Theory of Spin-Orbit Effects in the F Band in Alkali Halides*†

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A calculation of the spin-orbit splitting of the first optically excited state of the F center is reported. It is based on a tight-binding, static lattice model of the crystal and assumes a vacancy-centered electronic wave function for the F center. To satisfy the Pauli principle, the F-center state must be orthogonalized to the occupied states of the crystal. This modifies the vacancy-centered wave function by introducing states localized about the ions. These states undergo a spin-orbit interaction in the fields of the ionic nuclei, causing a splitting of the F band into two components. Explicit calculations for NaCl predict splittings of about 0.008 eV with the $P_{1/2}$ state lying above the $P_{3/2}$ state. This is in good agreement with the observed splittings. The calculations indicate that the spin-orbit splitting is determined primarily by the halide ion in the halides of light alkalies and generally increases with the atomic number of both ions. It further suggests that the structure in the F band of the cesium salts is due, at least in part, to a spin-orbit splitting.

I. INTRODUCTION

In the past year magneto-optical experiments have been reported that show that there is fine structure in the F-band absorption in the alkali halides.[1–6] This structure has been resolved by two methods: Karlov, Margerie, and d'Aubigné employed the dichroism for absorption of circularly polarized light that is induced by a magnetic field[1] and Lüty and Mort used paramagnetic Faraday rotation.[2] The structure has been tentatively ascribed to a spin-orbit splitting of the excited state to which optical transitions occur.

The present paper reports a model calculation of the spin-orbit splitting of the first optically excited state of the F center.[7] The splitting is found to arise from the spin-orbit interaction of the F-center electron with the shielded electric fields of the neighboring ions. The theory has been evaluated in detail for the F center in NaCl and is found to predict both the inversion of spin-orbit levels and the magnitude of the observed splitting.

Table I lists the observed splittings in the F-absorption band as reported up to the time of this writing.[1–6] The most striking feature of these data is that, considered as spin-orbit splittings, they are negative indicating that the $P_{1/2}(\Gamma_6^-)$ state lies above the $P_{3/2}(\Gamma_8^-)$ state. This order is inverted as compared with the usual configuration of energy levels for a system of one electron outside a closed shell and is at variance with the common single-force center models of the F center.

The next most striking feature is that the splittings generally increase with atomic number of both alkali and halide. For the lighter alkalies the splittings appear to be determined primarily by the second-nearest-neighbor halide ions and are relatively independent of the nature of the nearest-neighbor alkali ions. For the heavier alkalies, such as cesium, the situation is not clear because of the more complex structure of the F band.[8]

TABLE I. Observed splittings in the F-absorption band. With the exception of the values for KI, RbCl, and RbBr as observed by circular dichroism the values are derived from the difference between the maxima of the F-band components. In general the errors quoted for the splittings range from ±10% to ±20%. [For a discussion of a more accurate analysis of such spectra see Henry, Schnatterly, and Slichter (Ref. 25).]

Material	Circular dichroism (10^{-3} eV)	Faraday rotation (10^{-3} eV)
NaCl	−7.7	−5.1
NaBr	−28.2	···
KCl	−10	−11.4
KBr	−29.8	−19.2
KI	−57	−30.0
RbCl	−24	···
RbBr	−27	−32.4
CsCl	−55, −107	···
CsBr	−78	−42

II. THEORY

In the present calculation we shall adopt the well-substantiated de Boer model of the F center,[9] make the usual approximation of a static lattice, and use tight-binding, one-electron wave functions.[10]

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† A preliminary account of this work was given at the March 1964 meeting of the Americal Physical Society at Philadelphia [Bull. Am. Phys. Soc. **9**, 240 (1964)].

[1] N. V. Karlov, J. Margerie, and Y. Merle-d'Aubigné, J. Phys. Radium **24**, 717 (1963).

[2] F. Lüty and J. Mort, Phys. Rev. Letters **12**, 45 (1964).

[3] R. Romestain and J. Margerie, Compt. Rend. **258**, 2525 (1964).

[4] J. Margerie and R. Romestain, Compt. Rend. **258**, 4490 (1964).

[5] J. Gareyte and Y. Merle-d'Aubigne (private communication to Dr. R. P. Moran) and (to be published).

[6] J. Mort, F. Lüty, and F. Brown, preceding paper, Phys. Rev. **137**, A566 (1965).

[7] To the author's knowledge, the first considerations of the F center absorption to take account of the spin-orbit interaction were made by Professor D. L. Dexter in a letter to Dr. P. Sorokin in 1958.

[8] H. Rabin and J. H. Schulman, Phys. Rev. **125**, 1584 (1962), F. Hughes and H. Rabin, Phys. Chem. Solids **24**, 586 (1963).

[9] For a discussion of evidence for the de Boer model see J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillian Company, New York, 1962).

