

THE ELECTRONIC STRUCTURE OF THE F CENTER
IN KMgF_3

By

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CHAPTER I

INTRODUCTION

The F center lattice defect in a KMgF_3 crystal consists of an electron trapped at a vacant negative ion site. The KMgF_3 crystal has cubic perovskite structure with a lattice constant $a_0 = 3.754$ atomic units and in this structure the F center has a D_{4h} symmetry. The F center electron replaces a fluorine ion and has two magnesium ions as 1nn at a distance of a_0 (3.754 a.u.), four potassium ions as 2nn at $\sqrt{2} a_0$ (5.309 a.u.) and eight fluorine ions as 3nn at $\sqrt{2} a_0$ (5.309 a.u.) as shown in Figure 1.

Although extensive calculations of the electronic structure of the F center in crystals with the sodium-chloride structure have been done, similar calculations for crystals having the perovskite structure are more complex and have only recently been attempted. In this paper the calculations of the electronic structure of the F center in KMgF_3 are reported and the results compared with the experimental findings of Hall and Leggeat (1), Riley and Sibley (2) and Modine and Sonder (3), and with the calculations reported by Harker (4).

The absorption energies of a $A_{1g} \rightarrow A_{2u}$ transition and a $A_{1g} \rightarrow E_u$ transition are calculated using the model developed by R. F. Wood and U. Öpik (5) for alkali halides. This model treats the crystal as though it had two regions, an inner region and an outer region. The ions within the inner region, centered about the defect site, receive a

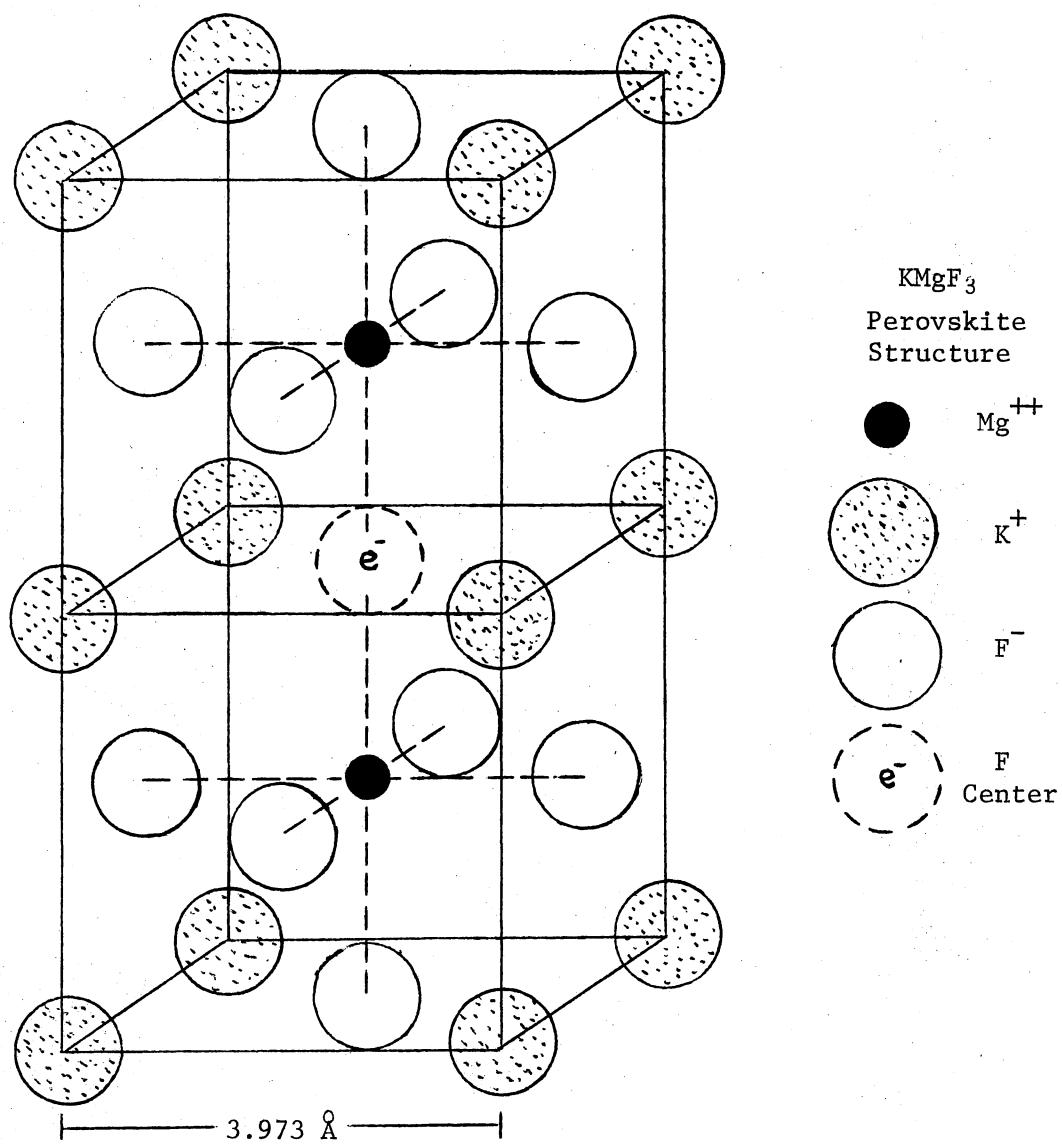


Figure 1. F Center in KMgF₃

detailed Hartree-Fock treatment by way of angular-momentum-dependent exchange potentials. The Hamiltonian for the outer region, which is composed of the rest of the crystal, is treated within the effective-mass approximation. Polarization effects are included according to the theory of THS (Toyozawa-Haken-Schottky) (5, 6).

