrons which dominate in A_i and B_i. Having made this assumption, the forces on the shells and cores follow straightforwardly. The forces on the cores are not zero, since there is an implicit dependence on the core coordinates in the factor $(\overline{V} - U_i)$. The forces on the shells are

$$F^{IS}_{A,S} = \frac{1}{1-\beta} \left[\beta \, F^{PI}_{A,S} + \frac{1}{3} B_+ R^2(a) \frac{\partial U_{nn}}{\partial Q_{AS}} \right.$$
$$\left. - \frac{1}{3} C_+ \frac{dR^2(r)}{dr} \Big|_a \right] ,$$

$$F^{IS}_{E,S} = \frac{1}{1-\beta} \left[\beta F^{PI}_{E,S} + \frac{1}{3} B_+ R^2(a) \frac{\partial U_{nn}}{\partial Q_{ES}} \right.$$
$$\left. - \frac{1}{3} C_+ \frac{dR^2(r)}{dr} \Big|_a \right] ,$$

$$F^{IS}_{T,S} = \frac{1}{1-\beta} \left[\beta F^{PI}_{TS} \right] , \qquad (4.10)$$

$$F^{IS}_{AA,S} = \frac{1}{1-\beta} \left[\beta F^{PI}_{AA,S} + \frac{1}{3} B_- R^2(\sqrt{2}\,a) \frac{\partial U_{nnn}}{\partial Q_{AAS}} \right.$$
$$\left. - \frac{1}{3} C_- \frac{dR^2(r)}{dr} \Big|_{(\sqrt{2})a} \right] ,$$

and the forces on the cores are

$$F^{IS}_{AC} = \frac{1}{1-\beta} \left[\beta F^{PI}_{AC} + \frac{1}{3} B_+ R^2(a) \frac{\partial U_{nn}}{\partial Q_{AC}} \right] ,$$

$$F^{IS}_{EC} = \frac{1}{1-\beta} \left[\beta F^{PI}_{EC} + \frac{1}{3} \beta_+ R^2(a) \frac{\partial U_{nn}}{\partial Q_{EC}} \right] ,$$

$$F^{IS}_{TC} = \frac{1}{1-\beta} \left[\beta F^{PI}_{TC} \right] , \qquad (4.11)$$

$$F^{IS}_{AAC} = \frac{1}{1-\beta} \left[\beta F^{PI}_{AAC} + \frac{1}{3} B_- R^2(\sqrt{2}\,a) \frac{\partial U_{nn}}{\partial Q_{AAC}} \right] .$$

In these equations C_+ is $[A_+ + B_+(\overline{V} - U_{nn})]$ and C_- is $[A_- + B_-(V - U_{nnn})]$, where U_{nn} and U_{nnn} are the values of U_i at the nearest- and next-nearest-neighbor sites. The suffixes S and C denote shell and core, respectively. The point-ion forces on the right-hand side of these equations come from derivatives of $\overline{V}$. For the T mode the only term is the point-

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TABLE I. Derivatives of U.

Derivatives with respect to motion of the nearest neighbors. In these expressions $X \equiv X_+$, $Y \equiv Y_+$.
Derivatives of U at the nearest-neighbor site:

$$U_{AS} = X_+(\tfrac{1}{4} + \sqrt{2}) + Y_+ (\tfrac{1}{2} + 2\sqrt{2}) + Z_+ ,$$

$$U_{ES} = X_+(\tfrac{1}{4} + \sqrt{2}) + Y_+(\tfrac{1}{2} + 1/\sqrt{2}) + Z_+ ,$$

$$U_{AC} = X_+(\tfrac{1}{4} + \sqrt{2}) ,$$

$$U_{EC} = X_+(\tfrac{1}{4} - 1/\sqrt{2}) ,$$

Derivatives of U at the next-neighbor site. Here $Q_Z \equiv X_+$ when the near-neighbor cores move, and Y_+ when the near-neighbor shell moves:

$$U_A = Q_Z \left(\frac{2(1-\sqrt{2})}{(5-2\sqrt{2})^{3/2}} + \frac{2}{5^{3/2}} + \frac{2(1+\sqrt{2})}{(5+2\sqrt{2})^{3/2}} \right) ,$$

$$U_E = Q_Z \left(\frac{(1-\sqrt{2})}{2(5-2\sqrt{2})^{3/2}} - \frac{1}{5^{3/2}} + \frac{(1+\sqrt{2})}{2(5+2\sqrt{2})^{3/2}} \right) .$$