[10] See, for example, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

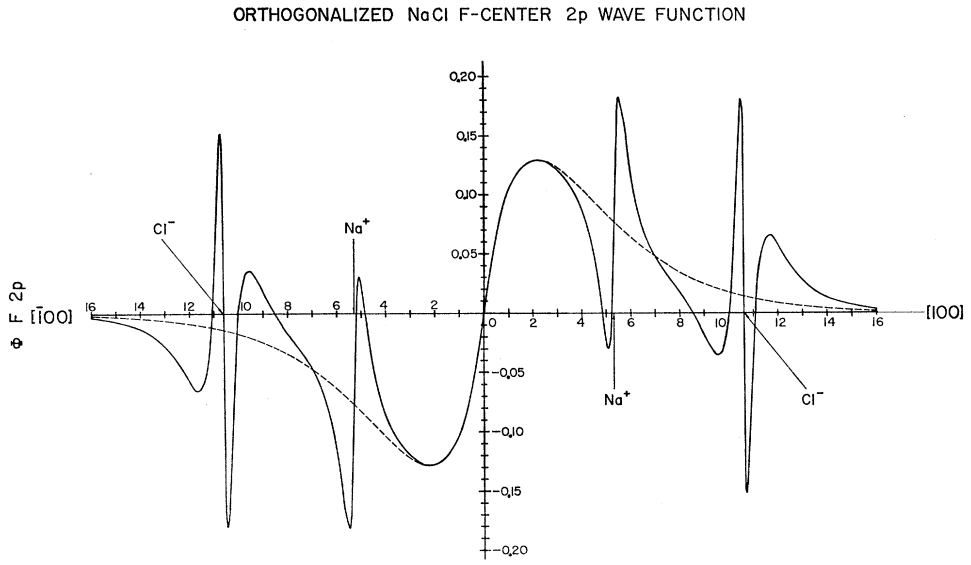

FIG. 1. A section along the [100] direction of the F-center $2p$ wave function orthogonalized to the outer-shell states of neighboring ions. The origin of coordinates is taken as the center of the vacancy. The dashed curve is Gourary and Adrian's type II point-ion wave function which is the starting function. Orthogonalization to the outer $2p$ states of the Na^+ ions and the $3p$ states of the Cl-ions yields the solid curve (the normalization correction was neglected in drawing these curves). Orthogonalization to deeper core states leads to still more structure in the neighborhood of the ion nuclei.

Ideally the wave functions for the F center and the crystal ion cores should be determined in a self-consistent manner such as that of Hartree and Fock for the crystal as a whole, with proper account taken of the ionic relaxation about the vacancy.[10] In the framework of the Born-Oppenheimer approximation,[11] an optical transition of the F center occurs when the crystal is raised to an excited state corresponding to an excitation of the one-electron function describing the F-center electron. After absorption the system of nuclei and electrons readjusts to minimize its energy. This leads to new ionic positions and a new set of electronic wave functions and energy levels.[12]

We are considering the spin-orbit interaction as exhibited in absorption, so that we are concerned with the first unrelaxed excited electronic state of the F center. If, on the other hand, we were calculating the spin-orbit splitting in emission, we would have to know the details of the relaxed excited state.

Since the calculation of even approximate self-consistent one-electron wave functions for a crystal defect is extremely difficult, we shall develop the present theory assuming that the F-center wave function may be taken as a one-electron function centered on the vacancy and subsequently orthogonalized to the occupied states of the crystal. The requirement of orthogonality simply ensures that the Pauli principle is satisfied and that the F-center electron does not occupy a state already occupied by another electron.

For a vacancy-centered wave function u and crystal ion functions, φ^α, the Schmidt orthogonalized vacancy-centered wave function ϕ is[13]

$$\phi=(1-\textstyle\sum_\alpha S_\alpha{}^2)^{-1/2}(u-\sum_\beta S_\beta\varphi^\beta)\,, \qquad (1)$$

where S_α is the overlap integral $\langle\varphi^\alpha|u\rangle$ and the sums over α and β are taken over all occupied states.

A comparison of a point ion function u and the resulting orthogonalized (but unnormalized) ϕ, for the "$2p$" state of the NaCl F center is given in Fig. 1. Here a Gourary and Adrian type II wave function[14–16] has been orthogonalized to the outer p functions of the ions along the [100] direction. The solid curve gives ϕ for points along the [100] direction while the dashed curve

[11] For a review of optical properties see D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

[12] W. B. Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962) and W. B. Fowler, *ibid.* **135**, A725 (1964).

[13] See, for example, R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 1.

[14] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[15] B. S. Gourary and F. J. Adrian in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

[16] Type I wave functions are simple hydrogenic functions of the form $u=(1/\pi)^{1/2}(\xi'/a)^{5/2}r\exp(-\xi'r/a)\cos\theta$, where a is the interatomic distance and ξ' a variational parameter. For NaCl Gourary and Adrian find $\xi'=2.40$. Type II wave functions are composite functions consisting of a square well solution inside the vacancy and a hydrogenic tail beyond. Thus,

$$u=A'(3/4\pi)^{1/2}j_1(\xi'r/a)\exp(-\eta')\cos\theta, \qquad r<a$$
$$=A'(3/4\pi)^{1/2}j_1(\xi')(r/a)\exp(-\eta'r/a)\cos\theta, \qquad r>a$$

where ξ' and η' are variational parameters, A' is a normalization constant and $j_n(x)$ is the spherical Bessel function of order n. For NaCl the values found for the variational parameters are $\xi'=3.26$ and $\eta'=3.40$.

is the original function u. This figure shows how radically the orthogonalized F-center electronic function differs from a simple form in the neighborhood of the ions. Processes depending on the details of the wave function near the ions such as the hyperfine splitting[14,15] and, as we shall see, the spin-orbit interaction, are determined almost exclusively by the terms introduced by orthogonalization. It is in this regard that the present calculation differs from a previous calculation by Suffczynski in which an approximate localized state formed from conduction band states was used.[17] The latter function was not accurately orthogonal to the occupied p states of the ions and important terms in the spin-orbit interaction were consequently not included.[18]

The Hamiltonian for the spin-orbit interaction of an electron is given in general by[19]

$$h_{so}=-e(2m^2c^2)^{-1}\mathbf{S}\cdot(\mathbf{E}\times\mathbf{p}), \tag{2}$$

where e is the electronic charge, m is the mass of the electron, c is the velocity of light, $\mathbf{S}$ is the electron spin operator, $\mathbf{p}$ the momentum operator, and $\mathbf{E}$ the electric field through which the electron moves. The electric field experienced by the F-center electron is not only that due to the point ions, but also that due to the potential within the ion cores. The crystal electric field is greatest in the immediate vicinity of the nuclei and hence the overwhelming portion of the above interaction arises there. To a good approximation the fields near the nuclei are radial so that Eq. (2) may be rewritten approximately as

$$\begin{aligned}h_{so}&=(2m^2c^2)^{-1}\textstyle\sum_I(\mathbf{r}-\mathbf{R}_I)^{-1}[\partial V_I/\partial(\mathbf{r}-\mathbf{R}_I)]\mathbf{L}_I\cdot\mathbf{S}\\&=\textstyle\sum_I\xi(\mathbf{r}-\mathbf{R}_I)\mathbf{L}_I\cdot\mathbf{S},\end{aligned} \tag{3}$$

where the index I labels the ion at point $\mathbf{R}_I$ and V_I is the potential of the Ith ion. Here the orbital angular momentum is measured with respect to the Ith nucleus so that $\mathbf{L}_I=(\mathbf{r}-\mathbf{R}_I)\times\mathbf{p}$.

