A PRELIMINARY THEORETICAL INVESTIGATION OF THE F^+ CENTER IN SrO AND BaO

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CHAPTER I

INTRODUCTION

The study of point defects in crystalline materials is an increasingly important branch of solid state physics. Many times such defects have a very direct effect on the electronic properties of a material, examples of which are transistors and solid state lasers. Point defects can be divided into the classes of impurity defects and radiation induced defects. (The defects of concern in this study are in the latter class.) A large part of the radiation-induced point defect research of the past several decades has been conducted in alkali halide crystals. These crystals have simple face-centered cubic structures and are easily grown both pure and with controlled dopants. Various point defects can easily be created in them by irradiation or additive coloration. A great deal of information about point defects has been obtained from this alkali halide research, and all of the current theoretical models, (including the model used in this study,) were first developed to treat point defects in the alkali halides.

Some of the major radiation-induced defects studied in the alkali halides and their nomenclature will be discussed in this paragraph. The class of these point defects of concern in this study are the trapped electron centers in which one or more electrons are trapped at a negative ion vacancy. If the center is neutral with respect to the rest of the lattice, it is called an F center. Thus, in the alkali halides the F center consists of one electron trapped at a halogen ion vacancy. If the center has a positive charge with respect to the rest of the lattice, it is termed an F^+ center, etc. There are several variations of the F centers, such as the F_A center, an F center in which one of the six nearest neighbors of the defect has been replaced by a different cation. Some complex trapped electron centers are the F_2 center, which is two adjacent F centers, and the F_3 center, which is three adjacent F centers, etc. Color centers can also be due to trapped holes. The most common trapped-hole center in alkali halides is the V_k center, which is a hole trapped by a pair of adjacent halogen ions to form a complex resembling an X_2^- ion. (X denotes a halogen atom.) The trapped hole analog to the F center in the alkali halides would be a hole trapped at a positive ion vacancy, but no such center has ever been identified. However, the trapped hole analog to the F^+ center in the alkaline earth oxides has been identified, that is one hole trapped at an oxygen ion vacancy.

These defects have characteristic optical properties, often in the visible region, which are used to identify the specific defects. And most of them have unpaired electrons which give rise to characteristic ESR properties. Thus, most of the experimental evidence concerning color centers has been acquired using absorption and luminescence optical spectroscopy and magnetic resonance techniques such as ESR and ENDOR.

More recently the alkaline earth oxides (MgO, CaO, SrO, and BaO) have been the subject of increasing interest. These compounds are the divalent analog to the alkali halides and present a logical extension of the alkali halide studies. The alkaline earth oxides have face-centered cubic structures and their binding is predominantly ionic (but becomes less classical ionic binding as one moves from MgO toward BaO.) They have electronic bandgaps ranging from approximately 8.0 eV in MgO to roughly 4.5 eV in BaO (1). Their melting points are much higher than those of the alkali halides, and this is partly responsible for the fact that, until recently, high quality samples of alkaline earth oxide crystals have been unavailable.

The object of this study is to theoretically investigate the F^+ center defects in SrO and BaO using a model developed by R. F. Wood and U. Opik (2) for alkali halides. This model has already been applied to the F and F^+ centers in MgO and CaO by T. M. Wilson and R. F. Wood (17).

In the alkaline earth oxides an F center consists of two electrons trapped at an oxygen ion vacancy, and an F^+ center is a single electron trapped in an oxygen ion vacancy. So the F center is effectively a neutral defect and the F^+ center is a singly ionized F center.

In some of these alkaline earth oxides it has been demonstrated that F centers can be converted to the F^+ centers by 'bleaching' with ultraviolet light which excites one of the electrons out of the F center, possibly into the conduction band where it is retrapped by some impurity defect such as an iron or chromium impurity. This leaves the one electron F^+ center. This F^+ center can be converted back to an F center by releasing the trapped electron using thermal (kT) excitation or optical irradiation so that it can fall back into the F^+ center to reform the two-electron F center.

TABLE I

OPTICAL ABSORPTION AND EMISSION VALUES FOR THE ALKALINE EARTH OXIDES (22)

Lattice	F^+ Center Absorption, eV ($^2A_{1g} \to {}^2T_{1u}$)	 Emission, eV ($^2T_{1u} \to {}^2A_{1g}$)	F Center Absorption, eV ($^1A_{1g} \to {}^1T_{1u}$)	 Emission, eV ($^3T_{1u} \to {}^1A_{1g}$)
MgO	4.92	3.13	5.01	2.4
CaO	3.70	3.3	3.10	2.0
				2.5 ($^1T_{1u} \to {}^1A_{1g}$) (30)
SrO	3.10	2.42	2.49	———
BaO	2.00	———	2.3 (4)	———

CHAPTER II

PREVIOUS EXPERIMENTAL STUDIES

The experimental study of color centers in the alkaline earth oxides has been in progress for about the last twenty years, but positive optical identification of their F centers and F^+ centers has been fairly recent. Until recently high quality samples of alkaline earth oxides were not available. Large dislocation densities occurred in these crystals since they have high melting points and were prepared by the arc-fusion method. Impurity concentrations were also fairly large and the optical characteristics of some of these transition-metal ion impurities made it very difficult to study the optical properties of the F and F^+ centers in these crystals (9).

The historical pecking order of the alkaline earth oxides is MgO, CaO, SrO, and BaO. BaO did receive some early attention due to its applications in oxide coated cathodes, but this order does hold as far as color centers are concerned. Thus SrO and BaO, the compounds of primary concern in this study, have received much less attention than MgO and CaO. This is partially due to the additional difficulties involved in obtaining and working with samples of BaO and SrO. Heavier elements, such as barium, are rather toxic (3) and both SrO and BaO are hydroscopic. However, progress is being made, and as a result some experimental data is now available for color centers in SrO and BaO.

The F and F^+ center absorption bands were positively identified in

SrO by Johnson and Hensley (5) in 1969, and in BaO by Rose and Hensley (4) in 1972. An F^+ center emission band in SrO was reported by Kemp and Evans in 1969. With the completion of the recent work in BaO, the absorption bands have now been positively identified for both F and F^+ centers in all four of the alkaline earth oxides. There is reliable identification of F and F^+ center luminescence in MgO and CaO, but the discovery of SrO F^+ center emission is very new and somewhat tentative. No F or F^+ center emission bands for BaO have been reported although such experiments are presently underway (4).

The optical absorption and emission values for F and F^+ centers in the series of alkaline earth oxides are summarized in Table I.

Lifetime evidence suggests that the observed F center emission in these alkaline earth oxides is a forbidden type ${}^3T_{1u} \rightarrow {}^1A_{1g}$ transition and the F^+ center emission is a ${}^2T_{1u} \rightarrow {}^2A_{1g}$ transition. Note that also a ${}^1T_{1u} \rightarrow {}^1A_{1g}$ F center emission band has been observed in CaO. The absorption bands for these alkaline earth oxides is assumed to be a ${}^1A_{1g} \rightarrow {}^1T_{1u}$ transition for the F center and a ${}^2A_{1g} \rightarrow {}^2T_{1u}$ transition for the F^+ center.

The halfwidths of the F^+ center absorption bands can be conveniently approximated from theoretical configuration coordinate diagrams by using a simple semiclassical model which assumes the nearest neighbors move in a single vibrational breathing mode of angular frequency w which results in a gaussian-shaped band. This model leads to a simple formula for the bandwidth H,

$$H = \hbar w \left[\underbrace{(8 \ln 2)}_{5,5452} S \coth (\hbar w / 2k_B T) \right]^{\frac{1}{2}},$$

where T is the temperature, and S is the Huang - Rhys factor, a measure of the linear coupling of the electronic states to the lattice vibrations. The effective frequency w is approximated from the curvature of the configuration coordinate diagrams.

The experimentalist uses this model in reverse to determine S and w by measuring the half-width of the F^+ center absorption band as a function of temperature.

Since the analysis of optical data requires knowledge of both the ground state and excited states, it would be advantageous to experimentally investigate these states individually. Magnetic resonance techniques (ESR and ENDOR) can be used to study the ground state individually.

The overlap of the F^+ center wavefunction onto the neighboring ions gives rise to measurable effects in the ESR spectrum of these centers. A shift in g-values is observed, and magnetic interactions with neighboring nuclei having non-zero nuclear spin result in hyperfine splittings. The isotropic part of this hyperfine interaction can be defined in terms of a parameter A, the Fermi contact term, which can be directly determined from experimental data. From Fermi-Segre' theory this quantity is given by

$$A = \frac{8}{3}\pi g \beta g_n \beta_n |\psi(\vec{r}_1)|^2$$

where $\vec{r}_1$ is the position of the particular nucleus, β and β_N are the electron and nuclear Bohr magnetons and g and g_n are the electron and nuclear g-values. This parameter should provide a good test for any theoretical wave function describing the ground state. Note that this isotropic parameter A depends upon the F^+ center wave function only at the nucleus of the particular ion involved.

There also exists an anisotropic interaction constant b which can be experimentally determined and can be calculated from

$$b = \frac{1}{2} g\beta\, g_n\, \beta_n \langle\psi|[3\cos^2\alpha - 1]/|\vec{r}^{\,3}|\,|\psi\rangle$$

for this symmetry. $\vec{r}$ is the electron nuclear separation and α is the angle between $\vec{r}$ and the symmetry axis z. This parameter is proportional to a weighted average of the defect electron wave function and provides another good test for any ground state theoretical wave function.

Due to the overlap of the defect electron wave function onto the nearest neighbor cations there is some mixing of orbital momentum into the ground state of the F^+ center which causes a shift in the electronic g-value of the center. This g-shift can be approximated by applying perturbation theory to this spin-orbit interaction. This leads to a complicated equation (1) which presents another challenge for any theoretical ground state wave function to meet.

Since several theoretical models give reasonable values for the transition energies of these defects (especially for MgO and CaO), it appears that the real test of any theoretical wave function will be how accurately it predicts these other experimentally measurable quantities. Unfortunately the calculation of these quantities, with the exception of half-widths, is very difficult and is beyond the scope of this study.

CHAPTER III

PREVIOUS THEORETICAL STUDIES

Most of the previous theoretical calculations on color centers have been based upon either the point-ion lattice model or the semi-continuum model. Of these two models the point-ion lattice model has been the more preferred for alkaline earth oxide calculations, although both models have been widely used for alkali halide calculations.

In the point-ion lattice model the potential seen by the color center electron(s) is approximated by the electrostatic potential due to the ions in the crystal treated as point charges; that is, by the Madelung potential,

$$V_m(\vec{r}) = \frac{-Nq^2}{|\vec{r}-\vec{d}|} + \sum_{v=o} \left[\frac{-Nq^2}{|\vec{r}-\vec{R}_v-\vec{d}|} + \frac{Nq^2}{|\vec{r}-\vec{R}_v|}\right] ,$$

where R_v is the position of the vth negative ion and $\vec{R}_v-\vec{d}_v$ is the position of the vth positive ion and v ranges over the number of shells of neighboring ions to be included in the calculation. N is the valence of the crystal ions.