Derivatives with respect to the motion of the next neighbors. In these expressions $X \equiv X_-$ and $Y \equiv Y_-$.
Derivative of U at the nearest-neighbor site.
Here $Q_Z = X_-$ when the next-neighbor core moves, and Y_- when its shell moves:

$$U_{AA} = Q_Z \left(\frac{4\sqrt{2}-2}{(5-2\sqrt{2})^{3/2}} + \frac{4\sqrt{2}}{5^{3/2}} + \frac{4\sqrt{2}+2}{(5+2\sqrt{2})^{3/2}} \right) .$$

Derivatives of U at a next-neighbor site:

$$U_{AAC} = X_- \frac{1}{2\sqrt{2}} \, \frac{9}{4} + \frac{2}{\sqrt{3}} + \frac{1}{\sqrt{2}} ,$$

$$U_{AAS} = X_- \frac{1}{2\sqrt{2}} \left(\frac{9}{4} + \frac{2}{\sqrt{3}} + \frac{1}{\sqrt{2}} \right) + Y_- \frac{1}{\sqrt{2}} \left(\frac{9}{4} + \frac{2}{\sqrt{3}} + \frac{1}{\sqrt{2}} \right) + \tfrac{1}{4} Z_+ .$$

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ion term, since the nearest-neighbor contribution to (4.7) cannot mix different p states. The contribution of the second neighbors is not restricted in this way. The various derivatives of the U_i can be written as

$$\frac{\partial U}{\partial Q_\alpha} = \frac{e^2}{a^2} \cdot U_\alpha . \qquad (4.12)$$

Apart from shell and core charges, the factors U_a are purely geometric. In Table I we list the U_α for both nearest-neighbor and next-neighbor sites. In the same way we may construct second derivatives for treating higher-order terms. These terms get progressively more complex and more tedious to derive, and we shall not quote the higher-order terms. In the rigid-ion limit of lattice dynamics we have $X \to 0$, $Y \to Z$, so that for the nearest-neighbor forces

$$U_A = Z (\tfrac{3}{2} + 2\sqrt{2}), \quad U_E = Z (\tfrac{3}{2} + 1/\sqrt{2}) . \qquad (4.12')$$

V. F CENTER IN KBr

We now discuss the application of these methods to the excited $2p$ state of the F center in KBr. Before giving details, we emphasize some of the assumptions which we shall make. Our aim in this

section is to illustrate the methods we have developed, rather than to provide an all-embracing theory of the center. Thus, we assume that the F-center wave function can be represented by a wave function with one variational parameter, λ. Further, we assume that the distortions and the changes in λ on distortion are sufficiently small that the higher-order terms are well given by (2.3'). Also, we ignore the effect of other close electronic states, such as the $2s$ state, even though these may be important in the real system.[15,16] It is possible to remove all these approximations using the method we have described, but only at the expense of some complexity which, for present purposes, we wish to avoid.

A. Choice of Wave Function

The variational trial function we adopt is the Gourary-Adrian type-II function, with

$$R(r) = g j_1(\xi r/a) e^{-\eta} \quad \text{for } r \leq a,$$
$$R(r) = g j_1(\xi)(r/a) e^{-\eta r/a} \quad \text{for } r \geq a, \tag{5.1}$$

in which ξ is the variational parameter, corresponding to λ; η is given by

$$\eta = 3 - \xi^2/(1 - \xi \cot\xi), \tag{5.2}$$

and $j(\chi) = (\sin\chi - \chi \cos\chi)/\chi^2$. For KBr the parameters for the undistorted lattice are

$$\lambda_0 \equiv \xi_0 = 3.22, \quad \eta_0 = 3.27, \tag{5.3}$$

using a point-ion model with ion-size corrections.[4]