The spin-orbit splitting of the F absorption band may now be calculated directly by finding the expectation value of the spin-orbit Hamiltonian, Eq. (3), for the unrelaxed $2p$ F-center wave function. Matters are particularly simple for p states in a cubic crystal since their degeneracy is not lifted by the crystal field.[20] The symmetry properties of the wave functions that diagonalize the spin-orbit interaction are therefore the same as in the free atom. In particular, the Γ_8^- level has the same basis as the $P_{3/2}$ state and that of the Γ_6^- level is the same as the basis for the atomic $P_{1/2}$ state.

Formally the spin-orbit interaction is the sum of three terms. The first involves the vacancy-centered function alone. The second is a cross term linear in S_α and the third is a crystal ion term with a coefficient quadratic in overlap. That is,

$$\begin{aligned}\Delta E_{so}&=\langle\phi|h|\phi\rangle\\&=N^2[\langle u|h_{so}|u\rangle\\&\quad+\textstyle\sum_\alpha S_\alpha\langle\varphi_\alpha|h_{so}|u\rangle+\sum_\beta S_\beta\langle u|h_{so}|\varphi_\beta\rangle\\&\quad+\textstyle\sum_{\alpha,\beta}S_\alpha S_\beta\langle\varphi_\alpha|h_{so}|\varphi_\beta\rangle],\end{aligned} \tag{4}$$

where N is the normalization factor $(1-\sum_\alpha S_\alpha^2)^{-1/2}$.

To compare the predictions of theory with experiment we need the difference in spin-orbit energy between the $P_{3/2}$ and the $P_{1/2}$ states. This may be found directly by evaluating Eq. (4) for both $P_{1/2}$ and $P_{3/2}$ states, but a simpler method is to take advantage of the fact that to first order the center of gravity of the p state is not changed by the spin-orbit perturbation. Thus, the difference in energy between the $P_{3/2}$ and the $P_{1/2}$ states is just three times the spin-orbit energy calculated from Eq. (4) for the $P_{3/2}$ state. To further simplify evaluation of this expression, we shall choose the angular dependence of the wave function u so as to reduce the algebra involved. In particular, we shall consider the p state with total angular momentum J equal to $\frac{3}{2}$ and projected angular momentum m_J equal to $\frac{3}{2}$. This state has spin up and an angular dependence given by the spherical harmonic Y_1^1 [proportional to $(x+iy)/r$].

The first term of Eq. (4) may be evaluated by using the definition of $\mathbf{L}_I$. The result is

$$\begin{aligned}\epsilon_1&=N^2\langle u|h_{so}|u\rangle\\&=(3\hbar^2N^2/16\pi)\textstyle\sum_I\Big[\int|\mathfrak{R}|^2x(x-X_I)r^{-2}\xi(\mathbf{r}-\mathbf{R}_I)d^3r\\&\quad+\int|\mathfrak{R}|^2y(y-Y_I)r^{-2}\xi(\mathbf{r}-\mathbf{R}_I)d^3r\Big],\end{aligned} \tag{5a}$$

where we define ϵ_1 to be the first terms in Eq. (4). $\mathfrak{R}$ is the radial part of u and X_I and Y_I are the x and y components of the ionic position vector $\mathbf{R}_I$. The integration is taken over all space. For the six nearest-neighbor ions at $|\mathbf{r}|=a$ in the NaCl crystal structure this reduces to

$$\begin{aligned}\epsilon_1&=(3\hbar^2N^2/8\pi)\Big\{\int|\mathfrak{R}|^2(x^2+y^2)r^{-2}\xi(0,0,a)d^3r\\&\quad+2\int|\mathfrak{R}|^2[x(x-a)+y^2]r^{-2}\xi(a,0,0)d^3r\Big\},\end{aligned} \tag{5b}$$

where the triplet of numbers, x, y, z, of the argument of ξ give the coordinates of the position about which the spin-orbit operator is centered.

The matrix element in the third term of Eq. (4) is of importance only when the wave functions φ_α and φ_β and the spin-orbit operator are located on the same center. The result is then an ionic spin-orbit matrix element times a product of overlap integrals. For the six nearest neighbors in the NaCl structure this term,

[17] M. Suffczynski, J. Chem. Phys. 38, 1558 (1963).
[18] See Ref. 15, p. 203.
[19] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).
[20] H. A. Bethe, Ann. Physik 3, 133 (1929).

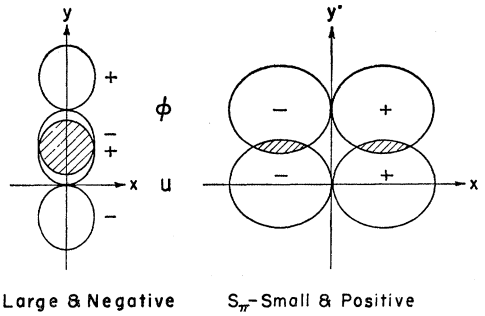

FIG. 2. Qualitative representations of the π and σ types of overlap for two $2p$ functions on different centers. In general, S_π and S_σ are opposite in sign and in almost all cases in this study the magnitude of S_σ was of the order of twice that of S_π.

abbreviated as ϵ_3, becomes

$$\epsilon_3 = 2N^2 \sum_{\alpha,\beta} S_{\pi,\alpha}(S_{\pi,\beta}+2S_{\sigma,\beta})\lambda_{\alpha\beta}. \quad (6)$$