Two sets of calculations using the ℓ -dependent potential are reported. Both sets include the explicit treatment of the electronic structure on the two 1nn magnesium ions and the four 2nn potassium ions inside the inner region. The absorption energies are calculated first with the trial wave function of the defect consisting of s and p Slater-type orbitals for the ground and excited states respectively. Then the calculations are repeated with the inclusion of d and f angular-momentum components to demonstrate their effect on the energies of the various states.

A third set of calculations was done using a point-ion potential to show the effect of the inclusion of d and f angular-momentum components in the absence of electronic structure on the magnesium and potassium ions. These results are compared with the calculations done by Harker (4) using a pseudopotential method, and demonstrate the importance of the inclusion of explicit electronic structure on neighboring ions.

In 1969, C. R. Riley and W. A. Sibley reported the experimental results of the investigation of color centers in KMgF_3 (2). The crystal was irradiated with electrons or ^{60}Co γ rays. Polarized bleaching revealed absorption in the range 190-800 nm and the absorption at 270 nm was attributed to F centers. The absorption energy of this peak was measured to be 4.569 eV at 78 K.

In their experimental study of the electronic properties of an F center in KMgF_3 , F. A. Modine and E. Sonder (3) attempted to resolve the placement of the A_{2u} and E_u states relative to the A_{1g} state. Measurements of the Magnetic Circular Dichroism (MCD) indicated an orbitally degenerate excited state and the energy splitting is consistent with an E_u excited state and a A_{1g} ground state. However, the experimental results could not resolve the question of the placement of the A_{2u} state but the absence of magnetic perturbation in the MCD spectrum implies that either the A_{2u} state is not near the E_u state in energy or it is so nearly degenerate that it is unresolved.

The primary purpose of this research is to determine if this accidental degeneracy does or does not exist.

CHAPTER II

THEORY AND NUMERICAL TECHNIQUES

The model and methods used in this calculation of the electronic structure of the F center were developed by R. F. Wood and U. Öpik. Extensive calculations have been done using this model for the F and U centers in alkali halides and the F and F' centers in MgO and CaO (6, 7). The results of these calculations indicate the reliability of the approximations made in order to reduce the magnitude of the problem.

The crystal is considered to have two regions; an inner region, centered about the defect site, containing the ions whose electronic structure is to be considered explicitly and an outer region which is treated within the effective-mass approximation.

Consider the situation where the F center electron is situated on one of the closed shell ions long enough to be considered a valence electron. Let ϕ_{vi} denote the i th core orbital on the v th ion and let Ψ denote the orbital of the F center electron. We wish to determine the orbital Ψ that will yield an expectation value of the Hartree-Fock Hamiltonian H_{HF} , i.e.,

$$\langle E \rangle = \langle \Psi | H_{HF} | \Psi \rangle / \langle \Psi | \Psi \rangle$$

that is stationary with respect to small variations in Ψ . The effective Hamiltonian is given by

$$H_{HF} = -\frac{1}{2}\nabla^2 + \sum_v (-) \frac{Z_v - N_v}{|r - R_v|} + U_v$$

where Z_v is the charge number, R_v is the position vector of the nucleus of ion v and N_v is the number of electrons on ion v . U_v is the numerical Hartree-Fock potential given by

$$U(r) = [\phi(r)]^{-1} V \phi_0(r)$$

$$V u(r) = \left(\frac{-N_v}{|r - R_v|} + 2 \sum_i \int \frac{[\phi_{vi}(r')]^2}{|r' - r|} dr' \right) u(r)$$

$$- \sum_i \phi_{vi}(r) \int \frac{\phi_{vi}(r') u(r')}{|r' - r|} dr'$$

and $u(r)$ is an arbitrary one-electron wave function.

This numerical function $U(r)$ and the core orbitals of each ion can be generated from Clementi's wave functions (8). The procedure of obtaining a self-consistent form of the potential function, core orbitals and energies is discussed in detail in Appendix A. Unless otherwise specified, Hartree atomic units will be used in this study. These units are defined in Table I.

TABLE I
HARTREE ATOMIC UNITS

Unit	Equivalent	Numerical Value
MASS	Rest mass of the electron	9.1091×10^{-28} gm
LENGTH	Radius of the first Bohr orbit of hydrogen	0.529167×10^{-8} cm
ENERGY	Twice the ionization energy of the ground state of hydrogen	27.2706 eV
CHARGE	Charge on the electron	1.6021×10^{-19} C

It is found that the numerical function $U(r)$ varies slightly with the energy E_0 used in the Hartree-Fock calculation but it is strongly dependent on the azimuthal quantum number ℓ . These results are illustrated in Table II and Table III.

TABLE II
ENERGY DEPENDENCE OF THE EFFECTIVE POTENTIAL*

$r \backslash 2E_0 =$	-0.8	-0.6	-0.3
0.005	0.13415	0.13393	0.13366
0.1	2.24294	2.24380	2.24610
1.0	1.30343	1.26356	1.22070
2.8	0.11764	0.11139	0.10359
3.6	0.04501	0.04379	0.04337
5.0	0.00575	0.00649	0.00898

*An illustration of the insensitivity of the effective exchange potential to the energy at which it is determined. The tabulated value is $\delta(2Zp)$ where $(-r^{-1})\delta(2Zp)$ is the exchange correction to the effective potential for a s electron in the field of a K^+ ion, r is the distance from the nucleus and E_0 is in atomic units.

