$$+\epsilon_{fz}\epsilon_{fx}\epsilon_{iz}\epsilon_{ix}] , \qquad (9)$$

where x, y, z refer to components along cube axes. Numerical techniques for computing $S_{11}(\omega)$ and $S_{44}(\omega)$ were very similar to those described above for the hcp lattice.

Results for $S_{11}(\omega)$ and $S_{44}(\omega)$ as a function of ω, together with the one-phonon density of states $g(\frac{1}{2}\omega)$, are plotted in Fig. 2. The bcc lattice structure is simple enough that there are relatively few critical points, and these show up quite prominently in the two-phonon scattering. To identify the critical points, we have searched, via phonon-frequency isopleths, the three symmetry planes of the first Brillouin zone together with the zone face. All critical points found on these planes are labeled in Fig. 2, and it can be seen that these include most of the prominent ones. It also appears that there are additional critical points in the bcc spectrum which do not lie on any bounding plane of the irreducible $\frac{1}{48}$ of the Brillouin zone, and hence are not required by symmetry. We are not aware of any study specifying the minimum number, let alone their location, of critical points in the bcc structure.

[1]N. R. Werthamer, R. L. Gray, and T. R. Koehler, Phys. Rev. B 2, 4199 (1970).
[2]N. R. Werthamer, Phys. Rev. 185, 348 (1969).
[3]N. S. Gillis, T. R. Koehler, and N. R. Werthamer, Phys. Rev. 175, 1110 (1968).
[4]T. R. Koehler, Phys. Rev. Letters 18, 654 (1967).
[5]R. A. Reese, S. K. Sinha, T. O. Brun, and C. R. Tilford, Phys. Rev. A 3, 1688 (1971).
[6]G. L. Morley and K. L. Kliewer, Phys. Rev. 180, 245 (1969).
[7]L. J. Raubenheimer and G. Gilat, Phys. Rev. 157, 586 (1967).
[8]C. B. Walker, Phys. Rev. 103, 547 (1956).

PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

Two-Electron F^- Centers in the Alkaline-Earth Fluorides

Herbert S. Bennett
National Bureau of Standards, Washington, D. C. 20234
(Received 9 April 1971)

The Hartree-Fock-Slater (HFS) equations for the two-electron orbitals localized about an anion vacancy in CaF_2, SrF_2, and BaF_2 have been solved numerically in the point-ion-lattice potential. It is found that the ground state $^1S(1s, 1s)$ contains bound electronic orbitals which are spatially compact. The existence of bound excited states for the F^- center in these crystals has been investigated. However, definitive statements on such excited states are not available at present.

I. INTRODUCTION

The F^- center in the alkaline-earth fluorides consists of two electrons, the defect electrons, localized about a vacant anion site.[1] Conclusive experimental evidence for the existence of the F^- center in CaF_2, SrF_2, and BaF_2 has not been reported in the literature.[2,3] This center has been proposed as one of several tentative models which might explain some of the many bands on the long-wavelength side of the M band in additively colored alkaline-earth fluorides. The M center consists of two F centers bound together at nearest-neighbor anion sites, and the F center consists of one electron localized about a vacant anion site. These give rise to the absorption bands which are formed during bleaching with F-band light. There are four bands situated in region from 600 nm (0.0760 a.u.) to 725 nm (0.0629 a.u.) for calcium fluoride and from 683 nm (0.0668 a.u.) to 805 nm (0.0566 a.u.) for strontium fluoride.[2,4] Only two bands have been observed on the long-wavelength side of the M band in barium fluoride. The bands which would correspond to the 805 and 775 nm bands in strontium fluoride have not been observed in barium fluoride because their intensities are too small.

F-band bleaching excites optically the F center, the M center, and other aggregate centers. Impurity centers such as rare earths are not considered in this paper. In the case of the alkali halide crystals, an excited defect electron of a color center may be assisted by thermal phonons into the conduction band. Once in the conduction band, it moves through the crystal until it is trapped again. The electron traps include ionized F^+ and M^+ centers and other ionized aggregate centers, and also the neutral F and M centers and other neutral aggregate centers. When an extra electron is trapped at a neutral center, a new center is formed. These centers are denoted, for example, by F^- and M^-,

respectively. Experiments on potassium chloride indicate that an absorption band due to the F^- center has a peak at a longer wavelength, 1000 nm (0.046 a.u.), than the neutral F center, 536 nm (0.085 a.u.). The F^- center in KCl is stable only at sufficiently low temperatures below 200 K.[5] If one assumes that the above process also may occur in the alkaline-earth fluorides, then the absorption band due to the F^- center is expected to be at a longer wavelength than the absorption band due to the F center.