Here $\lambda_{\alpha\beta}$ is the spin-orbit matrix element

$$\langle \varphi_\alpha(r-R_I)\,|\,\xi(\mathbf{r}-\mathbf{R}_I)\mathbf{L}_I\cdot\mathbf{S}\,|\,\varphi_\beta(\mathbf{r}-\mathbf{R}_I)\rangle.$$

$S_{\pi,\alpha}$ is the π overlap between the F-center $2p$ wave functions and the state φ_α centered on a neighboring ion, while $S_{\sigma,\alpha}$ is the corresponding σ overlap. The designations π and σ for the various overlap integrals refer to the orientation of the ionic p wave function and of the F-center p wave function with respect to the line joining the crystal ion and the vacancy center. These two cases are illustrated graphically in Fig. 2 which shows the overlap for typical $2p$ states centered on both the vacancy and on a neighboring ion. In general, the π and σ overlaps are opposite in sign and the σ overlaps are larger in magnitude than the π overlaps for the same functions. The ion-ion contribution therefore gives a negative spin-orbit interaction.

The second term in Eq. (4) is a sum of cross terms and may be evaluated in the same manner since the cross terms are important only when φ_α and V_I are centered on the same ion. The result for the six nearest-neighbor ions in the NaCl structure is

$$\epsilon_2 = -4N^2 \sum_\alpha (S_{\pi,\alpha}\lambda_{\pi,\alpha}+S_{\sigma,\alpha}\lambda_{\pi,\alpha}+S_{\pi,\alpha}\lambda_{\sigma,\alpha}), \quad (7)$$

where we have abbreviated the sum of the two cross terms as ϵ_2. Here $\lambda_{\pi,\alpha}$ and $\lambda_{\sigma,\alpha}$ are the π and σ like spin-orbit integrals between the vacancy-centered function u and the ionic state, φ_α. These are the analogs of $S_{\pi,\alpha}$ and $S_{\sigma,\alpha}$ but involve the spin-orbit operator rather than the unit operator.

Similar expressions may be found for the configurations of ions in other shells.[21] The relevant lattice sums have been performed for the first four shells in both the NaCl and the CsCl structures and it is found that the contribution per ion is of the same form for each shell, i.e., one-sixth of the above expressions.

The physical meaning of this analysis may be seen by considering the currents associated with the orthogonalized F-center wave function. A sketch of these currents for a crystal having the NaCl structure is given in Fig. 3. The vacancy-centered part of the state we have been considering has orbital angular momentum $\hbar$ in the z direction. Associated with this angular momentum there is an electric current due to the circulation of charge about the vacancy center. This current flows in loops lying in planes parallel to the x-y plane. As we shall see below, there are in addition localized current loops about each ion arising from the ionic functions introduced by orthogonalization. These currents may be thought of an forming ion-centered current swirls in the vacancy-centered current distribution.

The detailed analysis in the following paragraphs shows that in the case of ions in the x-y plane the swirls form back flows that locally have angular momentum pointing in the $-z$ direction. On the other hand, for ions located on the z axis, the swirls circulate in the same direction as the main current centered on the vacancy. Ions in intermediate positions have associated currents with localized angular momentum intermediate between the above extremes.

The spin-orbit interaction is the interaction between a moving electron and the screened nuclear electric fields. It is of importance only very close to the nuclei where the fields are large. Hence, the important electronic currents in the F-center spin-orbit interaction are those localized about the ions. As we shall demonstrate for the case shown in Fig. 3, the currents about ions in the x-y plane are greater than those about ions

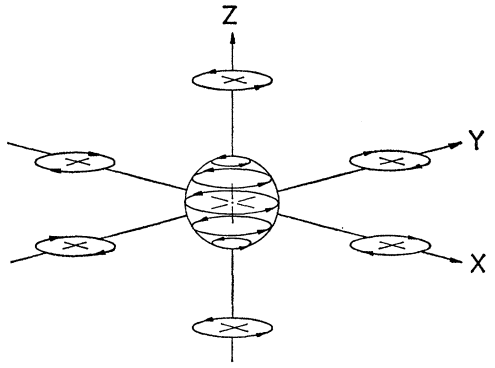

FIG. 3. The total current associated with an F center in a p state with $J=3/2$, $m_J=3/2$. The main current distribution is centered about the vacancy and rotates counterclockwise. Associated with this are currents from satellite states admixed by orthogonalization. These are centered about the neighboring ions (six of which are shown) and the associated currents flow counterclockwise about ions on the z axis, but *clockwise* about ions in the x-y plane (see text). Since these currents are in the electric field of the ionic nuclei, they give rise to the major spin-orbit interaction. The calculations show that the currents about ions in the x-y plane are the strongest and the reversal of their flow relative to that of the main distribution leads to the inversion of the spin-orbit levels.

[21] Evaluation of these lattice sums is simplified by the use of the tables for two center integrals with arbitrary choice of axes given by J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954), especially p. 1503.

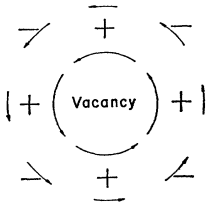

FIG. 4. Currents in the x-y plane associated with a vacancy-centered F-center p state with $J=3/2$, $m_J=3/2$. In the case illustrated, the current density is decreasing at the neighbors. For a sufficiently rapid decrease, this configuration of currents leads to a negative spin-orbit interaction.

on the z axis. Thus, the dominant spin-orbit interaction is that for currents with angular momentum opposite to that of the center as a whole. This is the source of the apparent anomalous inversion of spin-orbit levels.