The spherically symmetric part of this potential energy is constant and equal to the Madelung energy out to about the nearest-neighbor distance; then it increases rapidly to make a potential well, and oscillates as r increases, falling off as $\frac{-Ne^2}{r}$ on the average. In practice the calculations are carried out in such a way that the non-spherically symmetric parts of the potential are neglected. (The solutions, ϕ_i, are assumed to be s- and p-like only.) So for the one-electron center the equation to be solved is

$$[\frac{p^2}{2m} + V_m(r)]\ \phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r})\ .$$

This one electron wave equation for ϕ_i is typically solved using a variational technique with s- and p-like trial wave functions centered on the defect or on the nearest neighbor ion sights. These one electron functions can be orthogonalized to the nearest neighbor ions by computing

$$\phi_i' = \phi_i - \sum_{cv} (\phi_{cv},\phi_i)\ \phi_{cv}(\vec{r})$$

where ϕ_{cv} is the vth orbital on the cth ion and is obtained from a separate atomic calculation.

The semicontinuum model is essentially the effective-mass model except within the anion vacancy where it is square-well like. This model assumes that for large r the potential energy of the electron, measured from the bottom of the conduction band, behaves as $-Ne^2/K_{eff}r$ where K_{eff} is an "effective dielectric constant". The kinetic energy and perfect crystal potential terms are approximated by $\frac{p^2}{2m^*}$ where m* is the scalar effective mass at the bottom of the conduction band. So the resulting hamiltonian is

$$H = \frac{p^2}{2m^*} - \frac{Ne^2}{K_{eff}r}\ .$$

For this model the wave function should be written as $\psi_i(\vec{r}) = \phi_i(\vec{r})X_o(\vec{r})$ where $\phi_i(\vec{r})$ is a smooth envelope function and $X_o(\vec{r})$ is the k=0 Bloch function at the bottom of the conduction band. Then $\psi_i(r)$ would be orthogonal to the core orbitals at large r since ϕ_i will be approximately constant over the core and since $X_o(\vec{r})$ is by definition orthogonal to the core orbitals. In practice the Bloch function is "approximated" as a constant and thus the resulting wave function is not even approximately orthogonal to the core orbitals.

The effective mass model breaks down for small r since the potential inside the anion vacancy is certainly more square-well-like than it is hydrogenic. To correct for this a distance R (the Mott-Littleton radius) which is slightly smaller than the nearest neighbor separation is chosen. For r greater than R the effective mass model is used but for r less than R a square well potential is used and the hamiltonian is written

$$H_{r<R} = \frac{p^2}{2m} + V_o$$

where V_o, the depth of the square well, equals the Madelung energy plus corrections for polarization energy and for the energy zero being at the bottom of the conduction band.

Due to the discontinuity in the derivative of this potential at $r = R$ and the inflexibility of the trial wave functions usually used it is probable that this model is inaccurate for r just greater than R.

Note that neither the point-ion lattice model or the semi-continuum model explicitly takes into account the effects of the actual electronic structure of the crystal ions on the color center electron(s). This omission is surely very harmful in SrO and BaO where the cations are rather large and the binding is less typically ionic. (Note that BaO could even be considered a semiconductor since its bandgap is only about 4.5 eV.) Also these models do not require the wave functions of the defect electron(s) to be orthogonal to the valence and core states of neighboring ions.

Calculations of the F^+ center absorption energies using the point-ion lattice model have been carried out by Kemp and Neely (6) and Kemp (7), who used a linear combination of 3s and 3p hydrogenic wave functions centered on the nearest-neighbor cation sites for variational functions. They included a polarization energy correction and allowed for first nearest neighbor ion displacements.

Their calculated $^2A_{1g} \rightarrow {}^2T_{1u}$ transition energies are listed in Table II and agree with the experimental values to about 5% for MgO and 3% for CaO, but only to about 12% for SrO and 33% for BaO.

K. C. To and B. Henderson (8) also used the point-ion lattice model, with polarization and first nearest neighbor lattice distortion corrections, for calculation of these $^2A_{1g} \rightarrow {}^2T_{1u}$ F^+ center transition energies, but they used defect centered one-parameter s- and p-type hydrogenic wave functions for the variational functions. These calculated absorption energies are also tabulated in Table II and are all closer to the experimental values than Kemp and Neeley's results are. However, these energies are still very poor for BaO where they differ from experiment by more than 30% (and for SrO where they differ by about 9%.)

H. S. Bennett (9) has carried out calculations for F^+ center transition energies in MgO, CaO, and SrO using a polarizable-point-ion lattice model including electronic polarization and lattice distortion corrections. He used two-parameter hydrogenic s- and p-type variational functions centered on the defect. Bennett's F^+ center absorption energies are also listed in Table II. They are all smaller in magnitude than

TABLE II

THEORETICAL F^+ CENTER ABSORPTION ENERGIES

	K. C. To and B. Henderson (8)	J. C. Kemp and V. I. Neeley (7)	H. S. Bennett (9)
MgO	4.796 eV	4.70 eV	3.84 eV
CaO	3.731 eV	3.80 eV	3.45 eV
SrO	3.287 eV	3.40 eV	3.26 eV
BaO	2.865 eV	3.00 eV	---

Kemp and Neeley's or To and Henderson's results. This is closer to the experimental energy in SrO but further away in MgO and CaO. Results of this particular model for BaO are not reported. Bennett also used this model to calculate the F^+ center emission energies. For MgO, CaO, and SrO his calculated F^+ center emission energies were 3.45 eV, 3.237 eV, and 3.074 eV versus experimental energies of 3.13 eV, 3.30 eV, and 2.42 eV respectively.

H. S. Bennett (10) has also carried out F^+ center transition energy calculations in MgO and CaO using a semicontinuum model with corrections for the electronic polarization and lattice distortion included. These calculated energies were about 25 times smaller than the experimental energies. Bennett suggests that this failure could be due to the inflexibility of the hydrogenic type variational wave functions used. This inflexibility of trial wave functions is probably also responsible for part of the error in the point-ion lattice calculations.

There have been fewer theoretical calculations done for the F center (the two-electron center) in the alkaline earth oxides.

Neeley and Kemp (7) have done calculations for the F center absorption energies in the four alkaline earth oxides. They carried out a mixed point-ion lattice LCAO type calculation using Gaussian-type orbitals. Lattice relaxation and polarization corrections were not included but they "estimated" that corrections for these would change their transition energies by some 15% to 20%. These calculations for the $^1A_{1g} \rightarrow {}^1T_{1u}$ absorption energies gave values of 5.4 eV for MgO, 4.4 eV for CaO, 3.9 eV for SrO, and 3.5 eV for BaO, compared with experimental values of 5.0 eV, 3.1 eV, 2.5 eV, and 2.3 eV respectively. This MgO calculation differs from experiment by 8% but the others all differ by more than 40%.

Bennett (11) has also used the point-ion lattice model to calculate F center transition energies for MgO and CaO. He carried out a numerical solution of the Hartree-Fock-Slater equations to get the orbitals for the F center electrons. Terms for the effects of ionic polarization of nearest neighbor ions and an estimate for the correlation energy of the defect electrons were included. These calculations yielded absorption energies of 3.94 eV in MgO and 3.15 eV in CaO compared with experimental values of 5.0 eV and 3.1 eV respectively. Bennett also calculated emission energies from this model and got 2.53 eV for the $^3T_{1u} \rightarrow {}^1A_{1g}$ MgO transition, 1.93 eV for the $^3T_{1u} \rightarrow {}^1A_{1g}$ CaO transition and 3.1 eV for the $^1T_{1u} \rightarrow {}^1A_{1g}$ CaO transition compared with the experimental values of 2.4 eV, 2.0 eV, and 2.50 eV respectively. These calculations predict a negligibly small stokes shift for the $^1T_{1u} \rightarrow {}^1A_{1g}$ transition which is in sharp disagreement with experiment.

As far as the author knows no calculations have been reported for the emission energies for the F center in SrO or BaO.

CHAPTER IV

DEVELOPMENT OF THE MODEL

The model used in this study was developed primarily by R. F. Wood and U. Opik (2,12) in 1968. This model is essentially a variational L.C.A.O. technique using an approximate Hartree-Fock type hamiltonian. It treats the defect electron and the nearby ions as a large molecule embedded in an otherwise perfect crystal. In the following outline of the development of this model Hartree atomic units are used. These units are defined in Appendix A, and in equations using them $m = e = \hbar = 1$.

Let ϕ_{vi} represent the ith core orbital on the vth ion of the crystal. Since these ions have only closed subshells, the ϕ_{vi} are all taken to be doubly occupied. Let ψ denote the orbital of the F^+ center electron. Now to apply the variational principle one tries to determine the orbital ψ that makes the expectation value of this one electron Hartree-Fock hamiltonian, H_{HF}, that is

$$<E> \;=\; <\psi|H_{HF}|\psi>/<\psi|\psi> \qquad [1]$$

a minimum with respect to small changes in ψ, where ψ is constrained to be orthogonal to the core orbitals ϕ_{vi}. Since H_{HF} is hermitian the variational principle guarantees that this <E> will be an upper bound to the exact energy eigenvalue of H_{HF}. Thus when ψ has been adjusted so that <E> is minimized, the energy <E> has been determined as accurately as is possible for the form of the trial function used. The one electron hamiltonian used here is written (in atomic units) as

$$H_{HF} = -\frac{1}{2}\nabla^2 - \sum_v \frac{Z_v - N_v}{|\vec{r}-\vec{R}_v|} + \sum_v U_v \qquad [2]$$

where for an arbitrary one electron wave function u(r), the operatur U_v is defined by

$$U_v u(r) = \left(\frac{-N_v}{|\vec{r}-\vec{R}_v|} + 2\sum_i \int \frac{[\phi_{vi}(\vec{r}\,')]^2}{(\vec{r}\,'-\vec{r})} d\vec{r}\,'\right) u(\vec{r}) - \sum_i \phi_{vi} \int \frac{\phi_{vi}(\vec{r}\,')u(\vec{r}\,')}{|\vec{r}\,'-\vec{r}|} dr' \qquad [3]$$

where Z_v is the atomic number of ion v, N_v is the number of electrons on ion v, and R_v is the position vector of the nucleus of ion v. Note that all wave functions are taken to be real valued. The ϕ_{vi} are the ion core orbitals, and in a true Hartree-Fock calculation they would have to be determined in a self-consistent manner to take into account their dependence upon the defect electron. So the hamiltonian would require the addition of another operator containing terms for the coulomb and exchange interactions with the defect electron. (This additional operator would be similar to Equation [3] with the ϕ_{vi}'s replaced by ψ.) This would lead to an extremely difficult problem. Therefore in this model the ϕ_{vi} are taken to be the Hartree-Fock free-ion core orbitals and are obtained from a separate atomic calculation.