Since the numerical function $U(r)$ shows a strong dependence on the value of ℓ , its straightforward substitution for the potential operator would not be valid, but if it is defined by a different numerical function for each ℓ value, $V(r)$ would then be redefined as the $U'(r)$

TABLE III
ANGULAR MOMENTUM DEPENDENCE OF THE EFFECTIVE EXCHANGE POTENTIAL*

$\ell =$ $r \quad 2E_0 =$	0 -0.290	1 -0.191	2 -0.117	3 -0.04	4 -0.035
0.005	0.13366	0.12950	0.11006	0.07513	0.04995
0.1	2.24610	0.88760	0.77967	0.42726	0.21076
1.0	1.22070	1.40462	1.10615	1.14161	0.95915
2.8	0.10359	-0.00639	0.17000	0.07086	0.04856
3.6	0.04337	0.00966	0.05152	0.01744	0.01125
5.0	0.00898	0.00220	0.00689	0.00162	0.00092

*An illustration of the sensitivity of the effective exchange potential to the angular-momentum quantum number ℓ . The tabulated value is $\delta(2Zp)$ where $(-r^{-1})\delta(2Zp)$ is the exchange correction to the effective potential for an outer electron of a K^+ ion, r is the distance from the nucleus and E_0 is in atomic units.

satisfying the equation

$$U'(r)\phi_{0\ell}(r) = U_{\ell}(r)\phi_{0\ell}(r)$$

where $\phi_{0\ell}(r)$ is the solution to the equation

$$-\frac{1}{2}\nabla^2 - \frac{(Z-N)}{r} + U_{\ell} - E_{0\ell})\phi_{0\ell}(r) = 0$$

for corresponding values of ℓ . A new Hamiltonian H_u is defined for the ion as

$$H_u = -\frac{1}{2}\nabla^2 + \sum_n (-) \frac{(Z_n - N_v)}{|r - R_v|} + U_i$$

However, the Hartree-Fock core orbitals, ϕ_{vi} , of the various ions are not solutions to the equation

$$[H_u - E_{vi}] \phi_{vi}(r) = 0$$

thus the self-consistent procedure discussed in Appendix A was used to obtain core orbitals, ϕ'_{vi} , which satisfy the equation

$$(H_u - E'_{vi})\phi'_{vi} = 0. \quad (1)$$

In this treatment, the free-ion orbitals are regarded as good approximations to the Wannier orbitals that satisfy the relation

$$\langle \phi_{vi} | \phi_{vj} \rangle = \delta_{vu} \delta_{ij}.$$

The F center wave function Ψ can be expressed as a linear combination of the unoccupied orbitals centered on the surrounding ions, all of which are solutions to equation (1). Therefore Ψ is orthogonal to the core orbitals and is written as

$$\Psi(r) = f(r) - \sum_v \sum_i \phi'_{vi} \langle \phi'_{vi} | f \rangle. \quad (2)$$

If H'_u is defined as $H_u + q/r$, it represents the effective positive charge of a vacancy neutralized by an electron, i.e., a F center, so the function ϕ'_{vi} can be regarded as an eigenfunction of H'_u . We can write

$$H'_u \phi'_{vi} = E''_{vi} \phi'_{vi}$$

where E''_{vi} is the energy, corresponding to the wave function ϕ'_{vi} , with a Madelung potential correction. The generation of this Madelung correction term is discussed in Appendix B.

The above approximation allows us to write a simplified form of the matrix elements of H_u as

$$\begin{aligned} \langle \Psi_k | H_u | \Psi_\ell \rangle &\equiv H_{k\ell} = \langle f_k | H_u | f_\ell \rangle \\ &- \sum_v \sum_i E''_{vi} \langle f_k | \phi'_{vi} | f_\ell \rangle \langle \phi'_{vi} | f_\ell \rangle \\ &+ q \sum_v \sum_i \left(\langle f_k | r^{-1} | \phi'_{vi} \rangle \langle \phi'_{vi} | f_\ell \rangle \right. \\ &\left. + \langle f_k | \phi'_{vi} \rangle \langle \phi'_{vi} | r^{-1} | f_\ell \rangle \right) \\ &- q \sum_v \sum_i \langle f_k | \phi'_{vi} \rangle \langle \phi'_{vi} | r^{-1} | \phi'_{vi} \rangle \langle \phi'_{vi} | f_\ell \rangle \end{aligned} \quad (3)$$

$$\langle \Psi_k | \Psi_\ell \rangle \equiv S_{k\ell} = \langle f_k | f_\ell \rangle - \sum_v \sum_i \langle f_k | \phi'_{vi} \rangle \langle \phi'_{vi} | f_\ell \rangle \quad (4)$$

When Ψ is written as a linear combination of the functions Ψ_k defined in equation (2), the energies and wave functions can be obtained by solving the secular equation

$$\det [\mathbf{H} - E \mathbf{S}] = 0$$

where \mathbf{H} and \mathbf{S} are matrices whose elements are $H_{k\ell}$ and $S_{k\ell}$ as given in equations (3) and (4).

The smooth part f of the function Ψ is defined to be a Slater-type orbital of the form

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

where $Y_{\ell m}(\theta, \phi)$ is a spherical harmonic of degree ℓ and magnetic quantum number m . Each of the trial functions f is centered on the defect site and is expanded about each ion whose electronic structure is to be considered explicitly. The β 's of the STO's are treated as variational parameters in an iterative procedure of steepest descents to minimize the total energy of the crystal in its ground and excited states.

Wood and Öpik (5) present two methods of treating the ions in the outer region of the crystal, the method applied here is the effective-mass approximation. Let V_{per} be the periodic effective Hartree-Fock potential energy of an electron and let V' represent any additional polarization energy arising from the defect, polarization, etc. The energy of the bottom of the conduction band is denoted by ϵ_{HF} . Then for the inner region, we apply the equation

$$(-\frac{1}{2}\nabla^2 + V_{\text{per}} + V')\Psi = E\Psi$$

and the outer region is treated by the equation

$$[-(2m^*)^{-1}\nabla^2 + \epsilon_{\text{HF}} + V']g = E_g g$$

where g is the envelope function for the orbital and m^* is the effective mass.