This picture may be verified easily for the orthogonalized vacancy-centered function since each of the terms of Eq. (4) has a simple physical interpretation. The first term, Eq. (5), is just the spin-orbit interaction for the vacancy centered part of the wave function at the neighboring nuclei. The electric currents in the x-y plane associated with a vacancy-centered p state with $J=3/2$ and $m_J=3/2$ are indicated in Fig. 4. The nearest-neighbor ions are indicated with $+$ signs. For this example the current inside the vacancy is greater than that on the outside of the vacancy. Taking the spin-orbit interaction in the form $\mathbf{S}\cdot(\mathbf{E}\times\mathbf{p})$, one can show that the expectation value is proportional to that of $\mathbf{S}\cdot(\mathbf{E}\times\mathbf{j})$, where $\mathbf{j}$ is the electronic current. Using this form, it is easy to convince oneself that the net value of $(\mathbf{E}\times\mathbf{j})$ is of the opposite sign from that to be expected if the charges were all at the center of the vacancy (as in an atom). This situation is reversed, however, if the ions are in a region having currents greater outside the vacancy than inside. It should be pointed out that we are considering the screened nuclear field of the ions here. If just the point-ion potential were included, the spherically symmetric component of the electric field inside the vacancy would be zero.

The third term, Eq. (6), may be visualized as shown in Fig. 5. Here we have constructed an orthogonalized state from a $2p$ wave function having angular dependence $(x+iy)/r$ centered on the vacancy and $2p$ states centered on each of four ions in the x-y plane. Since orthogonalization mixes in "ghost" or "satellite" states on the neighboring ions (the wiggles introduced in Fig. 1) we have not only the main wave function with normal Y_1^1 character centered on the vacancy, but also additional satellite states about each of the neighbors. However, these arise from subtracting out ionic functions that overlap the vacancy-centered function in either a π-like or a σ-like manner. For overlapping $2p$ states, S_σ is negative and S_π is positive. Hence in every case either the x or y component of the satellite state is reversed giving a state having Y_1^{-1} character about the neighboring ion. These states then undergo a spin-orbit interaction which is the negative of that expected for a Y_1^1 state. This contribution is the source of the term $S_\pi S_\sigma$ in Eq. (6).

For ions located on the z axis the satellite states are introduced by subtracting out x- and y-like states both of which overlap the vacancy-centered part of the wave function with π-like overlaps. In this case both the x- and y-like states appear with coefficients of the same sign and there is no reversal of angular momentum. The two atoms on the z axis are therefore seen to give the S_π^2 term in Eq. (6).

The second group of terms, Eq. (7), may also be visualized from Fig. 5. They represent cross terms between p functions centered on the vacancy and those on neighboring ions. In verifying the terms in Eq. (7) it should be remembered that the orbital angular-momentum operator, L_z, rotates the x- and y-like p functions through 90°. Thus for ions in the x-y plane, a satellite state admixed by a π-like overlap is associated with a σ-like spin-orbit overlap integral, λ_σ, and vice versa. On the other hand, for ions on the z axis all p-function overlaps are π-like and terms of the form $S_\pi\lambda_\pi$ result.

A qualitative description of the spin-orbit interaction may also be developed for the linear combination of atomic orbitals (LCAO) model of the F center.[22] Figure

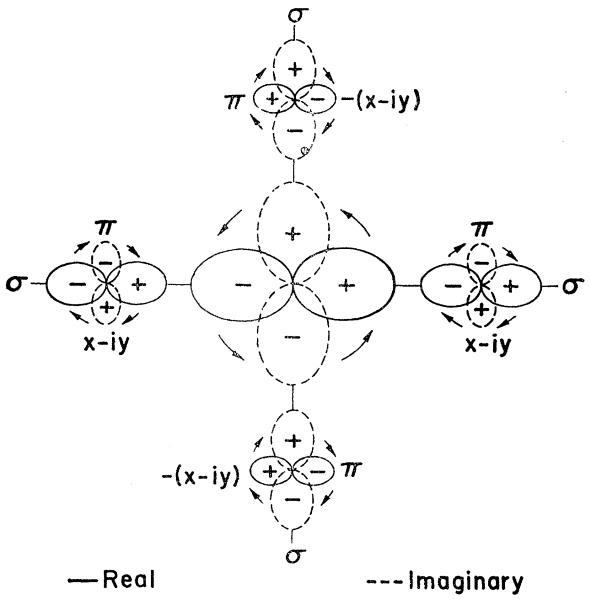

FIG. 5. A qualitative picture of an F-center p state with $J=3/2$, $m_J=3/2$ and its associated satellite states on neighboring ions in the x-y plane. Notice that in the immediate neighborhood of the ionic nuclei the angular dependence is like $Y_1^{-1}\approx(x-iy)/r$ while about the vacancy the dependence is $Y_1^1\approx(x+iy)/r$. This difference arises from the difference in sign between the π and σ overlap integrals which determine the sign of the satellite states.

[22] This picture was proposed by Dr. Beall Fowler as an alternative to the orthogonalized vacancy centered model, and the author is indebted to Dr. Fowler for permission to reproduce the argument here.

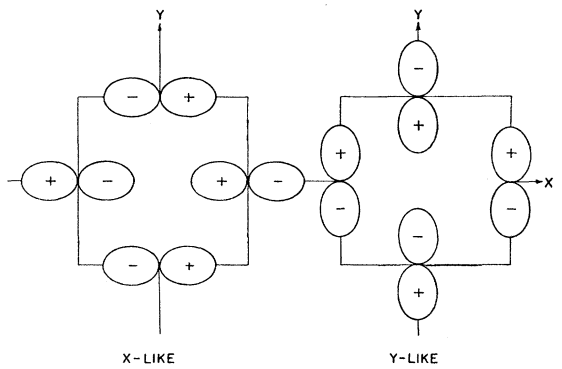

FIG. 6. F-center LCAO excited-state wave functions formed from $2p$ states centered on neighboring ions. The LCAO wave functions are either x-like or y-like within the vacancy.

6 shows two states made up of a linear combination of p states centered on neighbors that have x-like and y-like symmetry within the vacancy. Notice that in each case two of the p states on neighbors have been reversed in phase. The state with $(x+iy)$-like character within the vacancy is then easily seen to have $\pm(x-iy)$-like character locally about the neighbors. Calculations based on such a model are not possible at the present time because of the lack of satisfactory LCAO wave functions.