This neglect of the distortion of the ion core orbitals by the defect electron is probably not important for, say, the ground state of the F center in SrO or BaO since ψ would be compact and would mostly neutralize the effective charge of the defect. It is not clear how serious this approximation is for the F^+ center where the effective charge of the defect is not even approximately neutralized by ψ, but some corrections for electronic polarization are included in this model and will be considered later. Also the overlaps between the first nearest neighbor ions are nonzero when free ion orbitals are used but this is expected to cause a relatively small error.

Even using free ion core orbitals this model is still not tractible enough to use in practical computations because of the complicated form of the exchange term in U_v, (the last term in Equation [3]). During a variational calculation in which the trial wave function is expanded in some basis set, these complicated two-center exchange integrals would have to be evaluated a large number of times. This would be much too time consuming, so a simplified expression for the exchange part of U_v is needed. To develop this, consider first the interaction of the defect electron with only one of the crystal ions. Denote the "defect" electron wave function by ϕ_o. Then translating the origin to the nucleus of this ion and dropping the label v gives the Hartree-Fock equation for the atomic problem of one additional electron in the field of this ion.

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z-N}{\vec{r}} + U\right) \phi_o(\vec{r}) = E_o\phi_o(\vec{r}) \tag{4}$$

The troublesome exchange term is the last term of U as defined in Equation [3]. That is,

$$V_{HF}^{EXCH} = -\sum_i \phi_i(\vec{r}) \int \frac{\phi_i(\vec{r}\,')\phi_o(\vec{r}\,')}{(\vec{r}-\vec{r}\,')} d\vec{r}\,' .$$

These calculations would be simplified enough if the operator U were replaced by a numerical function U(r) such that $U\phi_o(\vec{r})$ is equal to $\phi_o(r)$ multiplied by U(r). There are several commonly used approximations of this type for V_{hf}^{exch}. One often used approximation to V_{HF}^{EXCH} is the Slater exchange potential which is the Hartree-Fock exchange averaged over all of the orbitals. The model that results from this exchange approximation is called the Hartree-Fock-Slater method (and was used in Bennett's F center calculations mentioned in section two). However, if an exchange potential is actually defined by

$$U(r) = [\phi_o(\vec{r})]^{-1} U\phi_o(\vec{r}),$$

it is found that the resulting U(r) depends rather strongly on the angular momentum quantum number ℓ of ϕ_o but only slightly on the energy E_0 so long as E_0 is well above the core state energies (2). The dependence of U(r) on E_0 and ℓ is illustrated in Table III and Table IV.

So it appears that while the Slater exchange approximation would significantly decrease the accuracy of the model, a satisfactory exchange approximation can be had by using a separate function $V_\ell^{EXCH}(\vec{r})$ for each different angular momentum quantum number ℓ, and replacing the troublesome operator U by $U_\ell(r)$, defined by $U\phi_{o\ell}(\vec{r}) = U_\ell(\vec{r})\phi_{o\ell}(\vec{r})$. V_ℓ is calculated in a manner similar to the Slater exchange except that the average includes only those orbitals having the same angular momentum quantum number.

Now the original exchange term in U is replaced by this ℓ-dependent exchange potential to get $U_\ell(r)$, and U in H_{HF} is replaced by $U_\ell(r)$. This new hamiltonian will be denoted by H_U. It is expected that H_{HF} and H_U will give practically the same results when operating on the orbital ψ of the defect electron.

The most straightforward way to require ψ to be orthogonal to the core orbitals ϕ_{vi} would be to write ψ in the form

$$\psi = f(\vec{r}) - \sum_v \sum_i \phi_{vi} \langle\phi_{vi}|f\rangle, \qquad [5]$$

as mentioned in section two. However, this leads to difficulties since

TABLE III

ENERGY DEPENDENCE OF THE ℓ-DEPENDENT POTENTIAL

E_0 =	- 0.83	- 0.4	- 0.05
R			
0.02	0.5066	0.5052	0.5042
0.06	1.104	1.101	1.098
0.18	1.298	1.284	1.274
0.80	1.064	1.015	0.979
2.8	.0729	0.0786	.0856
4.0	.0109	.0314	- .0576

An illustration of how "-r" times the exchange correction to the effective potential energy for an s electro of Ca++ depends upon the energy E_0 at which it is determined, and the radius r. E_0 and the exchange correction are given in rydbergs and r is in atomic units.

TABLE IV

ANGULAR MOMENTUM DEPENDENCE OF THE ℓ-DEPENDENT POTENTIAL

1 =	0	1	2	3	4	5
E_0 =	-.2915	-.18	-.11	-.0625	-.04	-.02778
0.02	.5016	.4384	.3708	.2621	.1780	.118
0.06	1.094	.776	.666	.436	.263	.146
0.18	1.240	1.182	1.034	.634	.377	.217
0.80	1.015	1.090	.839	.871	.789	.706
2.8	0.136	- .006	.209	.086	.058	.043
4.0	0.026	.005	.027	.007	.004	.003

An illustration of the manner in which "-r" times the exchange correction to the effective potential energy for the outermost electron of a potassium atom depends upon the angular momentum quantum number "ℓ" and the radius r. (E_0 is for the lowest free-atom state corresponding to the associated value of I.) The units are the same as in Table III.

$U_\ell(r)$ does not even approximate U when operating on the core orbitals. That is, $U_\ell(r)$ approximates U only when operating on a function which is orthogonal to the core orbitals ϕ_{vi} and which has an energy sufficiently higher than the core orbital energies. Thus the calculations of $H_U\phi_{vi}$ from the double summations in Equation [5] involved in obtaining matrix elements from $<\psi|H_{HF}|\psi>$ would probably be as complicated as using H_{HF} instead of H_U in the first place. This difficulty is avoided by noting that near the vth ion $\psi(\vec{r})$ can be approximated by a linear combination of solutions of the equation

$$(-\frac{1}{2}\nabla^2 - \frac{Z_v - N_v}{|\vec{r}-\vec{R}_v|} + U_v - E_o)\ \phi_o = 0 \qquad [6]$$

for E_0's well above the core energies, so that the dependence of U_v on the energy can be neglected. Then the solutions of Equation [6] that correspond to the core orbitals, call them ϕ'_{vi}, are orthogonal to these 'excited solutions' of Equation [6]. So instead of Equation [5] it should be acceptable to write

$$\psi_K \ = \ f_K(\vec{r}) - \sum_v \sum_i \phi'_{vi} <\phi'_{vi}|f_K> \qquad [7]$$

where K labels a particular choice of the smooth trial function $f_K(r)$.

Now it is not too difficult to determine the effect of H_U operating on ϕ'_{vi}. Notice that $H'_U = H_U + 2/r$ represents the effective positive charge of the oxygen vacancy as having been neutralized by a negative point charge, so that H'_U represents an approximate hamiltonian for the perfect crystal. When an ion is part of a crystal, the energies of its core orbitals differ from those of the free ion by approximately a_m/a where a_m is the Madelung constant and a is the nearest-neighbor separation (13). Thus one can assume that $H'_U\phi'_{vi} = E''_{vi}\phi'_{vi}$ with $E''_{vi} = E'_{vi} \pm \frac{a_M}{a}$, where E'_{vi} is the eigenvalue of Equation [6] corresponding to the solution ϕ'_{vi}. The "+" sign corresponds to the positive ions and the "-" sign is taken for negative ions.

Now that the energy eigenvalues of ϕ'_{vi} for H_U have been approximated, expressions for the matrix elements between functions of the form of Equation [7] say ψ_K and ψ_γ, can be written down:

$$\langle\psi_K|H_U|\psi_\gamma\rangle \equiv H_{K\gamma} = \langle f_K|H_U|f_\gamma\rangle - \sum_v \sum_i E''_{vi} \cdot$$

$$\times \langle f_K|\phi'_{vi}\rangle\langle\phi'_{vi}|f_\gamma\rangle + 2\sum_v\sum_i(\langle f_K|r^{-1}|\phi'_{vi}\rangle\langle\phi'_{vi}|f_\gamma\rangle + \langle f_K|\phi'_{vi}\rangle\langle\phi'_{vi}|r^{-1}|f_\gamma\rangle)$$

$$- 2\sum_u\sum_v\sum_i\sum_j \langle f_K|\phi'_{ui}\rangle \times \langle\phi'_{ui}|r^{-1}|\phi'_{vj}\rangle\langle\phi'_{vj}|f_\gamma\rangle \qquad [8]$$

$$\langle\psi_K|\psi_\gamma\rangle \equiv S_{K\gamma} = \langle f_K|f_\gamma\rangle - \sum_v\sum_i \langle f_K|\phi'_{vi}\rangle\langle\phi'_{vi}|f_\gamma\rangle \qquad [9]$$

In the actual calculations the last term of Equation [8] is approximated by

$$+ 2\sum_v\sum_i \langle f_K|\phi'_{vi}\rangle\langle\phi'_{vi}|r^{-1}|\phi'_{vi}\rangle\langle\phi'_{vi}|f_\gamma\rangle$$

In these calculations ψ is expressed as a linear combination with unknown coefficients of several functions of the form of Equation [7]. This leads to a set of simultaneous equations, and the energies and unknown coefficients are finally obtained by solving the secular Equation $|H-ES| = 0$. H is the matrix with elements H_{ij} from Equation [8] and S is the matrix with elements S_{ij} from Equation [9].

Since it is impractical in an actual calculation to treat many shells of ions with this detailed Hartree-Fock type method, an effective mass treatment is also included in this model. The crystal is divided by a radius R_A into two regions; an inner region R_1, and an outer region

R_2 (the remainder of the crystal.) Region R_1 will be treated using the ℓ-dependent Hartree-Fock model and region R_2 will be treated using an effective mass model. In this study only the first nearest neighbors are treated using the ℓ-dependent Hartree-Fock method and the rest of the crystal (R_2) is treated using the effective mass model.

Let V_{per} denote the Hartree-Fock approximation to the periodic perfect crystal potential for an electron in the crystal. Let V' represent any corrections to V_{per} to account for the defect, polarization, and etc. Let ε_{HF} be the energy of the bottom of the conduction band in the Hartree-Fock approximation. ψ denotes the orbital of the defect electron and let g be the envelope function for this orbital.