B. Calculation of the Linear Terms

The radial wave function $R(r)$ depends only on (r/a) and on ξ. Consequently, we can derive the point-ion forces F^{PI} in units of Ze^2/a^2 as functions of ξ. These are shown in Fig. 1. The forces on the shells should, of course, replace Z by Y, and those on the cores replace Z by X. The largest of the point-ion forces is F_A^{PI}, and F_E^{PI} is larger than F_T^{PI}. We shall find that, for most F centers, the tetragonal (E) distortions and the trigonal (T_2) distortions are comparable in magnitude. For KBr, the forces on the ion cores are

$$F_{AC}^{PI} = 0.3615 X_+ e^2/a^2, \quad F_{EC}^{PI} = -0.1999 X_+ e^2 a^2,$$
$$\tag{5.4}$$

$$F_{TC}^{PI} = 0.1772 X_+ e^2/a^2, \quad F_{AAC}^{PI} = 0.0410 X_- e^2/a^2.$$

The forces on the shells are found by replacing the core charges X_+ and X_- by shell charges Y_+ and Y_-. As we go through the sequence of alkali halides from the iodides to the fluorides the trigonal point-ion forces become progressively stronger compared with the tetragonal ones.

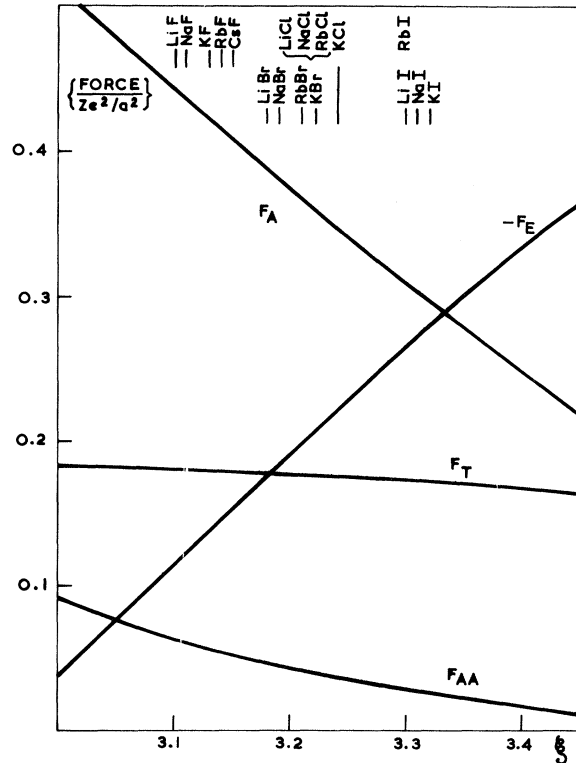The repulsive contribution to F_A is given by (4.5) and acts only on the shells:

FIG. 1. Point-ion forces in units of Ze^2/a^2 as a function of the variational parameter ξ, giving a measure of the extent of the excited-state F-center wave function. The values of ξ obtained in Ref. 4 for the different alkali halides are indicated.

$$F_{AS}^{REP} = -0.2913 Z^2 e^2/a^2. \tag{5.5}$$

The ion-size forces can be found directly from Eqs. (4.10)–(4.12). In these expressions, the $\partial U/\partial Q_\alpha$ depend on the shell and core charges, and cannot be given independently of the lattice dynamical model.[17] The other factors which depend on the wave function $[\beta, R^2(a), \text{ and } R^2(\sqrt{2}a)]$ may be found from knowledge of ξ and η. The B_i and C_i are given explicitly in Tables I, VI, and VIII of Ref. 4. The C_i make use of the reduced parameters $0.53 A_i$; we will not discuss the origin of the reduction factor here, and simply treat it as an empirical correction.

The ion-size forces on the nearest-neighbor shells are outward; the outward motion of the ions reduces a repulsive contribution to the energy. All three linear terms – the point-ion, repulsive, and ion-size contributions – are similar in order of magnitude. As various signs of term are possible, it is clear that all the terms must be considered, and that any model which does not include ion-size corrections or their equivalent is likely to be poor.