If an operator G is defined such that in the inner region

$$G = -\frac{1}{2}\nabla^2 + V_{\text{per}} + V'$$

and in the outer region

$$G = -\frac{1}{2}\nabla^2 + m^* \epsilon_{\text{HF}} + m^* V'$$

then

$$\begin{aligned} \langle E \rangle &= \left(\int_{\text{inner}} \Psi G \Psi d\tau + \int_{\text{outer}} g G g d\tau \right) \\ &\quad / \left(\int_{\text{inner}} \Psi^2 d\tau + m^* \int_{\text{outer}} g^2 d\tau \right) . \end{aligned}$$

Actually, in the application of this method to the KMgF_3 crystal, the formalism was violated in that the electronic structure of the 2nn potassium ions was included explicitly while the ions actually lie in the outer region. The radius that divides the two regions was treated as a variational parameter and was defined to be inside the 2nn ions.

Dielectric polarization effects have been included according to the theory of THS (Toyazawa-Haken-Schottky) (6). The polarization potential is divided into two parts: $U_{\text{el}}(r)$, the electronic potential and $U_{\text{ion}}(r)$, the ionic potential. $U_{\text{el}}(r)$ is given by

$$U_{\text{el}}(r) = (1 - \kappa_{\infty}^{-1}) \left\{ \frac{1}{2}(\rho_e + \rho_h) + \left(\frac{1}{r}\right) \left[1 - \frac{1}{2}(e^{-\rho_e r} + e^{-\rho_h r}) \right] \right\}$$

and $U_{\text{ion}}(r)$ is given by

$$U_{\text{ion}}(r) = (\kappa_{\infty}^{-1} - \kappa_{\text{st}}^{-1}) \left\{ \frac{1}{2}(V_e + V_h) + \left(\frac{1}{r}\right) \left[1 - \frac{1}{2}(e^{-V_e r} + e^{-V_h r}) \right] \right\}$$

where κ_{∞} and κ_{st} are the high-frequency and static dielectric constants. The parameters ρ_e and V_e are associated with the electron and ρ_h and V_h are associated with the hole. Their values are determined by THS theory.

The effective Hamiltonian for the outer region of the crystal can be expressed as

$$H_{\text{HF}} = -(2m^*)^{-1} \nabla^2 - \frac{1}{r} + \epsilon_{\text{HF}}$$

where ϵ_{HF} represents the bottom of the conduction band. The value of ϵ_{HF} is given by

$$\epsilon_{\text{HF}} = \epsilon_{\text{expt}} + \frac{1}{2}(1 - \kappa_{\infty}^{-1})\rho_e - \frac{1}{2}(\kappa_{\infty}^{-1} - \kappa_{\text{st}}^{-1})V_e$$

where ϵ_{expt} is the experimental electron affinity.

Since the bottom of the conduction band has not been determined experimentally, the magnitude of the energies of the various states have no valid physical interpretation and only their values relative to each other is of importance.

The calculation of the transition energies and the determination of the placement of the A_{2u} state were of primary importance in this paper, but a secondary calculation was done to determine the transition probability in terms of the oscillator strength for the various states. The energy of a state is relatively insensitive to slight variations in the wave function of the defect but the oscillator strength is highly dependent on the coefficients of the linear combination of the Slater-type orbitals composing the optimized trial defect wave function.

Because of this sensitivity, the oscillator strength provides a check on the accuracy of the form of the defect wave function.

The values of the oscillator strengths were calculated using the expressions

$$\begin{aligned}
f_{A_{1g} \rightarrow A_{2u}} = & \left(\frac{2}{3} \Delta E_{A_{1g} \rightarrow A_{2u}} \left\{ \frac{1}{\sqrt{3}} \sum_{sp} C_s C_p \langle f_s | r | f_p \rangle \right. \right. \\
& + \sqrt{\frac{9}{35}} \sum_{df} C_d C_f \langle f_d | r | f_f \rangle \\
& \left. \left. + \sqrt{\frac{4}{15}} \sum_{dp} C_d C_p \langle f_d | r | f_p \rangle \right\}^2 \right) / N_{A_{1g}} \cdot N_{A_{2u}}
\end{aligned}$$

$$\begin{aligned}
f_{A_{1g} \rightarrow E_u} = & \left(\frac{4}{9} \Delta E_{A_{1g} \rightarrow E_u} \left\{ \sum_{sp} C_s C_p \langle f_s | r | f_p \rangle \right. \right. \\
& - \frac{1}{\sqrt{5}} \sum_{dp} C_d C_p \langle f_d | r | f_p \rangle \\
& - \sqrt{\frac{27}{140}} \sum_{df_1} C_d C_{f_1} \langle f_d | r | f_{f_1} \rangle \\
& \left. \left. - \sqrt{\frac{45}{140}} \sum_{df_2} C_d C_{f_2} \langle f_d | r | f_{f_2} \rangle \right\}^2 \right) / N_{A_{1g}} \cdot N_{E_u}
\end{aligned}$$

where ΔE is the transition energy between the states indicated. C denotes the coefficients of the components, f , of the trial wave function that yields the optimal energy. N represents the appropriate normalization factor.

CHAPTER III

PREVIOUS THEORETICAL WORK

A calculation of the electronic structure of the F center in KMgF_3 was recently reported by A. H. Harker (4). He used the point-ion model of Gourary and Adrian (9) in two sets of calculations; Case 1 includes angular momentum components up to and including $\ell = 1$ and Case 2 includes angular momentum components up to and including $\ell = 3$.