Then for region R_1 write $(-\frac{1}{2}\nabla^2 + V_{per} + V')\ \psi = E\psi$ where $V_{per} + V'$ is the potential energy operator given in Equation [2] plus a polarization correction which is discussed below. For region R_2 the effective mass approximation is used to write

$$\left(-\frac{1}{2m^*}\nabla^2 + \varepsilon_{HF} + V'\right) g = Eg$$

where $V' = -2/r$ plus a polarization correction, and m* is the effective mass at the bottom of the conduction band.

Wood and Opik define an operator G as $G = -\frac{1}{2}\nabla^2 + V_{per} + V'$ in R_1, and $G = -\frac{1}{2}\nabla^2 + m^*\varepsilon_{HP} + m^*V'$ in R_2, and this operator G can be shown to be hermitian (2).

$$\begin{array}{ll} \text{So in } R_1 & G\psi = E\psi \\ \text{and in } R_2 & Gg = m^*Eg \end{array}$$

This implies that the expectation value of E, <E>, is

$$\langle E\rangle = \left(\int_{R_1}\psi G\psi d\tau + \frac{1}{m^*}\int_{R_2} gGg d\tau\right)\Big/\left(\int_{R_1}\psi^2 d\tau + \int_{R_2} g^2 d\tau\right) \qquad [10]$$

It can be shown that the variational principle can be applied to G to determine ψ, g, and E only if ψ and its normal derivative are continuous with g and its normal derivative at the boundary of region R_1 and R_2. (2) This requirement constitutes an approximation whose effects are unknown. (It makes the trial wave function less flexible.) In the actual calculations the same linear combination of Slater type orbitals is used for both ψ and g.

It has been noted in previous color center calculations with this model that dielectric polarization effects must be included in order to obtain satisfactory agreement with experiment. The dielectric polarization effects of the defect are accounted for in this model by adding a polarization correction potential to the hamiltonian operator. The form of this polarization correction term is taken from THS (Toyozawa-Haken-Schottky) polarization theory (14). This THS polarization potential term U(r) is written as the sum of an electronic polarization potential $U_{el}(r)$, which is to account for the distortion of the ion electronic orbitals by the defect electron, and an ionic potential $U_{ion}(r)$ which is to account for displacement of the ions. So $U(r) = U_{el}(r) + U_{ion}(r)$. The expressions for $U_{el}(r)$ and $U_{ion}(r)$ given by THS theory for the F center in an alkali halide are:

$$U_{el}(r) = (1-K_\infty^{-1})\left\{\frac{1}{2}(P_{el} + 4Ph) - \left(\frac{1}{r}\right)\left[\frac{1}{2}\exp(-P_{el}r) + \frac{3}{2}\exp(-P_h r) - 2\right]\right\} \qquad [11]$$

and

$$U_{ion}(r) = (K_{\infty}^{-1}-K_{st}^{-1})\{-\tfrac{1}{2}\ (v_{el}+4v_{h}) - (\tfrac{1}{r})[\tfrac{1}{2}\ \exp(-v_{el}r)+3/2\ \exp(-v_{h}r)-2]\} \qquad [12]$$

where K_{∞} and K_{st} are the high frequency and static dielectric constants; P_{el} and P_{h} are parameters associated with the self-energy due to the electronic polarization associated with the electron and vacancy, respectively; and v_{e} and v_{h} are parameters associated with the polarization self-energies due to displacement of the ions. The values of these parameters are specified by the THS theory; however, these THS prescriptions are not all followed in this model and choosing the values of these parameters seems to be a point of some confusion (2,12,15,17). Wood and Opik report that in order to obtain satisfactory results provision must be made to cut off the electron and vacancy polarization potentials inside arbitrary radii R_{ce} and R_{ch} respectively (12). The values of these parameters used in this particular study will be considered in the discussion.

Now the total energy E of this system equals the sum of the defect electron's energy E_{F} (including the THS polarization contributions) and the potential energy of the crystal lattice E_{L}. That is $E(R) = E_{F}(R) + E_{L}(R)$ where R represents the position of the first nearest-neighbor ions. In this study only the "breathing" mode of the first nearest neighbor ion displacement is considered, i.e., all first nearest neighbors move on line with the fourth nearest neighbor negative ions and in the same direction with respect to the defect site. See Figure 1. Note that the removal of a negative ion from the perfect lattice causes the first nearest neighbor positive ions to move outward from the vacancy

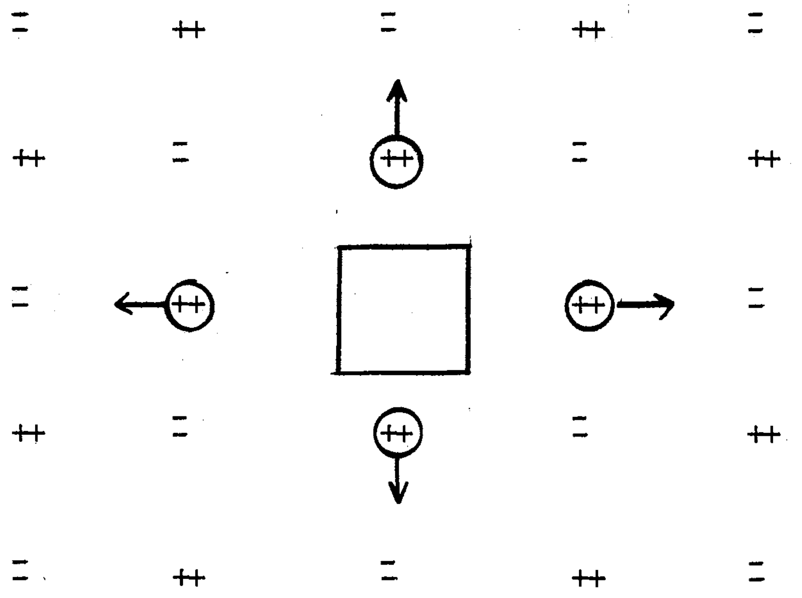

Figure 1. An Illustration of the "Breathing" (A_{1g}) Mode of Displacement of the First Nearest Neighbor Positive Ions of an Oxygen Vacancy

site since the vacancy is positive with respect to the perfect lattice and thus the positive nearest neighbors are "repelled".

The lattice potential energies used in this study were calculated by T. M. Wilson (17) using the type of classical ionic crystal theory techniques formulated by Boswarva and Lidiard (18).

The lattice potential energy E_L is written as $E_L(\delta) = E_C(\delta) + E_R(\delta)$, where δ is the displacement of the first nearest neighbor ions from the perfect crystal positions; $E_C(\delta)$ is the coulomb energy of the ions, treated as point charges; and $E_R(\delta)$ represents the repulsive potential due to the finite extent of the ions; and the lattice potential energy at zero percent distortion is taken as the zero energy point. The repulsive potential is taken to be the Born-Mayer potential with Van-der Waals corrections included. This potential between ion u and ion v separated by a distance R_{uv} is written as

$$V_{uv} = B_{uv} \exp(-|R_{uv}|/p) - \frac{c}{R_{uv}^6} - \frac{d}{R_{uv}^8}$$

where the values of the constants are given in Appendix B. The expressions for $E_C(R)$ and $E_R(R)$ as used in this calculation and the values of the parameters used in these equations for BaO and SrO are listed in Appendix B.

The actual computations required in this study were carried out on the Oklahoma State University computer center's IBM 360/65 computer using a sequence of four computer programs.

The first program used was written by C. Froese Fischer (19). It carries out non-relativistic multi-configuration self-consistent field Hartree-Fock calculations for the one electron wave functions and energies of an atom or ion in a bound state. This excellent program was used to obtain accurate free ion orbitals, the ϕ_{vi} above, for Sr^{++} and Ba^{++}. Free ion orbitals for Mg^{++}, Ca^{++}, and K^{+} were also calculated with this program and were used with the other programs for testing and comparison purposes.

The second program is named ZP2COUL. This program reads in one electron wave functions and computes twice the "effective nuclear charge for potential", ZP2, using techniques discussed in detail by D. R. Hartree (20). Then ZP2COUL punches out the one electron wave functions and ZP2 on meshes which conform to the input requirements of the next program EXCH POT. Program ZP2COUL was originally written to use the analytical wave functions of Clementi (21). Since analytical wave functions are not available for Sr^{++} or Ba^{++}, program ZP2COUL was modified in this study to use the numerical wave functions produced by C. Froese Fischer's program mentioned above. This modified ZP2COUL was tested on the K^{+} ion using numerical orbitals from the first program above, and the results compared very well with the K^{+} results obtained using the original ZP2COUL and Clementi's analytic orbitals.

The third program in the sequence is named EXCH POT and was written by U. Opik. This program calculates the effective nuclear charge for potential, radial wave functions, and energy eigenvalues for an electron moving outside a spherically symmetrical closed-shell core. For input it requires the wave functions for the core electrons, and the "effective nuclear charge for potential" function of the core, both of which are produced in the proper format by ZP2COUL. The numerical technique used in this program is described in detail by D. R. Hartree (20). It is essentially an iterative technique in which the wave equation is integrated outwards from zero, integrated inwards from some large radius, and the energy is adjusted until the solutions match at some arbitrary intermediate radius. Choosing the starting values for the first iteration is somewhat arbitrary and required several trials in a few cases.

This program was originally capable of dealing only with cores with no more than five different core orbitals so it had to be modified for this study to handle more core orbitals in order to treat Sr^{++} and Ba^{++}. In this study EXCH POT was used to determine the ℓ-dependent potentials $U_\ell(r)$. Then these potentials were used as input to EXCH POT to determine the "approximate core functions", ϕ'_{vi}. ℓ-dependent potentials for $\ell = 0,1,\ldots 5$ were calculated using EXCH POT as outlined above, and the $\ell = 5$ potential, $U_5(r)$, was used in place of $U_\ell(r)$ for ℓ greater than five.

The final program in the sequence was written by R. F. Wood and U. Opik and performs the variational L.C.A.O. calculation of the F^+ center electronic energies and wavefunctions.

This program reads in the ℓ-dependent potentials and approximate core orbitals and energies (corrected for Madelung energy) from program EXCH POT. Of course, it also requires other input describing the symmetry and dimensions of the defect, information defining the initial trial function, the THS polarization parameters, and etc. The program then carries out the entire L.C.A.O. procedure (including the polarization corrections) and prints out the energies, trial function coefficients, average radius of the wave function, defect electron charge inside first nn and second nn, and other information which is primarily of diagnostic value. This program required no modification and is relatively complex, so the exact internal procedures employed by this program were not investigated by the author.