The results of the linear calculations are given in Table II. These show ΔE, the change in total en-

TABLE II: Results for KBr. These use the nuclear (core) coordinates, and are expressed as a percentage of the nearest-neighbor distance. Q_A is positive for outward motion; Q_E is positive when two neighbors move out and four in, and Q_T is positive when the neighbors move towards the (111) direction. In all cases, the second-neighbor cores move in by 1 to 3%. ΔE is the total (lattice and electronic) energy reduction.

Lattice dynamics		Linear	Second order in Q_A
Rigid ion[a]	Q_A (%)	6.2	3.3
	Q_E (%)	1.8	1.8
	$\Delta\xi, \Delta\eta$		0.006, 0.021
	ΔE (eV)	0.40	0.29
Fitted model[a]	Q_A (%)	7.1	6.2
	Q_E (%)	−4.2	−4.2
	$\Delta\xi, \Delta\eta$		−0.016, −0.058
	ΔE (eV)	0.81	0.78
300° lattice-dynamic data[a]	Q_A (%)	4.7	0.92
	Q_E (%)	2.3	2.3
	$\Delta\xi, \Delta\eta$		0.0017, 0.0060
	ΔE (eV)	0.69	0.59
Rigid ion[b]	Q_A (%)	6.2	3.3
	Q_T (%)	6.7	6.7
	ΔE (eV)	0.73	0.52
Fitted model[b]	Q_A (%)	7.1	6.2
	Q_T (%)	8.2	8.2
	ΔE (eV)	1.33	1.26
300° lattice-dynamic data[b]	Q_A (%)	4.7	0.92
	Q_T (%)	7.3	7.3
	ΔE (eV)	0.61	0.49

Lattice Dynamics	Tetragonal linear		Trigonal linear	
Rigid ion[c]	Q_A (%)	1.54	Q_A (%)	1.54
	Q_E (%)	−7.85	Q_T (%)	1.12
	ΔE	0.151	ΔE	0.044
Fitted model[c]	Q_A (%)	3.43	Q_A (%)	3.43
	Q_E (%)	−12.14	Q_T (%)	1.36
	ΔE	0.501	ΔE	0.32
300° lattice dynamic data[c]	Q_A (%)	0.83	Q_A (%)	0.83
	Q_E (%)	−7.46	Q_T (%)	1.22
	ΔE	0.195	ΔE	0.071

[a]Tetragonal case with ion-size effects.
[b]Trigonal case with ion-size effects.
[c]Tetragonal and trigonal cases: no ion-size terms.

ergy (electronic plus elastic) from relaxation, and the various distortions. A number of points emerge clearly. First, the relaxation energy ΔE depends strongly on the lattice-dynamic model chosen. Second, the symmetry, and sometimes even the sign of the asymmetric distortions, depends on the lattice dynamics because the shell and core charges enter in the forces. It is clear that the problem of lattice distortion and polarization near defects is sensitive to lattice-dynamic models, and that adequate models are not always available, even for well-studied crystals'like the alkali halides.

C. Higher-Order Terms

In the earlier section it became obvious that some, at least, of the higher-order corrections must be included. For the excited state of the F center, the linear theory with ion-size corrections predicts rather large distortions of A_{1g} symmetry, and, at least, we must treat the second-order terms in these totally symmetric modes. We will ignore terms which are of higher order in other distortions, since we can then simplify the calculation considerably. This simplification would not be valid in some circumstances. Thus, if there were appreciable mixing of the 2s and 2p levels we would have to treat other modes in detail.