The energies of the A_{1g} , A_{2u} and E_u states obtained by using this model are listed in Table VI and from these results, Harker (4) concluded that

. . . Our results for the energy levels suggest that the point-ion theory of Gourary and Adrian (1957) becomes unreliable when terms other than the first (spherically symmetric) in the expansion of the point-ion potential have non-vanishing matrix elements with the variational wave function. (p. 3351)

Harker introduced a correction for the finite sizes of the ions according to the method developed by Bartram, Stoneham and Gash (10) and reported the calculations for the same two cases. The results of these calculations are listed in Table IV. This model does not yield the anomalously low energy for the A_{2u} state that resulted from the point-ion calculation. However, for Case 1 the A_{2u} and E_u states are relatively close to each other in energy while inclusion of higher-order angular momentum terms in Case 2 created a separation of several electron volts.

Harker concludes that

While simple (the point-ion and ion-size) approximations yield ground state wave functions which give reasonable values of the hyperfine interactions which accurately predict spin-orbit effects, more sophistication is required in calculating the energies. (p. 3353)

TABLE IV

HARKER'S CALCULATED ENERGY LEVELS OF F CENTER IN KMgF_3

Wave Function	Symmetry	Point-Ion Energy (eV)	Ion - Size Energy (eV)
Case 1	A_{1g}	-7.60	-6.56
	A_{2u}	-6.99	-1.99
	E_u	-3.17	-1.87
Case 2	A_{1g}	-10.63	-6.81
	A_{2u}	-12.73	-2.13
	E_u	-4.56	-3.33

CHAPTER IV

RESULTS AND DISCUSSION

The calculation of the electronic structure of the F center in KMgF_3 was done on an IBM 360/65 computer. The programs used were modified versions of the set of programs written by U. Öpik for calculations of the energies of an F center in sodium chloride-structured crystals.

The first step in the calculation was the generation of the radial part of the one-electron wave function for each closed shell and a tabulated numerical potential represented by an effective nuclear charge. Atomic wave functions from Clementi's tables (8) were used to obtain tabulated wave functions and potentials for a potassium ion, a magnesium ion and a fluorine ion.

These tabulated numerical values were used as input to a second program which is capable of generating a self-consistent set of core wave functions, effective potentials and energies. The program calculates an exchange correction to the effective potential, V_{eff} , according to the equation

$$V_{\text{eff}} = Z_p(r) - I_c + \delta Z_p(r)$$

where $Z_p(r)$ is one-half the effective nuclear charge for the potential, I_c is the charge of the core and $\delta Z_p(r)$ is the exchange correction to $Z_p(r)$. This potential is generated for each angular-momentum number ℓ

by introducing an additional correction according to

$$-\frac{2Z_p(r)}{r} + \frac{\ell(\ell+1)}{r^2}$$

where $Z_p(r)$ does not contain the exchange correction. The process of attaining self-consistency is discussed in Appendix A.

The self-consistent forms of the core orbital wave functions, the effective exchange potentials and the energies corresponding to the core orbitals with a Madelung potential correction are used as input to a third program which calculated the electronic energies and wave functions of the F center.

The trial wave function used in determining the matrix elements of the effective Hamiltonian and overlap matrices defined by equations (3) and (4) is composed of Slater-type orbitals where the β 's are the variational parameters. Orbitals of angular-momentum quantum number $\ell = 0, 1, 2$ and 3 were included in the wave functions and the spherical harmonics that composed the angular parts of the orbitals for the three states are listed in Table V (11). Two combinations of spherical harmonics were used for the $\ell = 3$ angular momentum component for the E_u state.

The explicit electronic structure on the 1nn magnesium ions and the 2nn potassium ions is included by a ℓ -dependent Hartree-Fock treatment but overlaps between core orbitals on positive ions have been ignored because they are small in magnitude compared to overlaps between outer electrons on these ions with the F center wave function. Since in the equations considered these overlaps have a power of two, this approximation seems reasonable. But the overlaps between positive and negative ions are not negligible as can be seen in Table VI. This

fact will be of importance when considering the inclusion of the explicit structure on the fluorine ions.

TABLE V
ANGULAR PART OF THE SLATER-TYPE ORBITALS OF THE BASIS WAVE FUNCTION

Symmetry	ℓ -Value	Real Spherical Harmonic Representation	Cartesian Coordinate Representation
A_{1g}	0	$Y_{0,0}$	$\sqrt{\frac{1}{4\pi}}$
	2	$Y_{2,0}$	$\sqrt{\frac{5}{16\pi}} \frac{1}{r^2} (3Z^2 - r^2)$
A_{2u}	1	$Y_{1,0}$	$\sqrt{\frac{3}{4\pi}} \frac{Z}{r}$
	3	$Y_{3,0}$	$\sqrt{\frac{7}{16\pi}} \frac{Z}{r^3} (5Z^2 - 3r^2)$
E_u	1	$\sqrt{\frac{1}{2}} (Y_{1,1} + Y_{1,-1})$	$\sqrt{\frac{3}{4\pi}} \frac{y}{r}$
	3	$\frac{1}{4} [5(Y_{3,3} + Y_{3,-3}) + 3(Y_{3,1} + Y_{3,-1})]$	$\sqrt{\frac{7}{16\pi}} \frac{y}{r^3} (5y^2 - 3r^2)$
	3	$\frac{1}{4} [\sqrt{3}(Y_{3,3} + Y_{3,-3}) - \sqrt{5}(Y_{3,1} + Y_{3,-1})]$	$\sqrt{\frac{105}{16\pi}} \frac{y}{r^3} (x^2 - z^2)$

The polarization energy is included according to the theory previously discussed and a list of the values of the parameters ρ_e , ρ_h ,

v_e , v_k , κ_∞ , κ_{st} and χ_{expt} appear in Table VII. The high-frequency and static dielectric constants, κ_∞ and κ_{st} , were the only parameters for which experimental values were used and were determined by C. H. Perry and E. F. Young (12). The other polarization parameters were allowed to vary but were not radically different from values used in alkali-halide calculations from which the initial estimates of their values were obtained.