CHAPTER V

RESULTS AND DISCUSSION

The electronic energies $E_F(\delta)$ of the F^+ center in SrO and BaO were calculated at several different outward distortions, δ, of the first nearest neighbor positive ions using the model outlined in the previous chapter. The sum of these $E_F(\delta)$'s and the corresponding lattice potential energies, $E_L(\delta)$, give the total energy of the F^+ center, $E(\delta) = E_F(\delta) + E_L(\delta)$. Plots of the total energy versus the percent outward distortion of the first nearest neighbors were constructed from these calculated points. The resulting plot is termed a configuration-coordinate diagram of the F^+ center (see Figure 2). From this configuration-coordinate diagram the minimum energies and corresponding percent distortions of the nearest neighbor ions predicted by this model for the $^2A_{1g}$ state and the $^2T_{1u}$ state can be determined. In accordance with the Frank-Condon principle, which assumes the nuclear coordinates do not change during an electronic transition, the electronic transitions between these two states are taken to be vertical on the configuration-coordinate diagram. Thus, the absorption ($^2A_{1g} \rightarrow {}^2T_{1u}$) energy is predicted by measuring the vertical energy difference between the two total energy curves at the percent distortion corresponding to the $^2A_{1g}$ minimum and the emission ($^2T_{1u} \rightarrow {}^2A_{1g}$) energy is predicted to be the vertical energy difference at the percent distortion corresponding to the $^2T_{1u}$ minimum.

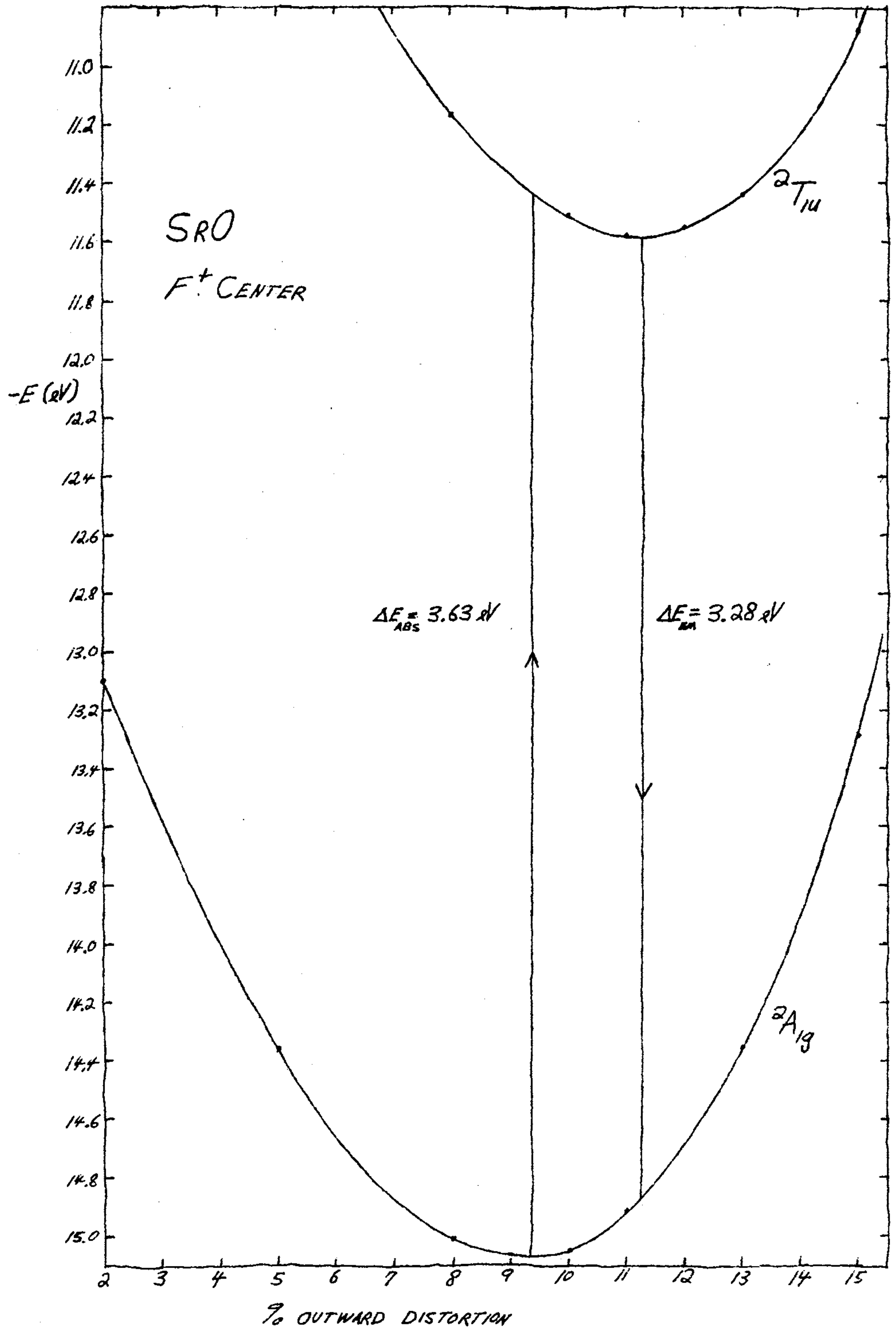

Figure 2. Configuration Coordinate Diagram for F^+ Center in SrO

TABLE V

THE CALCULATED F^+ CENTER ELECTRONIC ENERGIES E_F

% Dist.	Q_1	Q_2	Electronic Energy	Ave Radius
For SrO. $^2A_{1g}$ State:				
2%	.963	.996	-10.8943 eV	2.544 au
5%	.960	.992	- 9.4021 eV	2.636 au
8%	.951	.984	- 8.0382 eV	2.769 au
10%	.940	.976	- 7.2003 eV	2.901 au
11%	.933	.971	- 6.7811 eV	2.962 au
13%	.912	.956	- 6.0108 eV	3.154 au
15%	.877	.929	- 5.2744 eV	3.430 au
For SrO. $^2T_{1u}$ State:				
2%	.691	.923	- 6.3014 eV	4.294 au
5%	.676	.900	- 5.1842 eV	4.501 au
8%	.583	.814	- 4.1976 eV	5.114 au
10%	.506	.730	- 3.6605 eV	5.713 au
11%	.430	.649	- 3.4453 eV	6.214 au
12%	.380	.589	- 3.2534 eV	6.642 au
13%	.330	.524	- 3.0894 eV	7.144 au
15%	.203	.365	- 2.8575 eV	8.210 au
For BaO. $^2A_{1g}$ State:				
2%	.869	.973	- 8.7375 eV	2.805 au
5%	.941	.982	- 7.3631 eV	2.475 au
8%	.975	.987	- 6.1128 eV	2.354 au
9%	.981	.987	- 5.7313 eV	2.352 au
11%	.985	.986	- 4.9762 eV	2.389 au
13%	.9787	.9793	- 4.2850 eV	2.524 au
15%	.9696	.9699	- 3.6306 eV	2.667 au
For BaO. $^2T_{1u}$ State:				
5%	.320	.561	- 2.5102 eV	7.289 au
7%	.188	.378	- 2.2835 eV	8.707 au
8%	.141	.291	- 2.2085 eV	9.457 au
9%	.116	.271	- 2.1398 eV	9.553 au
11%	.070	.166	- 2.0563 eV	10.68 au
13%	.049	.125	- 1.9903 eV	11.11 au
15%	.040	.116	- 1.9103 eV	11.41 au

Q_1 = The charge inside the first nearest neighbors; Q_2 = The charge inside the second nearest neighbors; % Dist. = The percent outward distortion of the 1nn positive ions.

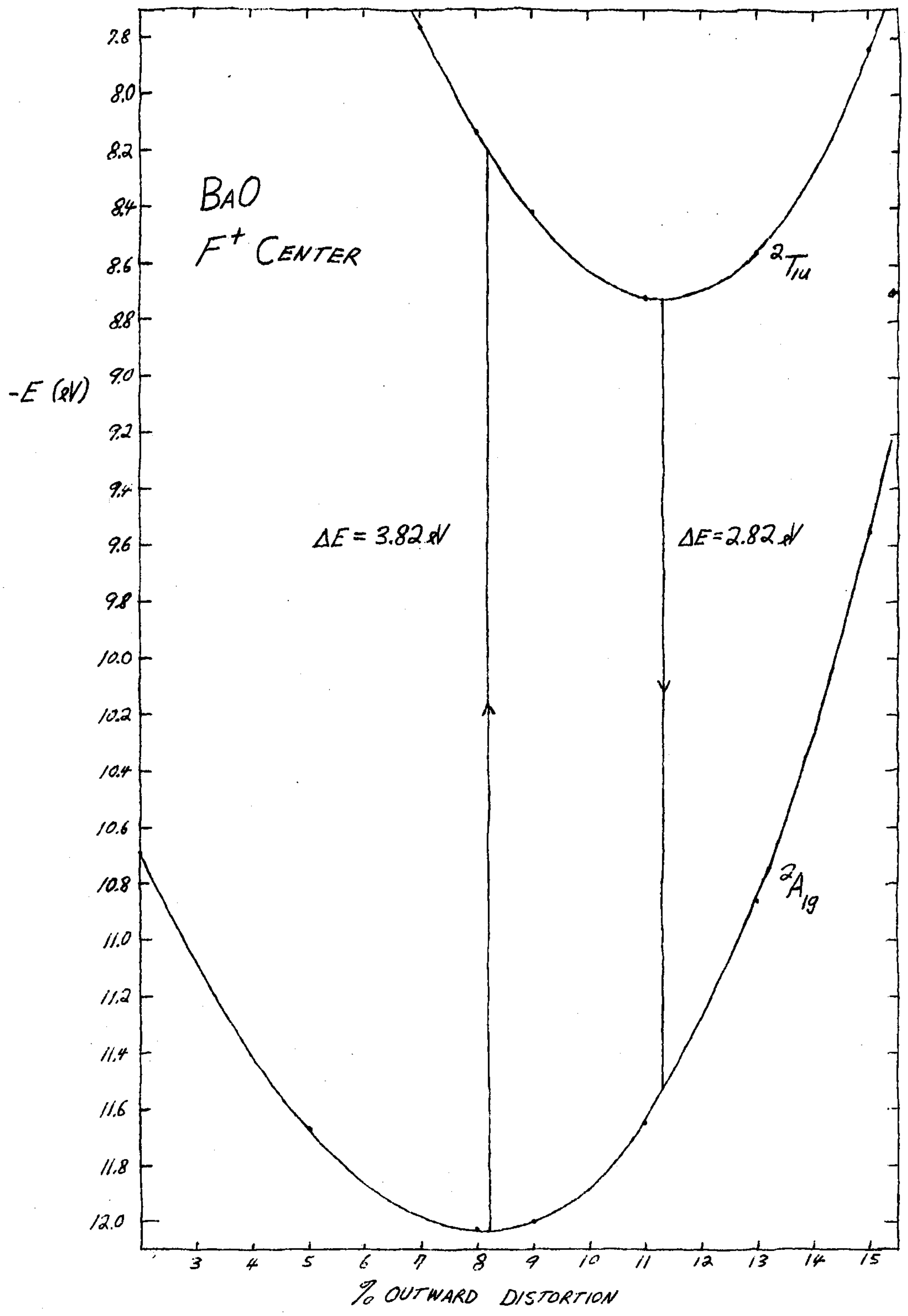

Figure 3. Configuration Coordinate Diagram for F^+ Center in BaO

The actual configuration-coordinate diagrams given by these calculations for the F^+ centers in SrO and BaO are shown in Figure 2 and Figure 3, respectively. The numerical results of these calculations for the electronic energy, E_F, for the $^2A_{1g}$ and $^2T_{1u}$ states of the F^+ centers in SrO and BaO are listed in Table V. The average radius $<r>$ of the smooth part of the theoretical wave function for each distortion and the charge of the defect electron inside the first nearest neighbors and inside the second nearest neighbors for each distortion are also listed in Table V. The numerical results for the lattice energies, E_L, are listed in Table VI. A graphical representation of E_F and E_L versus the nearest neighbor ion distortion is given in Figure 4 for SrO and in Figure 5 for BaO.