The calculation of the higher-order terms follows very closely the treatment of the linear terms. For this reason we will only mention the points of difference. We now have derivatives of $W(\lambda, x)$ with respect to $(\lambda - \lambda_0)$, including those which enter into the variational condition. The simplest of these is Λ', which can be found during the variational (computer) calculation to determine λ_0. Since this parameter is not readily obtained at other times, we give values of Λ' for all alkali halides in Table III. Values are given for both the point-ion model and for the model including ion-size corrections. The other derivatives are obtained analytically. It is important to note that the ion-size corrections to the potential [Eq. (4.7)] already involve $\overline{V}$ which is a function of the variational parameter λ. The variational condition is to be taken as

$$\frac{\partial}{\partial \lambda} \langle \phi(\lambda) | T + V(\lambda') | \phi(\lambda) \rangle |_{\lambda = \lambda'} = 0 , \qquad (5.6)$$

where $| \phi(\lambda) \rangle$ is normalized to unity. This form was correctly used in Ref. 4, and its use introduces a number of changes in detail.

Another point of difficulty arises because the particular variational trial function we use has a discontinuous second derivative $d^2 R/dr^2$, at $r = a$. We have estimated the second derivative in several ways, by taking the limit as r tends to $r = a$ from both larger and small values of r, by setting $d^2 R/dr^2$ equal to zero, and also by setting $d^2 R^2/dr^2$ equal to zero. The various choices give negligible differences in the results.

For simplicity of exposition, we assume that only two coordinates Q_{AC} and Q_{AS} become sufficiently large for the second-order term to be appreciable. It is clear from Sec. IV that nonlinear terms in these coordinates may be large. It is useful to write out some of the equations of Sec. II B in a form which can be applied directly. We abbreviate Q_{AC} to x and Q_{AS} to y. The forces which correspond to x and y are F_C and F_S, respectively. The linear theory gives results corresponding to (2.11):

$$x = \alpha_{CC} F_C + \alpha_{CS} F_S, \qquad (5.7)$$

TABLE III. Values of Λ' for F centers in various hosts. $E(\xi) = E(\xi_0) + \frac{1}{2}\Lambda'(\xi - \xi_0)^2$; $\xi \equiv \lambda$. Results are ordered in increasing (anion radius/cation radius). Units for Λ' are Ry.

Crystal	Ground state (point-ion model)	Excited state	Ground state (with ion-size corrections)	Excited state
CsF	0.731 95	0.494 72	0.724 79	0.368 95
RbF	0.807 64	0.516 18	0.743 87	0.367 16
KF	0.870 23	0.537 63	0.743 87	0.314 71
RbCl	0.662 21	0.460 15	0.529 29	0.302 79
RbBr	0.613 93	0.442 27	0.454 19	0.258 68
NaF	1.077 65	0.566 24	0.791 55	0.316 50
KCl	0.691 41	0.482 20	0.517 96	0.301 60
KBr	0.653 27	0.460 15	0.446 44	0.252 13
RbI	0.556 11	0.419 02	0.424 98	0.272 39
KI	0.590 68	0.433 33	0.423 79	0.278 95
NaCl	0.808 84	0.515 58	0.563 86	0.324 85
LiF	1.297 00	0.540 61	0.944 14	0.352 26
NaBr	0.742 08	0.503 66	0.478 63	0.259 88
NaI	0.674 13	0.469 68	0.460 74	0.309 94
LiCl	0.915 53	0.544 19	0.634 19	0.382 66
LiBr	0.842 21	0.537 04	0.529 89	0.305 18
LiI	0.739 10	0.497 70	0.514 98	0.355 84

$$y = \alpha_{sc}F_c + \alpha_{ss}F_s .$$

But these forces are themselves linear in x and y because of the higher-order terms. Consequently, we have

$$F_c = F_{co} + F_{co}x + F_{cs}y,$$
$$F_s = F_{so} + F_{sc}x + F_{ss}y. \tag{5.8}$$