TABLE VI
OVERLAPS BETWEEN CORE ORBITALS

Ions = R =	$\langle F^- F^- \rangle$ 5.309	$\langle F^- Mg^{++} \rangle$ 3.754		$\langle F^- K^+ \rangle$ 5.309	$\langle Mg^{++} K^+ \rangle$ 6.502
Overlap			Overlap		
1S 2S	0.1334E-03	0.4436E-04	1S 3S	0.8170E-04	0.4088E-05
1S 2P	0.2729E-02	0.3445E-03	1S 3P	0.6515E-03	0.5958E-04
2S 2S	0.6657E-02	0.1495E-01	2S 3S	0.7063E-02	0.1086E-03
2S 2P	0.4022E-01	0.2059E-01	2S 3P	0.1970E-01	0.9434E-03
2P 1S	0.2729E-02	0.6666E-02	2P 3S	0.4541E-01	0.2691E-03
2P 2S	0.4022E-01	0.6667E-01	2P 2P	0.1882E-02	0.4035E-05
2P 2P	0.6908E-01	0.4871E-01	2P 3P	0.5910E-01	0.1446E-02
2PP 2PP	0.2274E-01	0.1503E-01	2PP 3PP	0.1477E-01	0.1492E-03

The radius that divides the crystal into two regions is R_a and this value was chosen to be 4.0, between the 1nn magnesium ions and the 2nn potassium ions. This choice of R_a was found to be necessary in order to obtain a calculated transition energy close to that seen experimentally. The fact that R_a is less than the 2nn radius appears to be due to the treatment of the fluorine ions as point ions while taking the electronic structure on the potassium ions explicitly into account. The effective mass was set at 0.6, comparable to alkali-halide calculations. These values are also listed in Table VII. The values of the parameters listed there apply to all calculations reported unless explicitly stated otherwise.

TABLE VII
PARAMETERS USED IN THE F CENTER ENERGY CALCULATIONS

Parameter	Value
R_a	4.0
κ_∞	2.04
κ_{st}	5.96
ρ_e	0.2
ρ_h	0.2
v_e	0.0
v_h	0.0
χ_{expt}	0.11
m^*	0.6

The first calculations of the energies of the A_{1g} , A_{2u} and E_u states were made with $\ell = 0$ and 1 angular momentum components in the trial defect wave function. The A_{1g} state's basis function consisted of 1s, 2s, 2s and 3s STO's; the basis function for both the A_{2u} and E_u states were composed of 2p, 2p, 3p and 4p STO's.

The program was allowed to find an "optimal, minimal" energy for the lowest states of each symmetry by performing a pattern search from an algorithm by A. F. Kaupe (13). The description "optimal, minimal" is relative to the calculation being performed, the calculation was optimal in that the minimal energy was found to be within the tolerances desired. The determination of the energy to machine precision loses its meaning when considering the approximations made in the theory of the model.

With this restriction in mind, the optimal energies for the three states are listed in Table VIII. Other relevant properties, such as the electronic polarization energy and the average radius at which the F center electron is found, are listed in Table IX. Also listed is the percentage of the total charge enclosed in spheres centered on the defect site and defined by the radii of the Inn ions and R_a .

The only change involved in the second set of calculations was the addition of a $\ell = 2$ angular momentum component to the basis set of the A_{1g} state and the addition of a $\ell = 3$ component to the basis sets of the A_{2u} and E_u states. The explicit descriptions of these orbitals are listed in Table VIII and the energies and electronic properties of the three states are listed in Table IX.

A comparison of the states in the first calculations show that the transition energy from the A_{1g} state to the E_u state to be 4.3 eV with

TABLE VIII
CALCULATED ENERGY LEVELS OF A F CENTER IN KMgF_3

Wave Function	Symmetry	Energy (eV)
$\ell = 0, 1$	A_{1g}	-4.7736
	A_{2u}	-0.5889
	E_u	-0.4774
$\ell = 0, 1, 2, 3$	A_{1g}	-5.0320
	A_{2u}	-0.6533
	E_u	-0.5146

TABLE IX
THEORETICAL PREDICTIONS OF ELECTRONIC PROPERTIES*

Wave Function	Symmetry	R_{ave}	$C_{lnn}(5)$	$C_{Ra}(\%)$	$E_{pol}(\text{eV})$
$\ell = 0, 1$	A_{1g}	2.313	92.96	95.88	-0.590
	A_{2u}	15.122	6.81	7.55	-1.091
	E_u	21.043	0.12	0.13	-1.243
$\ell = 0, 1, 2, 3$	A_{1g}	2.373	91.39	94.64	-0.607
	A_{2u}	10.673	17.64	19.55	-0.968
	E_u	17.966	1.62	1.83	-1.164

* R_{ave} is the expectation value of the position of the F center electron; C_{lnn} and C_{Ra} represent the total charge found inside a sphere centered on the defect site with a radius defined by the distance to the l_{nn} ions and R_a respectively; E_{pol} is the electronic polarization energy expressed in eV's.

a 0.11 eV separation of the A_{2u} and E_u states. The transition energy compares with the experimental value of 4.6 eV. In the second calculations, the expected lowering of the energies of all states due to the additional element of the basis set is observed. The transition energy of 4.52 eV is closer to the experimental value and a 0.14 eV separation of the A_{2u} and E_u states is now observed. Several other calculations were done using different values for the parameters of Table VII and the two excited states were never separated by more than a few tenths of an electron volt.