III. NUMERICAL RESULTS AND DISCUSSION

The foregoing expressions for the contributions to the spin-orbit interaction were evaluated in detail for NaCl using Gourary and Adrian's types I and II wave functions for the F center.[14,16] Free ion functions for Na^+ and Cl^- calculated by Hartree and Hartree[23] were used for the crystal ion functions. All overlaps and overlap spin-orbit integrals were evaluated using the "α-function" technique.[24]

Calculations were carried out correct to terms in the square of the overlap integrals, i.e., the "S^2" approximation was made.[24] This approximation is equivalent to neglecting the overlap corrections to the free-ion wave functions in forming the crystal ion functions φ_α and to neglecting the normalization correction $(1-\sum_\beta S_\beta^2)^{-1/2}$. Since some of the overlap integrals are large (see Appendix) this approximation is somewhat crude. However, it is easily shown that inclusion of overlap corrections to the crystal-ion functions tends to decrease the spin-orbit splitting while the inclusion of the normalization correction tends to increase it. Hence, higher overlap corrections tend to compensate one another and the S^2 approximation probably yields better than order of magnitude accuracy.

In the calculations no effect of lattice relaxation about the vacancy has been taken into account. This is consistent with the approximations used by Gourary and Adrian in their calculation of F-center wave functions,[14] but of course would not be permissible in a discussion of spin-orbit effects in emission. A more extensive discussion of the effects of using approximate wave functions, estimates of errors introduced, and possible improvements are given in the Appendix.

Tables II and III give the results for Gourary and Adrian's type I and type II wave functions.[16] The contribution of each of the three terms of Eq. (4) to the difference in energy between the F-center $P_{3/2}$ and $P_{1/2}$ levels is listed for each shell of ions out to the fourth nearest neighbors. The total $P_{3/2}-P_{1/2}$ energy difference is also given.

TABLE II. Calculated contributions to the spin-orbit splitting of the $P_{1/2}$ and $P_{3/2}$ excited states of the NaCl F center. Gourary and Adrian's type I wave function were used. Values are in units of $eV\times10^{-3}$.

	1st neighbor 6 Na^+ at 5.3 a_0	2nd neighbor 12 Cl^- at 7.5 a_0	3rd neighbor 8 Na^+ at 9.2 a_0	4th neighbor 6 Cl^- at 10.6 a_0
Vacancy-centered term	0.009	−0.013	0.000_8	-0.000_6
Vacancy-ion cross term	0.028	−0.038	0.004	−0.003
Ion-ion term	−0.324	−6.27	−0.053	−0.768
Total	−0.288	−6.32	−0.048	−0.772

Grand total for four shells of neighbors $=-7.43\times10^{-3}$ eV

It is clear that the major contribution to the effect is from the third term, Eq. (6). This could have been anticipated from Fig. 1 which shows that almost all the variation in the F-center electronic wave function near the neighboring ions arises from orthogonalization. Since the spin-orbit interaction depends on this variation in the wave function, it is now evident why Suffczynski's calculation,[17] which did not explicitly include effects of orthogonalization, could not have correctly predicted the magnitude of the effect.

The total contribution of each shell is given in the fourth row. At first glance these results are somewhat

TABLE III. Calculated contributions to the spin-orbit splitting of the $P_{1/2}$ and $P_{3/2}$ excited states of the NaCl F center. Gourary and Adrian's type II wave function were used. Values are in units of $eV\times10^{-3}$.

	1st neighbor 6 Na^+ at 5.3 a_0	2nd neighbor 12 Cl^- at 7.5 a_0	3rd neighbor 8 Na^+ at 9.2 a_0	4th neighbor 6 Cl^- at 10.6 a_0
Vacancy-centered term	0.007	−0.013	0.000_6	0.000_0
Vacancy-ion cross term	0.068	−0.043	0.002	−0.001
Ion-ion term	−0.696	−7.80	−0.031	−0.414
Total	−0.621	−7.86	−0.028	−0.415

Grand total for four shells of neighbors $=-8.92\times10^{-3}$ eV

[23] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936); **A193**, 299 (1948).
[24] P. O. Löwdin, Advan. Phys. **5**, 1 (1956).

surprising since the contribution of the next-nearest Cl^- neighbor is the largest, indeed, much larger than that for the nearest-neighbor Na^+ ions. The reason for this is clear when one compares the extent of the Na^+ and Cl^- wave functions. The outer shell of the Cl^- ion is more weakly bound and extends out many times the distance of the strongly bound outer shell of the Na^+ ion. This results in larger overlap integrals and consequently larger spin-orbit interactions.

The sum of the contributions from the four shells is given at the bottom of the tables. Since the falloff of spin-orbit splitting is rapid, contributions from more distant shells are neglected. Considering the approximations, the calculated spin-orbit splittings -7.43×10^{-3} eV for type I and -8.92×10^{-3} eV for type II are in good agreement with the observations of -5.1×10^{-3} eV (Lüty and Mort) and -7.7×10^{-3} eV (Romestain and Margerie). Surprisingly, there is a relatively small difference between the total results for type I and II wave functions even though there is a large difference in the "tails" of the two functions. The type II function falls off much more rapidly than the type I functions. However, this lack of extent is offset by correspondingly larger contributions from the near neighbors.

A possible serious objection to the present treatment is the assumption of a static lattice. Noncubic lattice vibrations even at absolute zero give rise to noncubic crystal fields which destroy the quantization scheme for a cubic crystal. The correct electronic wave functions are then linear combinations of wave functions for the static case and in general their orbital angular momentum is largely quenched since the effect of lattice vibrations, as measured by the breadth of the F band, is generally large compared with the spin-orbit interaction. This problem has been resolved by Henry, Schnatterly, and Slichter who have shown that even in the case in which noncubic lattice vibrations are included, the relevant parameter for describing spin-orbit effects is the spin-orbit splitting for the static lattice.[25] In particular they demonstrate that the difference in the first moment of the components of the F band in a circular dichroism or Faraday rotation experiment is not affected by lattice vibrations and consequently is just that calculated in the present paper based on the static lattice model.