The smooth part, f, of the trial function used in this variational model outlined in the previous chapter consists of a linear combination with unknown coefficients of Slater-type orbitals of the form

$$f(r) = [(2\beta)^{2n+1}/(2n)!]^{\frac{1}{2}} r^{n-1} \ell^{-Br} Y_{\ell 0}(\theta,\phi),$$

where $Y_{\ell 0}$ is a spherical harmonic of degree "ℓ" and magnetic quantum number of zero. The $^2A_{1g}$ state calculations for both SrO and BaO employed a linear combination of five of these Slater-type orbitals (STO's). The $^2T_{1u}$ state calculations for SrO were all carried out using a linear combination of three STO's. Some of the $^2T_{1u}$ state calculations for BaO were carried out using five term trial functions and some employed three term trial functions. In these $^2T_{1u}$ BaO calculations it was found that the five term trial function did not give significantly different results from the three term trial function, and, of course, the five term trial function required much more computer time than the

TABLE VI

LATTICE POTENTIALS FOR SrO AND BaO (17)

% Dist.	E_L For SrO	E_L For BaO
0%	0.0 eV	0.0 eV
1%	-1.141 eV	-1.010 eV
2%	-2.209 eV	-1.948 eV
3%	-3.202 eV	-2.811 eV
4%	-4.119 eV	-3.598 eV
5%	-4.958 eV	-4.306 eV
6%	-5.715 eV	-4.932 eV
7%	-6.387 eV	-5.472 eV
8%	-6.971 eV	-5.921 eV
9%	-7.460 eV	-6.273 eV
10%	-7.850 eV	-6.522 eV
11%	-8.133 eV	-6.660 eV
12%	-8.301 eV	-6.680 eV
13%	-8.346 eV	-6.571 eV
14%	-8.256 eV	-6.323 eV
15%	-8.020 eV	-5.922 eV

% Dist. = The percent outward distortion of the 1 nn positive ions.

E_L = The lattice potential energy.

TABLE VII

FINAL PARAMETERS FOR SOME IMPORTANT VARIATIONAL WAVE FUNCTIONS

STO#	n-value	ℓ-value	β-value	coefficient
For SrO $^2A_{1g}$ 13% Distortion:				
1	1	0	1.25	- 4.297927
2	1	0	0.48	17.42786
3	2	0	0.88	- 9.072655
4	2	0	0.49	- 7.886480
5	3	0	0.41	.7223983
For SrO $^2A_{1g}$ 10% Distortion:				
1	1	0	1.25	3.951217
2	1	0	0.48	-15.96222
3	2	0	0.88	8.481639
4	2	0	0.49	7.132539
5	3	0	0.41	- .6810565
For SrO $^2T_{1u}$ 10% Distortion:				
1	2	1	0.768	- .1838047
2	3	1	0.6048	- .8357322
3	2	1	0.2592	- .1609917
For SrO $^2T_{1u}$ 12% Distortion:				
1	2	1	.768	- .1615408
2	3	1	.504	- .8895595
3	2	1	.2592	- .1027084
For SrO $^2T_{1u}$ 13% Distortion:				
1	2	1	.896	.07295097
2	3	1	.504	.6443295
3	2	1	.3024	.4073326
For BaO $^2A_{1g}$ 9% Distortion:				
1	1	0	1.25	-10.84199
2	1	0	0.48	44.58764
3	2	0	0.88	-22.77718
4	2	0	0.49	-18.50013
5	3	0	0.41	1.510491

TABLE VII (Continued)

STO#	n-value	ℓ-value	β-value	coefficient
For BaO $^2A_{1g}$ 13% Distortion:				
1	1	0	1.25	- 8.840262
2	1	0	0.48	36.23794
3	2	0	0.88	-18.14609
4	2	0	0.49	-16.61357
5	3	0	0.492	2.279598
For BaO $^2A_{1g}$ 11% Distortion:				
1	1	0	1.25	- 9.998940
2	1	0	0.48	41.90400
3	2	0	0.88	-21.00867
4	2	0	0.49	-17.16651
5	3	0	0.41	1.418204
For BaO $^2T_{1u}$ 13% Distortion:				
1	1	1	.5376	- 1.969008
2	2	1	.6144	20.34102
3	2	1	.896	1.256571
4	2	1	.64512	-20.69688
5	3	1	.400	- 1.940961
For BaO $^2T_{1u}$ 11% Distortion:				
1	1	1	.43008	- 1.762672
2	2	1	.7680	15.01527
3	2	1	.7168	-29.25900
4	2	1	.64512	14.94596
5	3	1	.4	- 1.767580
For BaO $^2T_{1u}$ 9% Distortion:				
1	2	1	.59774	- .9801323
2	3	1	.379	- 4.361214
3	2	1	.31	3.989647
For BaO $^2T_{1u}$ 8% Distortion:				
1	1	1	.64512	- .0041449
2	2	1	.6144	57.00790
3	2	1	.640	-37.95255
4	2	1	.4608	-30.43719
5	3	1	.480	13.58431
For BaO $^2T_{1u}$ 8% Distortion:				
1	2	1	.62917	- .5940375
2	3	1	.3780	- 2.938301
3	2	1	.30996	- 2.257726

See text for an explanation of these labels.