Solving (5.7) and (5.8) simultaneously we find that the displacements can be calculated from (5.7) using

$$F_c \equiv F_c^{\text{eff}} = \gamma_{cc}F_{co} + \gamma_{cs}F_{so},$$
$$F_s \equiv F_s^{\text{eff}} = \gamma_{sc}F_{co} + \gamma_{ss}F_{so}, \tag{5.9}$$

where

$$\gamma_{cc} = (1 - F_{sc}\alpha_{cs} - F_{ss}\alpha_{ss})/\Delta \equiv \delta_{cc}/\Delta,$$
$$\gamma_{ss} = (1 - F_{cs}\alpha_{sc} - F_{cc}\alpha_{cc})/\Delta \equiv \delta_{ss}/\Delta,$$
$$\gamma_{cs} = (F_{cc}\alpha_{cs} + F_{cs}\alpha_{ss})/\Delta \equiv \delta_{cs}/\Delta, \tag{5.10}$$
$$\gamma_{sc} = (F_{sc}\alpha_{cc} + F_{ss}\alpha_{sc})/\Delta \equiv \delta_{sc}/\Delta,$$
$$\Delta = \delta_{cc}\delta_{ss} - \delta_{cs}\delta_{sc} .$$

The results of taking the terms in the spherically symmetric distortions to second order are shown in Table II. The main effects are a significant reduction in the symmetric distortion, and small changes in the electronic wave function. In part, the smallness of the change in the wave function may arise from our use of a simple one-parameter trial function. Consequently the results in Table I are not sufficiently accurate to test the hypothesis (Ref. 18; see also the comments in Ref. 5) that the wave function is very widespread in the relaxed excited state. The methods we have described can, of course, be extended to discuss this point.

VI. DISCUSSION

We have developed a general method for treating the polarization and distortion near color centers. Two basic approximations are made: The host lattice is assumed to respond to the average, consistently chosen charge distribution of the defect electrons, and the shell model or some equivalent model is used to describe the host. There are no restrictions on the symmetry of the distortions which result, nor on the range of the distortions. Terms in the electron energy which are very sensitive to the lattice configuration can be treated provided that the harmonic approximation remains valid. However, such terms usually reduce the value of knowledge of the static distortion since many of the observable properties depend on the details of the defect lattice dynamics; in particular, the Condon approximation (Ref. 19, for example) may break down.

The methods have been illustrated by a discussion of the $2p$ excited state of the F center in KBr. This state is electronically degenerate and exhibits a JT effect. The calculations give the change in total energy, the totally symmetric and JT distortions, and the change in defect-electron wave function. Since these calculations were designed to illustrate the method rather than to provide a full treatment of this very complex system, two simplifying approximations were made. The first approximation was the use of a one-parameter variational trial function, and the second the neglect of the influence of the nearby $2s$ state. However, a number of conclusions are apparent. First, it is

essential to go beyond the point-ion model[13] for the defect-electron–host-lattice coupling. We have used the ion-size corrections described in Ref. 4. Second, our knowledge of the lattice dynamic and dielectric properties of the host lattice may not be good enough to predict defect properties accurately. This is because there are a number of models, differing only in actual magnitudes of parameters and in some small terms, all of which give perfect crystal properties with comparable accuracy. The anharmonic properties of the host lattice are even less well known. We emphasize that the use of simple approximations, such as Born-Mayer interactions or even continuum models, does not resolve any of these difficulties; at best, such simplifications merely hide the problems. For all the lattice-dynamic models we have used, we find an outward motion of the nearest neighbors to the vacancy, together with a JT effect in which the trigonally and tetragonally distorted configurations are comparable in energy. The change in total energy on distortion is of order 0.5 to 1 eV, depending on the detailed model. This change is clearly in line with the substantial Stokes shifts observed for F centers. The change in wave function on distortion is relatively small, probably because of the restricted form of variational function.

In the past, many calculations of color-center properties have used intuition as a major constituent. We have attempted to show, both in an earlier paper[4] and here, that detailed atomic calculations are practical, and that the methods developed are sufficiently general to treat complicated systems without restrictive approximations or sophisticated computation.

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APPENDIX: SHELL-MODEL PARAMETERS

These parameters, the shell charges Y_+ and Y_- and the shell-core force constants k_+ and k_-, can be fitted from neutron data. Here we describe one other approach, a least-squares fit from elastic, dielectric, and infrared data.