It is important to note that there was no erratic displacement of the energies of the states relative to each other with the addition of the $\ell = 2$ and 3 angular momentum components as was observed in the calculations done by Harker (4). So a third set of calculations was performed using a point-ion potential instead of the ℓ -dependent effective exchange potential. The Hamiltonian was defined to be

$$H_{PI} = -\frac{1}{2} \nabla^2 - \sum_i V_i(r)$$

where $V_i(r)$ is the point-ion potential of each of the ions inside the inner region defined by R_a . The parameters in this calculation are those given in Table VII except R_a which is now defined to be 10.5. The energies generated using the point-ion potential both with and without $\ell = 2$ and 3 angular momentum contributions are listed in Table X along with Harker's results for his point-ion calculation.

The probability of a transition from the ground state to the A_{2u} and to the E_u states was calculated in terms of the oscillator strengths. The coefficients of the linear combination of the optimized basis functions that yielded the energies in Table VIII were used in

these calculations with an effective mass of 0.6 and the value of R_a set to 4.0. Although no experimental data is available for a comparison, the theoretically predicted values as listed in Table XI seem anomalously small.

TABLE X
COMPARISON OF THE RESULTS OF TWO POINT-ION CALCULATIONS

Wave Function	Symmetry	Energy (eV)	
		Whisenhunt	Harker
$\ell = 0, 1$	A_{1g}	-7.611	-7.60
	A_{2u}	-7.042	-6.99
	E_u	-3.166	-3.17
$\ell = 0, 1, 2, 3$	A_{1g}	-9.651	-10.63
	A_{2u}	-11.219	-12.73
	E_u	-4.167	-4.56

TABLE XI
OSCILLATOR STRENGTHS

Wave Function	Transition	Oscillator Strength
$\ell = 0, 1$	$A_{1g} \rightarrow A_{2u}$	0.0248
	$A_{1g} \rightarrow E_u$	0.0013
$\ell = 0, 1, 2, 3$	$A_{1g} \rightarrow A_{2u}$	0.0848
	$A_{1g} \rightarrow E_u$	0.0114

CHAPTER V

CONCLUSIONS

It would appear from the energy calculations that the model as applied to alkali halides can be extended to crystals of lower symmetry. The predicted transition energy of 4.52 eV compares quite favorably with the experimental value of 4.6 eV but reflected in this value is the fact that many constants of the calculation had to be treated essentially as variational parameters because an experimental determination of their values has not yet been affected, namely the energy of the bottom of the conduction band and the effective mass.

A comparison of the energies in Table VIII shows that the inclusion of angular momentum terms greater than $\ell = 0$ and 1 have little effect on the energies of the various states as was reported in an earlier publication (14). The expected lowering of the energies of all states due to the expansion of the basis set of the trial defect wave function is observed but no large displacement of the states relative to each other occurs.

The point-ion calculation performed exhibits a behavior of the A_{2u} state similar to that shown by Harker and appears to indicate that explicit inclusion of the electronic structure on the ions neighboring the defect has a marked influence on the energy of the state, especially when higher-order angular-momentum terms are considered.

Although the energies of the states yield a reasonable transition energy, the small oscillator strengths pose a question as to the accuracy of the form of the trial defect wave function. The size of these transition probabilities might be a reflection of the fact that the fluorine ions at the edges of a cube centered on the defect site are treated as point ions even though they are the same distance from the defect as the 2nn potassium ions. The size of the overlaps of the fluorine core orbitals with orbitals on potassium, magnesium and other fluorine ions could have a pronounced effect, especially when considering that there are eight equivalent fluorine ions.

It might be argued that the effect of leaving these ions as point ions in the calculations up to the present has been counter-balanced by defining the value of R_a to be inside the 2nn potassium ions since the effect of including the orthogonalization terms on the fluorine ions would be to decrease the overlaps while moving the radius R_a inward tends to increase the effective mass contribution. The explicit inclusion of these fluorine ions is in progress now and will be continued by T. M. Wilson at Oak Ridge National Laboratory.

As can be seen from the values in Table IX, the A_{1g} state is an extremely localized state while both the A_{2u} and E_u states are more delocalized and effective-mass-like. Therefore the inclusion of the fluorine ions would be expected to have a more pronounced effect on the ground state than on the diffuse excited states.

The conclusion that can be drawn at this stage of the calculations is that the E_u and A_{2u} states have so nearly the same energy that the states would not easily be resolved experimentally and so appear to have a near accidental degeneracy. Furthermore, this near degeneracy

was evident regardless of the variation of parameters of the calculation. The separation of these states from the ground state implies a transition energy that agrees favorably with experiment. But further calculations are needed to remove approximations and provide further checks with experiment.

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APPENDIX A

METHOD OF SELF-CONSISTENT CALCULATION

The model of the F center used in this paper is based on an angular-momentum dependent exchange potential and the process of deriving this potential will be outlined in this appendix.

First, the core wave functions and an effective nuclear charge form for the potential are generated in tabulated form using Clementi's atomic orbitals (8). The effective form for this potential is represented by the total charge of the nucleus with the coulombic interaction of the closed shell electrons subtracted from it. Let these core wave functions be denoted by ϕ_{0i} and the effective nuclear charge for potential by $Z_p(r)$.