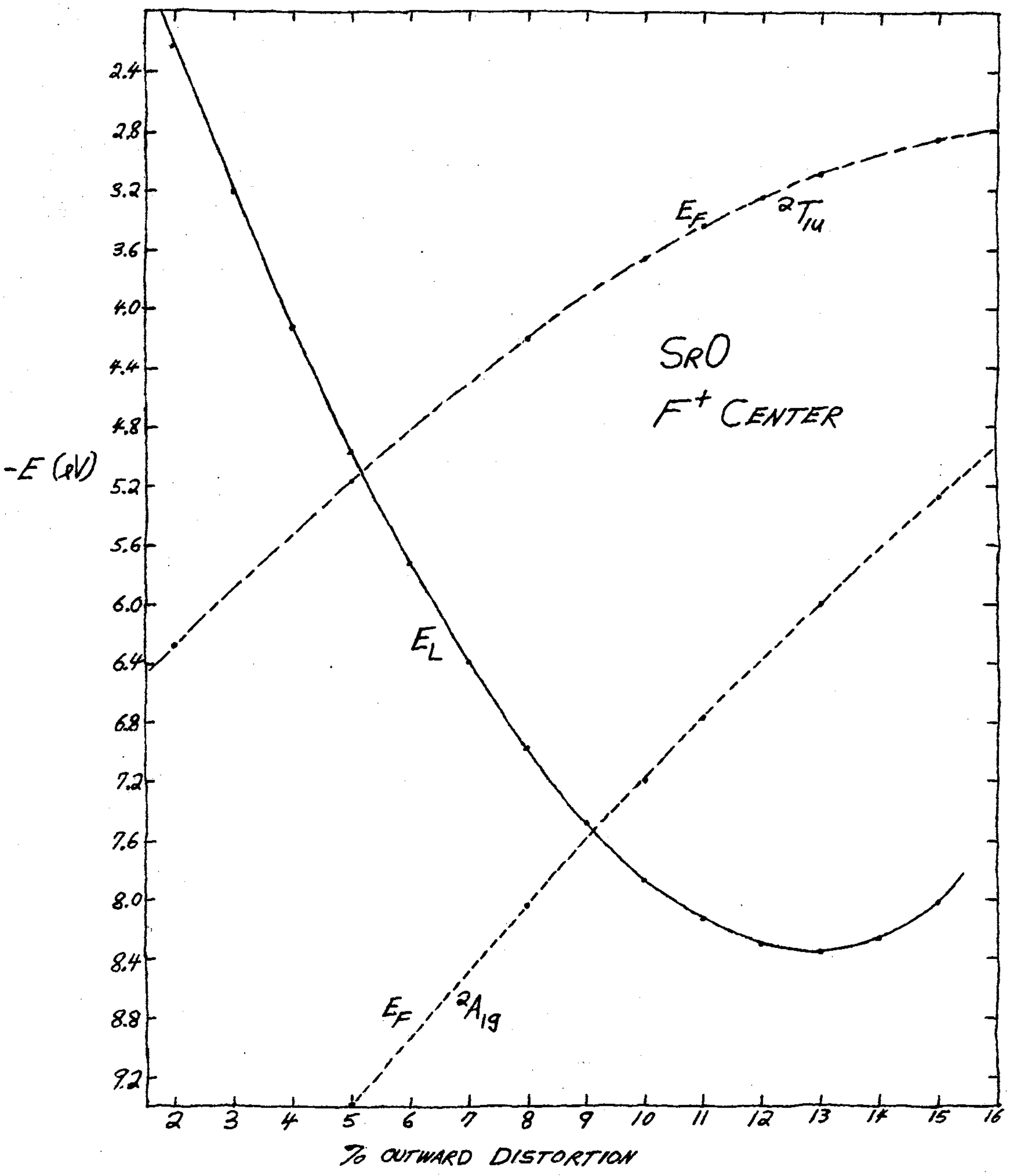

Figure 4. E_F and E_L for SrO F^+ Center

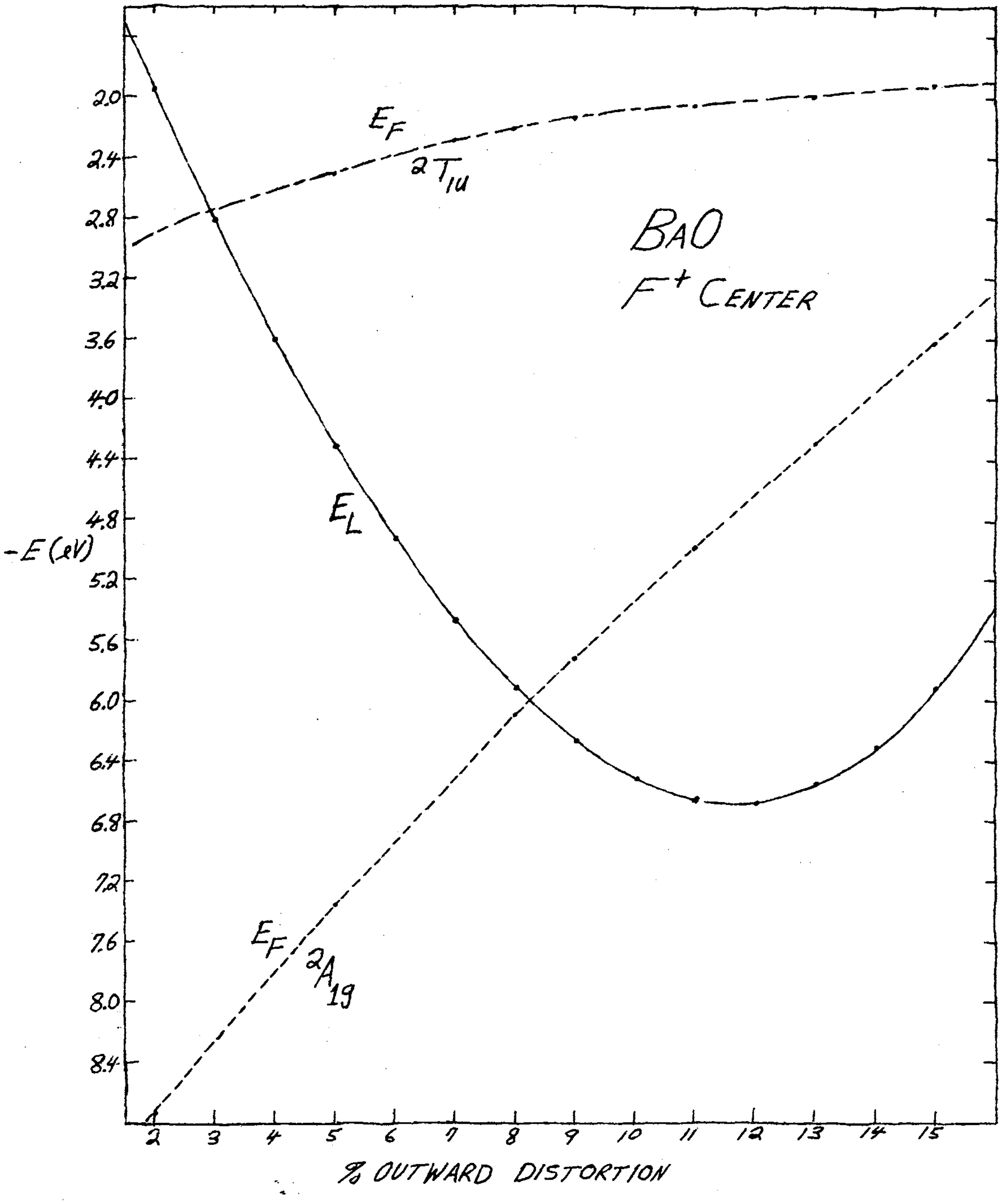

Figure 5. E_F and E_L for BaO F^+ Center

three term trial functions did. In the minimization procedure both the β's and the linear coefficients are varied.

The final β-array, n-array, ℓ-array, and linear coefficients for some of the final wave functions at or near important nearest neighbor distortions are listed in Table VII.

Due to difficulties in assigning values to some of the necessary parameters, the THS polarization corrections discussed in the preceding chapter were not used in these calculations. They are built into the computer program, though, and can be used whenever the necessary parameters have been determined. So, in these calculations the values $K_\infty = K_{st} = 1$ were used for the THS polarization input to make it vanish. (See Equations [11] and [12]. It is expected that the polarization corrections would be rather large for SrO and especially large for BaO. The polarization energy will be discussed in more detail later in this section.

The first nearest neighbor distance a_0 was taken to be 4.875 au (33) for SrO and 5.22 au (33) in BaO. The radius R_A beyond which the Hartree-Fock type model is replaced by the effective mass model was chosen to be $R_A = (1 + \sqrt{2})a_o/2$. Thus, only the first nearest neighbor positive ions were treated by the ℓ-dependent Hartree-Fock model, but in previous calculations with this model this has given fairly satisfactory results (2). The actual values were $R_A = 5.87$ au for SrO and $R_A = 6.30$ au for BaO.

In these calculations the trial function was required to be orthogonal only to the outermost five core orbitals of the nearest neighbor positive ions. For the Sr^{++} ion and Ba^{++} ion the neglect of the overlap of the trial function with the innermost three and six core orbitals, respectively, should not cause too much error since they are all fairly compact about the nucleus. This approximation was used since Opik and Wood's program is capable of orthogonalizing the trial function to only five core orbitals and it seemed probable that the error incurred would not be great enough to warrant modification of the program at this time.

For all of these calculations the effective mass was taken to be the electron rest mass, one au. The electron affinity was taken to be about 1.2 eV for SrO, and about 1.5 eV for BaO. It is now thought that the electron affinity for BaO is actually about .9 eV (28) and this value would cause the calculated BaO transition energies to be a little larger, but this error is so overwhelmed by the error due to not including polarization corrections that the electronic energies were not recalculated to use the more realistic electron affinity.

The integrals $<\phi'_{ui}|r^{-1}|\phi'_{ui}>$ required in the calculation of the elements H_{ij} of the hamiltonian matrix (see Equation [8] were all approximated in these calculations by $1/R_1$ where R_1 is the distance to the first nearest neighbor positive ions at the particular distortion under consideration. This approximation is motivated by assuming that $\phi'_{ui}(r)$ will be large only in the vicinity of ion u, and that r will be nearly equal to R_1 in that vicinity. So one can write $<\phi'_{ui}|r^{-1}|\phi'_{ui}> \cong \frac{1}{R_1} <\phi'_{ui}|\phi'_{ui}> = \frac{1}{R_1}$.

So from the configuration-coordinate diagrams resulting from using the parameter values and approximations above in the model outlined in the previous section (Figure 2 and Figure 3), the predicted absorption and emission energies not including polarization are determined to be about 3.63 eV and 3.28 eV, respectively, for the F^+ center in SrO and about 3.82 eV and 2.82 eV, respectively, for the F^+ center in BaO. See

Table VIII for a comparison of these values with the experimental values and the theoretical values given by the previous calculations discussed in Chapter III.

It is difficult to compare these results with the previous calculations mentioned in Chapter III since all of those calculations did include polarization, but the polarization corrections are not included in this study and are expected to be fairly large.

As might be expected these no-polarization results are not as close to the experimental energies as any of the calculations mentioned in Chapter III. The most consistantly best results of the calculations mentioned in that chapter were from K. C. To and B. Henderson's work. In their paper (8) they also listed the results of their model when the corrections for polarization energy and first nearest neighbor distortions are not included. These results for the F^+ center absorption energies are: 5.647 eV for MgO, 4.606 eV for CaO, 4.144 eV for SrO, and 3.705 eV for BaO. This energy for SrO is much worse than the value predicted by this study, and the energy for BaO is about the same, but again it is questionable whether this is a fair comparison since the first nearest neighbor distortions are not included in the above results. (In their paper, To and Henderson do not make it clear to the author how the distance to the nearest neighbors was chosen for these no polarization, no lattice distortion calculations.)

In order to obtain some estimate of the magnitude of the polarization corrections that were neglected in this study, some calculations including these polarization corrections were carried out for the F^+ center in CaO. The F^+ center in CaO has previously been investigated rather extensively using this model (24,17), and suitable values for the

TABLE VIII

SUMMARY OF THE THEORETICAL AND EXPERIMENTAL VALUES OF THE F^+ CENTER ABSORPTION ENERGIES

Lattice	Wood and Opik's Model	To and Henderson (All N.P.)	Kemp and Neely (All P.)	H. S. Bennett (All P.)	To and Henderson (All P.)	Experimental
MgO	————	5.647 eV	4.70 eV	3.84 eV	4.796 eV	4.92 eV
CaO	3.84 eV (P)	4.606 eV	3.80 eV	3.45 eV	3.731 eV	3.70 eV
SrO	3.63 eV (NP)	4.144 eV	3.40 eV	3.26 eV	3.287 eV	3.10 eV
BaO	3.82 eV (NP)	3.705 eV	3.00 eV	————	2.865 eV	2.00 eV

N.P. = Polarization corrections are not included.

P. = Polarization corrections are included.

parameters in the THS polarization potential equations have been determined. In this study calculations for the F^+ center in CaO were carried out both with and without the THS polarization corrections. The calculations were done only at five percent outward distortion of the nearest neighbor ions for convenience. The results of these calculations are listed in Table IX. From the complete investigation of the F^+ center in CaO using this model it is reported that the theoretical absorption energy is 3.84 eV at about 8.5% outward nearest neighbor distortion and the theoretical emission energy is 2.78 eV at 11% distortion (32). The experimental values for the CaO F^+ center absorption and emission energies are 3.7 eV and 3.3 eV, respectively.

For the sample CaO calculations results shown in Table IX the $^2A_{1g}$ - $^2T_{1u}$ energy difference is decreased by about 1.5 eV when the THS polarization corrections are included, but this is at 5% distortion of the nearest neighbors which is far from either the $^2A_{1g}$ or $^2T_{1u}$ equilibrium distortions. In any case these calculations on CaO do show that the THS polarization corrections can be large and do significantly lower the transition energies and alter the wave functions predicted by the model used in this study.

In reported calculations for the F center in NaCl and KCl using this same model, the use of the THS polarization potentials lowered the absorption energies by about .5 eV (12). Note that this is just about the correction needed for the SrO F^+ center results of this study to agree with experiment. The BaO results are farther away from the experimental values but BaO also has a much larger static dielectric constant than any of these other crystals, and this is expected to cause a significant increase in the magnitude of the polarization corrections for

TABLE IX

RESULTS OF CaO F^+ CENTER ELECTRONIC ENERGY CALCULATIONS WITH AND WITHOUT POLARIZATION CORRECTIONS AT FIVE PERCENT OUTWARD DISTORTION OF THE NEAREST NEIGHBOR IONS

State	Electronic Energy, E_F	Ionic Polarization Energy	Electronic Polarization Energy	Q Inside 1NN	Q Inside 2NN	Ave. Radius
$^2T_{1u}$	- 10.792 eV	+.54009 eV	- 8.8784 eV	.176	.289	9.54 au
$^2T_{1u}$	- 4.647 eV	0.0	0.0	.742	.907	3.94 au
$^2A_{1g}$	- 14.683 eV	+.12601	- 6.5146	.953	.991	2.67 au
$^2A_{1g}$	- 10.055 eV	0.0	0.0	.974	.998	2.48 au

BaO.