The input data consisted of the static and optical dielectric constants ϵ_0 and ϵ_∞, the lattice parameter a, the ionic polarizabilities α_+ and α_-, the ionic masses M_+ and M_-, the restrahlen frequency ω_0, and the elastic constant c_{11}. From these, we define variables which may be related to the shell-model parameters:

$$\alpha_0 = \frac{3}{4\pi} \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \quad , \quad \alpha_\infty = \frac{3}{4\pi} \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \quad ,$$

$$\mu = M_+ M_- / (M_+ + M_-) \ , \quad v = 2a^3 \ ,$$

$$R = 2c_{11}/(e^2/va) + 2.718\,94\,Z^2 \ .$$

In terms of the shell-model parameters Y_+, Y_-, k_+, and k_- we have

$$\alpha_+ = Y_+ v/k_+, \quad \alpha_- = Y_-^2 v/k,$$

$$\alpha_\infty = [(Y_+ + Y_-)^2 R + (Y_+^2 k_- + Y_-^2 k_+)]/\Delta \ ,$$

$$\alpha_0 = \alpha_\infty + \frac{[Z - (Y_+ k_- - Y_- k_+)R/\Delta]^2}{1 - (k_+ + k_-)R/\Delta} \ ,$$

where

$$\Delta = k_+ k_- + R(k_+ + k_-)$$

and

$$\mu \omega_0^2 = \left[\frac{(1 - \frac{4}{3}\pi\alpha_0)}{(1 - \frac{4}{3}\pi\alpha_\infty)}\right] \frac{R}{\Delta} k_+ k_- \ .$$

We used a least-squares fit in which we minimized the sum

$$\sum_{i=1}^{5} W_i \left(\frac{x_i^{fit} - x_i^{exp}}{x_i^{exp}}\right)^2 \ ,$$

with x_i given by $\alpha_+, \alpha_-, \alpha_\infty, \alpha_0$, and $\mu\omega_0^2$, to find values of k_+, k_-, Y_+, and Y_-. The problem was, thus, overdetermined, and the residuals gave an estimate of the accuracy of the fit. The weights W_i were usually unity, but could be varied to reduce the importance of any poor data.

For KBr we use the data[20,21] given in Table IV. The other data used were taken from the fit to dispersion data of Ref. (22). A number of different sets of parameters appear in the literature, for example, those given by Havinga[23] and by Bron.[24] We have not made use of these other sets.

TABLE IV: Lattice dynamic data.

$\alpha_+ = 0.83 \times 10^{-24}$ cm^3,
$\alpha_- = 4.77 \times 10^{-24}$ cm^3,
$M_+ = 39.100$ amu,
$M_- = 79.916$ amu,
$\epsilon_0 = 4.78$,
$\epsilon_\infty = 2.33$,
$\omega_0 = 2.13 \times 10^{13}$ rad/sec,
$c_{11} = 3.46 \times 10^{11}$ dyn/cm^2,
$a = 3.30$ Å.

*Perliminary accounts of this work appear in Abstracts of the Conference on Color centers in Ionic Crystals, Rome, 1968 (unpublished); and in Bull. Am. Phys. Soc. 14, 375 (1969).

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Influence of Impurities on the Room-Temperature Coloration Processes in Alkali Halides

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The F-center growth curves for undoped KCl and KCl crystals doped with Ba, Co, and Cd have been obtained by x irradiation at room temperature. These growth curves are fitted to an equation with two exponential terms and a linear term, and the parameters occuring in the equation are evaluated. Two exponential terms have been found to be adequate to describe the first-stage coloration, with which this paper is mainly concerned. The analysis shows that the slower exponential component is strongly influenced by the presence of impurities; specifically, the rate of coloration during the process responsible for this component decreases, and the saturation level for the process increases, on account of the impurities. The faster exponential component appears to be relatively insensitive to the presence of impurities. These results are discussed with reference to certain mechanisms that have been put forward to account for the first stage.

I. INTRODUCTION

There has been considerable interest in recent years in the mechanisms of color center production by ionizing radiation in alkali halides.[1] Among other methods employed, the analysis of the plots of F-center growth versus time of irradiation (or radiation dose) has yielded useful information regarding