A numerical function $Z'_p(r)$ is defined to be

$$Z'_p(r) = Z_p(r) - I_c - \delta Z_p(r)$$

where I_c is the net charge of the core and $\delta Z_p(r)$ is the exchange correction to $Z_p(r)$.

Then twice the radial potential is calculated according to the equation

$$V_\ell(r) = \frac{-2Z'_p(r)}{r} + \frac{\ell(\ell + 1)}{r^2}$$

where ℓ is the angular momentum quantum number of the outer orbital to be considered.

The radial Schrödinger equation for this outer orbital is solved by integrating outward over the core orbitals. This equation is given by

$$[-\frac{1}{2}\nabla^2 - (Z - N)/r + V_\ell(r) - E_\ell]\Psi_\ell(r) = 0 \quad (7)$$

where E_ℓ is the energy corresponding to the outer electron Ψ_ℓ and V_ℓ is given by equation (6). Equation (7) is solved for values of $\ell = 0, 1, 2, 3, 4$ and 5 .

Another calculation is performed to define the core orbitals corresponding to the corrected form of the potential $V_\ell(r)$ obtained from equation (7). These core orbitals are calculated by solving the equation

$$[-\frac{1}{2}\nabla^2 - (Z - N)/r + V_\ell(r) - E_i]\phi_i(r) = 0 \quad (8)$$

where $V_\ell(r)$ is the potential for the corresponding angular-momentum number ℓ of the core orbital ϕ_i and the equation is integrated outward over only the orbitals within ϕ_i .

If a self-consistent calculation is desired, at this point redefine ϕ_{0i} and the corresponding E_{0i} to be the ϕ_i 's and E_i 's obtained from equation (8). Then recalculate the exchange correction $\delta Z_p(r)$ in equation (5) with these new values for ϕ_{0i} and proceed through the calculations defined by equations (6), (7) and (8).

At this stage, a comparison is made between the core orbitals ϕ_{0i} and the core orbitals ϕ_i from equation (8). If the numerical form of the two sets of wave functions are self-consistent to within acceptable tolerances, the calculation is terminated. Otherwise return to equation (5) and iterate again. It has been observed that acceptable self-consistency can be attained after two iterations.

If the calculations are determined to have reached self-consistency, the numerical potential $V_\ell(r)$ of equation (7) for values $\ell = 0, 1, 2, 3, 4$ and 5 are defined to be the potentials for the outer electrons in the F center calculation. The core orbitals corresponding to these potentials are the ϕ_{0i} 's used to determine the exchange corrections in equation (5), not the ϕ_i 's with their corresponding E_i 's in equation (8).

These values of $V_\ell(r)$, ϕ_{0i} and E_{0i} are used as input to the program that calculates the energy of the F center. It should be noted that the energies, E_{0i} , must be corrected for the Madelung potential contribution; the derivation of this correction is discussed in Appendix B.

APPENDIX B

Madelung Correction to the Energy

The energy for each core orbital must be corrected for the electrostatic interaction ($\pm q^2/r$) between the ions called the Madelung energy. The Madelung correction terms were calculated according to a method which employs Born's and Hund's basis potentials (15). The total potential at a point is given by the equation

$$\phi = \sum_{\alpha} q_{\alpha i} \psi_i$$

where α represents groups made up of ions within the same unit cell. The charge $q_{\alpha i}$ is calculated according to an ion's position in the unit cell; charges in the interior, on the face, on the edge, or on the corner of the cube assume weights of 1, $\frac{1}{2}$, $\frac{1}{4}$, or $\frac{1}{8}$ respectively. The ψ 's are Hund's basic potentials (15) that are chosen according to the position of the ion in the cell.

Using this method, the potential on the potassium ion would be given by the expression

$$\phi_K = \psi_0 + 2\psi_1 - 3\psi_3$$

where ψ_0 , ψ_1 and ψ_3 correspond to the potassium, magnesium and fluorine ions, respectively.

The Madelung correction term is given by

$$M_d = -k_d \sum_i q_{\alpha i} \psi_i$$

where k_d is dependent on the structure of the crystal (16). The Madelung corrections, calculated with respect to the first nearest neighbor ions, for KMgF_3 were: K^+ : +0.3588, Mg^{++} : +0.8243, and F^- : -0.4299 a. u.

This correction is added to the energy, E_{0i} , of each core orbital for all ions. The resultant energy, E' , is used as input to the F center program.

APPENDIX C

POINT-ION POTENTIALS

The F center program is capable of generating point-ion potentials for ions out to an arbitrary radius R . The form of the potential for $r < R$ and through $\ell = 6$ is

$$\begin{aligned} V_{D_{4h}}(r) = & \gamma_{00} Z_{00} + \gamma_{20} r^2 Z_{20} + \gamma_{40} r^4 Z_{40} \\ & + \gamma_{44} r^4 Z_{44} + \gamma_{60} r^6 Z_{60} + \gamma_{64} r^6 Z_{64} \end{aligned}$$

where $Z_{\ell 0} = Y_{\ell,0}$

and $Z_{\ell m} = \sqrt{\frac{1}{2}}(Y_{\ell,m} + Y_{\ell,-m})$.

The coefficients, $\gamma_{\ell m}$, are determined for the n th shell of ions by the equation

$$\gamma_{\ell m}^n = \gamma_{\ell m}^\infty - \sum_{i=1}^{n-1} \gamma_{\ell m}^i$$

where $\gamma_{\ell m}^\infty$ represents the shell where the coefficients cease to change relative to the previous shell. In our calculations, this occurred at the fifteenth nearest neighbor shell which includes 8,810 ions.

This method of expressing the point-ion potential was presented by M. T. Hutchings (17) and the program used to determine the coefficients, $\gamma_{\ell m}$, was provided by Harold L. Davis (18).

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