R. F. Wood and U. Opik also report that including these polarization corrections increases the magnitude of the predicted Stokes shift (12). This increased Stokes shift will improve the agreement of the results of this study with experiment when the polarization corrections are included. The wave functions generated in Wood and Opik's calculations mentioned above were used to calculate oscillator strengths and the spin density at the nuclei of the nearest neighbors and other shells of XTAL ions (27,24). The results of these calculations were in fairly good agreement with experiment.

It is apparent that when the polarization corrections are included the transition energies and corresponding Stokes shift will most likely be in much better agreement with the experimental values. It is not clear just how accurate these values including polarization effects will be, and to settle this the calculations including polarization will have to be carried out.

CHAPTER VI

CONCLUSION

A preliminary theoretical investigation of the F^+ centers in SrO and BaO has been carried out. The electronic energy of these F^+ centers was calculated using a model developed by R. F. Wood and U. Opik in 1969 (2). The first nearest neighbor positive ions are treated using a detailed ℓ-dependent Hartree-Fock type model and the rest of the crystal is accounted for by an effective mass model. Polarization corrections were not included in this study due to difficulties in assigning values to some of the necessary parameters. The lattice potential energy was calculated by T. M. Wilson using a model based on classical ionic crystal lattice theory. A Born-Mayer type potential was employed in his calculations for the repulsive interaction.

The electronic energy plus the lattice potential energy was plotted against the percent outward distortion of the first nearest neighbor ions to give configuration-coordinate diagrams for the F^+ center in SrO and BaO. (Figure 2 and Figure 3, respectively.) From these configuration-coordinate diagrams the emission and absorption transition energies of these F^+ centers have been predicted. These predicted absorption and emission energies for SrO are 3.63 eV and 3.28 eV versus experimental values of 3.10 eV and 2.42 eV respectively, and for the F^+ center in BaO the predicted absorption and emission energies are 3.82 eV and 2.82 eV respectively. The experimental absorption energy for BaO is 2.00 eV and emission from F^+ centers in BaO has not yet been reported.

The magnitude of the difference between these calculated energies and the experimental energies is not too disappointing since the polarization corrections were not included in these results. It is known from previous calculations using this same model that the polarization corrections are large and their inclusion causes the calculated transition energies to be smaller. The inclusion of the polarization potential in this model also causes the Stokes shift of the theoretical transition energies to be smaller, and this will also give closer agreement with experiment for the SrO theoretical transition energies when polarization is included. In previous color center calculations this model has proven itself to be somewhat better than the other models in predicting such quantities as oscillator strengths, Fermi contact terms, and half-widths as well as the transition energies of color centers in the alkali halides (12,27,24). Since these "no polarization" calculations for the F^+ centers in SrO and BaO yielded transition energies which were greater than the experimental values by a fairly reasonable amount, it is expected that when polarization corrections are included this model will give good transition energies (and other results) for SrO and BaO, also.

Much of the "future work" for this problem is either already in the calculation phase or in the programming stage. Of course, the most obvious needed work is to complete the calculations of SrO and BaO within the context of the model used in this study by rerunning these calculations with the THS polarization corrections included. This will most likely be accomplished very soon. The wave functions generated by this calculation should be used to calculate some other measurable quantities such as the oscillator strengths and Fermi-contact terms. As mentioned previously, this is expected to verify that this model is indeed fairly satisfactory.

Computer programs are now available which would allow the model utilized in this study for the one electron F^+ center calculations to be applied to the two-electron F center in SrO and BaO. F center calculations for MgO and CaO have already been carried out using this model (17) and the SrO and BaO F center calculations will undoubtedly be completed shortly. These MgO and CaO F center results were in fairly good agreement with experiment.

Work is underway at Oklahoma State University to apply this very same model to the F center in $KMgF_3$ and in other crystals having the perovskite structure (25). The results of these calculations are also expected to be available in the next few months.

Programs utilizing a more sophisticated molecular-orbital type model which will be superior to the one used in this work are currently being developed by T. M. Wilson (24). This model is intended to eliminate several of the more serious approximations made by the model used in this study. The proposed molecular-orbital model calculations would allow distortion of the crystal ion core orbitals, would allow for a more flexible trial function (especially for r greater than R_A), would treat the exchange term more exactly, and would evaluate the multicenter integrals more accurately. Considering the fairly good results given by the comparatively unsophisticated model considered in this study, the proposed molecular-orbital model can be expected to generate much more satisfactory energies and wave functions and, hopefully, will answer some of the more difficult questions such as the apparent lack of emission from the excited state of the two-electron F center in BaO.

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APPENDIX A

HARTREE ATOMIC UNITS

Hartree atomic units are often used in atomic structure calculations because of their convenience. In the usual quantum mechanical wave equations $m = e = \hbar = 1$ when Hartree atomic units are employed.

These Hartree atomic units, their physical equivalents, and their equivalents in more common units of measure are given in Table X below.

TABLE X

HARTREE ATOMIC UNITS

Unit	Physical Equivalent	Numerical Equivalent
Mass	rest mass of the electron	9.1091×10^{-28} gm
Length	radius of first Bohr orbit of hydrogen	$.0529167 \times 10^{-8}$ cm
Energy	twice the ionization energy of the ground state of hydrogen	27.2106 eV
Charge	the charge of the electron	1.6021×10^{-19} Coul

APPENDIX B

EQUATIONS AND PARAMETERS EMPLOYED FOR CALCULATION OF THE LATTICE POTENTIAL ENERGIES USED IN THIS STUDY (18,32)

The lattice potential energy is written as $E_L(\delta) = E_C(\delta) + E_R(\delta)$. ΔE_C represents the change in the electrostatic energy of the first nearest neighbor ions, treated as point charges, when they are distorted outward from the vacancy site by a distance δ.

The equation used for $\Delta E_C(\delta)$ is:

$$\Delta E_c(\delta) = \frac{24}{a_o}\left(\frac{1.25 + \sqrt{2}}{1+\delta} - \frac{1}{2+\delta} - \frac{1}{[1+(1+\delta)^2]^{\frac{1}{2}}} + \sqrt{2} - .75\right)$$

$\Delta E_R(\delta)$ represents the change in the repulsive energy due to the finite size of the ions. This repulsive energy term is written as $\Delta E_R(\delta) = W_R(\delta) + W_{RR}(\delta) + \Delta W_{RR}(\delta)$. The expressions for these quantities given by I. M. Boswarva and A. B. Lidiard (18) are:

$$W_R(\delta) = 12c_+[\exp[-\sqrt{2}(1+\delta)a_o/\rho] - \exp[-\sqrt{2}\ a_o/\rho]]$$

$$\frac{-12c_{++}}{(\sqrt{2}\ a_o)^6}\left[\frac{1}{(1+\delta)^6} - 1\right] - \frac{12d_{++}}{(\sqrt{2}\ a_o)^8}\left[\frac{1}{(1+\delta)^8} - 1\right]$$

and

$$W_{RR}(\bar{\xi}_s,\delta) = 6[\phi_R([1-\delta_o+\bar{\xi}_1]a_o) - \phi_R([1+\bar{\xi}_1]a_o)]$$

$$+ 24[\phi_R(a_o\sqrt{(1+\bar{\xi}_2/\sqrt{2})^2 + (8 - \bar{\xi}_2/\sqrt{2})^2}) - \phi_R(a_o\sqrt{(1+\bar{\xi}_2/\sqrt{2})^2 + \bar{\xi}_2{}^2/2})]$$

$$+24[\phi_{RR}(a_o\sqrt{(\delta-\bar{\xi}_3/\sqrt{3})^2+2(1+\bar{\xi}_3/\sqrt{3})^2} - \phi_{RR}(a_o\sqrt{\bar{\xi}_3{}^2/3 + 2(1+\bar{\xi}_3/\sqrt{3})^2})]$$

$$+24[\phi_{RR}(a_o\sqrt{(1-\delta + 2\bar{\xi}_4/\sqrt{5})^2 + (1+\bar{\xi}_4/\sqrt{5})^2}$$

$$- \phi_{RR}(a_o\sqrt{(1+2\bar{\xi}_4/\sqrt{5})^2 + (1+\bar{\xi}_4/\sqrt{5})^2})]$$

and

$$\Delta W_{RR}(\delta) = -\tfrac{1}{2} \sum_{s=1}^{4} \{\bar{\xi}_s[\frac{\partial W_{RR}(\partial,\xi_s}{\partial\xi_s}]_{\xi_s=\bar{\xi}_s}\}$$

where $\bar{\xi}_1 = \frac{-M'}{4}$, $\bar{\xi}_2 = \frac{-M'}{2}$, $\bar{\xi}_3 = \frac{M'}{3}$, $\bar{\xi}_4 = \frac{M'}{5}$, and M' is a parameter defined by Boswarva and Lidiard in Reference 29. In these calculations the Born-Mayer potential with Van der Waals corrections is used and are given by:

$$\phi_R(r) = B \exp(-r/\rho) - \frac{c_{\pm}}{r^6} - \frac{d_{\pm}}{r^8}$$

and

$$\phi_{RR}(r) = C_+ \exp(-r/\rho) - \frac{c_{++}}{r^6} - \frac{d_{++}}{r^8}$$

where

$$B = b \exp[(r_+ + r_-)/\rho]$$

and

$$C_{\mp} = b\ (1 \pm \frac{4}{n_{\pm}}) \exp\ (2r_{\pm}/\rho)$$

The actual values assigned to these parameters in the calculations carried out for use in this study are listed below.

TABLE XI

INPUT DATA AND REFERENCES FOR LATTICE ENERGY CALCULATION (32)

		SrO	BaO
	ρ (a)	.224 (31)	.25 (32)
	b (eV)	.525 (31)	.55 (32)
	a_o (Å)	2.58 (33)	2.762 (33)
	r_+ (Å)	1.114 (35)	1.327 (35)
	r_- (Å)	1.336 (35)	1.336 (35)
	$n_+ = n_-$	8	8
	α_+ (Å^3)	1.795 (34)	3.188 (34)
	α_- (Å^3)	1.657 (34)	1.657 (34)
	K_{static} (ε_o)	13.3 (37)	34.0 (36)
(33)	c_+ - (eV-Å^6)	43.6	66.2
	d_+ - (eV Å^8)	76.6	133.0
	c_{++} (eV Å^6)	46.3	110.0
	d_{+-} (eV Å^8)	82.9	261.0
	c_{--} (eV Å^6)	41.0	41.0
	d_{--} (eV Å^8)	70.7	70.7

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