Extension of these calculations to the other alkali halides is straightforward. Without going through the numerical work several predictions may be made. From the relative contributions of the various shells it is to be expected that, neglecting changes in lattice constant, the spin-orbit splittings for crystals of a given halide should increase slightly with alkali atomic number. However, except for salts of the heaviest alkalies, the most important factor should be the spin-orbit splitting due to the halide ions. In the case of the lithium salts the spin-orbit splittings should be determined almost entirely by the halide ion since lithium ions have only s states occupied and these do not contribute to the spin-orbit interaction. The experimental observations given in Table I are in general agreement with these speculations.

For the two components of the F band to be resolved in absorption of unpolarized light, their spin-orbit splitting must be at least as great as their half-width. Generally this condition is not satisfied, so the spin-orbit structure is masked and only a single smooth band is observed. The cesium salts are an exception to this since their F bands exhibit a complex structure.[8] From estimates based on the present calculation and from the experimental results of Margerie and Romestain[4] and Mort, Lüty, and Brown,[6] it appears that the spin-orbit interaction may be an important factor in this structure. In any event, the cesium salts appear to represent an intermediate case where lattice vibrations and the spin-orbit interaction are of comparable importance. One should therefore, be cautious in attributing the entire structure to the spin-orbit interaction alone.[26,27]

Aside from its application to the F-center problem, the present treatment of the spin-orbit interaction in a solid suggests that previous treatments have overlooked the importance of the spin-orbit interaction of a properly orthogonalized electronic function centered on one lattice site with the electric fields of the nuclei of neighboring ions or atoms. In analogy with a similar effect on the hyperfine interaction one might denote this contribution to the spin-orbit splitting as a "transferred spin-orbit interaction."

A considerable body of literature has developed pointing out the importance of the effects of covalency,[28] renormalization of wave functions,[29] crystal field effects,[29] and configuration interaction[30] in the general problem of spin-orbit interactions in solids. However, the "transferred spin-orbit interaction" has been omitted as small[30] up to now. Studies of some simple impurity systems are being pursued to demonstrate this effect in systems more complicated than the F center.

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[26] For various possible explanations of the F-band structure in the cesium halides see D. W. Lynch, Phys. Rev. **127**, 1537 (1962); R. S. Knox, *ibid.* **133**, A498 (1964), and P. R. Moran (to be published).

[27] A detailed analysis by C. Henry and S. Schnatterly of the data of Margerie and Romestain for cesium salts suggests that the spin-orbit splitting accounts for only about half of the energy difference between the peaks in the CsCl and CsCl F bands.

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APPENDIX

In evaluating the equations for the spin-orbit splitting approximate wave functions and potentials were used. A short discussion of these approximations is in order.

The F-center wave functions have been taken as vacancy-centered point-ion functions. Detailed discussions of this approximation have been given elsewhere.[15,31] In the case of the ground state of the F center, the success in predicting hyperfine interactions[14,15] suggests that wave functions derived from the point ion approximation provide a good approximation to the state of affaris at neighboring nuclei provided orthogonality is taken into account. Since the point ion solution does not include the effects of either lattice or ionic polarization, excited-state wave functions derived from it are probably reasonably good representations of the state to which optical transitions occur, but not of the relaxed excited state.[12]

The F-center functions of Gourary and Adrian are simple analytical functions with parameters derived by applying the variational principle before orthogonalization to the core functions. An alternate approach in which orthogonalization is performed before minimization has been reported by Wood and Koringa.[32] The latter method was found to yield improved energies and hyperfine interactions in the case of LiCl, but wave functions for NaCl have not been published. The use of simple analytical variational functions is probably satisfactory for the ground state. However, excited states are more extended and sample the complex "tail" of the F-center point ion potential and so cannot be expected to be simple functions. In fact, preliminary calculations for excited s states using the spherically symmetric component of the point ion potential indicate that structure develops in the wave functions in the region of attractive potential between the second and sixth nearest neighbors.[14,33]

The use of free-ion wave functions for the ion core functions is reasonable as a first approximation. However, functions on different ion sites are not orthogonal, and the wave functions are not consistent with the crystal field. The former shortcoming could be remedied by some scheme such as Löwdin's symmetric orthogonalization.[24] The second is more difficult to correct for,[34] but the effects of the correction may be visualized easily. The negative ions are in a crystal-field potential well similar to that for the F center. This well tends to bind the electrons more tightly with a resulting contraction of the ionic wave functions. Conversely, a positive ion is a potential hill for electrons and so an expansion of its wave functions is to be expected.

In the one-electron picture the potential, V_I, to be used in evaluating the spin-orbit interaction, Eq. (3), includes the self-consistent screened potential due to the nuclear charge and the electron cloud plus exchange corrections. Almost all the spin-orbit interaction arises from interactions within a few tenths of a Bohr unit of the nucleus and within this region all effective potentials are roughly the same since electronic exchange corrections are negligible compared to the strong nuclear field. In the numerical calculations of the present work, V_I was approximated by the Hartree-Fock self-consistent field.

In addition to the effects calculated in the body of this paper which arise from the diagonal matrix elements of the spin-orbit interaction, off-diagonal matrix elements which mix higher excited states into the first excited state may contribute to the spin-orbit interactions.[35] In general, the matrix elements are of the form $\langle\psi^1|\mathcal{H}+h_{so}|\psi^m\rangle$ where ψ^1 is the first excited state with energy ϵ_1 and ψ^m is a higher excited state of energy ϵ_m. Here $\mathcal{H}$ is the crystal Hamiltonian excluding the spin-orbit interaction h_{so}.

In second-order perturbation theory the correction to the diagonal energies due to off-diagonal terms is

$$E^{(2)}=\sum_m{}'|\langle\psi^1|\mathcal{H}+h_{so}|\psi^m\rangle|^2/(\epsilon_1-\epsilon_m). \quad \text{(A1)}$$

If ψ^1 and ψ^m are exact solutions to the crystal Hamiltonian, the matrix elements of $\mathcal{H}$ are zero and $E^{(2)}$ is quadratic in h_{so}. If, on the other hand, inexact solutions, φ^1 and φ^m of energy E_1 and E_m are used rather than the exact solutions ψ^i, there is a correction to the energy E_1 from $\mathcal{H}$ which is given by

$$E^{(2)}(\mathcal{H})=\sum_m{}'|\langle\varphi^1|\mathcal{H}|\varphi^m\rangle|^2/(E_1-E_m)\approx\epsilon_1-E_1. \quad \text{(A2)}$$

In addition there are cross terms between $\mathcal{H}$ and h_{so} given by

$$E^{(2)}(h_{so})=2\sum_m{}'\langle\varphi^1|\mathcal{H}|\varphi^m\rangle\langle\varphi^m|h_{so}|\varphi^1\rangle/(E_1-E_m). \quad \text{(A3)}$$

The latter term is linear in the spin-orbit interaction and is a correction to the diagonal part of the interaction.

To estimate this term we shall assume a dielectric continuum model for the higher excited states of the F center and assume that there is a connection only to one excited state φ^m. We expect that the major errors in φ^1 are in the tail of the wave function and around the

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[35] The author is particularly indebted to Professor C. P. Slichter for a discussion of this point.

TABLE IV. Overlap integrals for F-center $2p$ states at neighboring sites. Columns labeled I and II correspond to Gourary and Adrian type I and type II functions, respectively. [In calculating these overlaps the center of coordinates has been taken at the ion.]

	1st neighbor Na^+		2nd neighbor Cl^-		3rd neighbor Na^+		4th neighbor Cl^-	
	I	II	I	II	I	II	I	II
$1s$	−0.0161	−0.0186	−0.00429	−0.00328	−0.00479	−0.00266	−0.00149	−0.000636
$2s$	0.158	0.179	0.0341	0.0264	0.0498	0.0289	0.0120	0.00516
$2p\sigma$	−0.0375	−0.0598	−0.00449	−0.00555	−0.0175	−0.0160	−0.00178	−0.00117
$2p\pi$	0.0309	0.0345	0.00190	0.00147	0.00574	0.00339	0.000471	0.000203
$3s$	···	···	−0.218	−0.183	···	···	−0.0849	−0.0431
$3p\sigma$	···	···	0.159	0.202	···	···	0.0945	0.0793
$3p\pi$	···	···	−0.0967	−0.0817	···	···	−0.0307	−0.0178

neighboring ions. Both of these factors imply that the state φ^m must be a highly excited state which extends well into the crystal.

If we assume that only one higher excited state is important, we may drop the summation and combine Eqs. (A2) and (A3) to get

$$|E^{(2)}(h_{so})| = 2[(\epsilon_1 - E_1)/(E_1 - E_m)]^{1/2}\langle\varphi^m|h_{so}|\varphi^1\rangle. \tag{A4a}$$

Since φ^m extends far out into the crystal its slope will probably be considerably more gentle than that of φ^1 and the off-diagonal spin-orbit matrix element will be smaller than the diagonal matrix element. Assuming that $\langle\varphi^m|h_{so}|\varphi^1\rangle \approx 0.5|\langle\varphi^1|h_{so}|\varphi^1\rangle|$, which is probably an overestimate, we have,

$$|E^{(2)}(h_{so})/\langle\varphi^1|h_{so}|\varphi^1\rangle| = [(\epsilon_1 - E_1)/(E_1 - E_m)]^{1/2}. \tag{A4b}$$

We shall assume $\epsilon_1 - E_1$ is of the order of the difference between the observed F band energy and that predicted by Gourary and Adrian which is of the order of 0.2 eV when corrected for lattice distortions.[14] In our model, φ^m represents a highly excited state. We will therefore take $E_1 - E_m$ as the energy necessary to ionize the F center from the first excited state which for the high-frequency dielectric constant of 2.25 for NaCl is approximately 0.7 eV. This yields a value of $|E^{(2)}(h_{so})/\langle\varphi^1|h_{so}|\varphi^1\rangle| \approx 0.5$.

This method of estimating errors is in general an overestimate since it ascribes all the correction to a single state making a single contribution to Eq. (A3). In the real problem many states enter. Some would have positive spin-orbit matrix elements while others would have negative ones and considerable cancellation should occur in Eq. (A3). On the other hand, the estimate is rather general in that it does not depend on a particular form of wave function or on the assumption of a crystal or pseudopotential. The important assumption is that $\langle\varphi^m|h_{so}|\varphi^1\rangle$ is generally of the order of $\langle\varphi^1|h_{so}|\varphi^1\rangle$.

In the present calculation, this assumption seems justified since φ^1 is orthogonal to the occupied crystal states and the excited states admixed as corrections are presumably reasonably smooth and diffuse. On the other hand, the assumption would not be valid if φ^1 were not orthogonal to the lattice ion states. Then the correction functions, φ^m, would be localized largely about the ions and would have a large gradient where h_{so} is important. These considerations are relevant to a comparison between Suffczynski's effective mass calculations[17] and the present treatment.

In any event this treatment suggests that at the very worst, the diagonal elements give the correct sign and order of magnitude for the spin-orbit interaction. The form of Eq. (A4a) also points out the general rule that in order to calculate an observable to a given accuracy from a wave function, the wave function must predict the energy to far greater accuracy. It is also interesting to note that the difference in predicted spin-orbit interaction for type I and type II wave functions is of the order of 20%. Presumably the "correct" excited state lies close to these approximations, particularly to the type II function (provided orthogonalization is included). One would therefore expect that the difference in the spin-orbit interaction for type I and type II solutions would be of the same order and probably greater than that for the correct wave function and the type II solution. Our estimate of error is not in disagreement with this conjecture.

For reference the calculated overlap integrals for Gourary and Adrian's type I and type II NaCl F-center wave functions with Na^+ and Cl^- free ion states are included in Table IV.[16] These were calculated using alpha functions[24] and Simpson's rule numerical integration with functions specified at intervals of $0.05a_0$.