Studies on the intrinsic optical properties of simple color centers in the alkaline-earth fluorides are hindered by the presence of impurities and the high probability with which F centers form aggregate centers and impurity associated centers. In fact, positive experimental identifications of the F- and M-center in calcium fluoride have been made only in the last decade.[6,7]

In this paper, calculations on some states of the F^- center in CaF_2, SrF_2, and BaF_2 are reported. A point-ion-lattice model which incorporates the Hartree-Fock-Slater (HFS) procedure to compute the defect electron orbitals is used. In addition, the model contains estimates for the correlation energy of the defect electrons.[8] These approximations constitute the model and make it solvable on a computer. The formalism which leads to an estimate for the correlation energy is analogous to the formalism by which Slater estimates the exchange energy for the free-electron gas.[8,9] To the author's knowledge, no calculations on the electronic states of the F^- center in CaF_2, SrF_2, and BaF_2 have appeared previously in the literature. It is hoped that such calculations on the F^- center will aid researchers in understanding the optical properties of color centers in the alkaline-earth fluorides. Because no ionic and electronic polarizations of the lattice are included in the model, the present calculations are not physically precise and any future agreement with experiment should be considered as being fortuitous. However, the methods and procedures used here have had some success for the F^- center in KCl and for the F center in CaO.[10] Therefore, the calculations reported here indicate what one might expect in optical experiments on the fluorides of calcium, strontium, and barium. Such calculations also would be informative if the F-center to F^--center photochromic process were found to exist.

The HFS equations for the F^- center given by the model outlined in the preceding paragraph are solved numerically. These numerically computed solutions give the exact properties of the model. The model has for the ground state ^1S $(1s, 1s)$ bound electronic orbitals which are spatially compact. An orbital is referred to as compact whenever its spatial extent is less than or of the order of magnitude of the nearest-neighbor distance. The same model is used to compute the ground-state energies of the F center (one electron) in CaF_2, SrF_2, and BaF_2. The theoretical binding energies of the F^- centers in the above three fluorides have been estimated. The existence of bound excited states for these F^- centers remains uncertain. The attempts to solve for the singlet excited state ^1P $(1s, 2p)$ of the model suggest that the $1s$-like orbital is spatially compact but that the $2p$-like orbital is either spatially very diffuse (but bound) or bandlike (not bound). The uncertainty of the spatial extent of the second electron orbital arises from two related and practical considerations. The numerical integration procedure converges more slowly the more diffuse the orbital becomes (or, equivalently, the smaller the magnitude of its energy eigenvalue becomes).

II. POINT-ION MODEL

We shall examine here the orbitals and energies of the two defect F^- electrons localized about an anion vacancy in an otherwise perfect point-ion fluorite lattice. This corresponds to the case for which the electronic and ionic polarizations are zero. We shall study the possible optical transitions which the defect electrons may undergo. We denote the state of the F^- center by $|\eta\rangle$, where the symbol η represents the electronic configuration of the two defect electrons. We shall consider here the ground state ^1S $(1s, 1s)$ and shall determine whether any low-lying excited states such as ^1P $(1s, 2p)$ exist with both $1s$-like and $2p$-like orbitals bound.

Before presenting an expression for the total F^--center energy, we introduce some notations and definitions. The F^--center electronic wave function $\Psi_\eta(x, y)$ has the representation

$$\Psi_\eta(x, y) = \langle x, y | \eta \rangle \ . \tag{1}$$

The spatial charge density due to the two defect electrons in the configuration η is

$$\rho_{F^-}(\vec{r}; \eta) = -2e \int d^3y \, \Psi_\eta^*(r, y)\Psi_\eta(r, y) \ , \tag{2}$$

where d^3y is the volume element in the coordinate, and spin space y and the integration is over only the spatial coordinates. We also specify in Eq. (2) that the wave function is normalized to unity.

We create a vacancy at the fluorine anion site $\vec{r}_0 = \vec{0}$ of charge $Z_0 = -1$ by adding an effective vacancy charge $Z_v - Z_0 = 1$ at $\vec{r}_0$. We treat the effective vacancy charge as a point charge and write the charge density $\rho_v(\vec{r})$ due to the vacancy in terms of a three-dimensional δ function $\delta^3(\vec{r})$:

$$\rho_v(\vec{r}) = Z_v \, \delta^3(\vec{r}) \ . \tag{3}$$

We define for future use $Z_F = -e$, where the magni-

tude of the electronic charge is e. The total F^--center charge density becomes the sum of the above charge densities,

$$\rho_d(\vec{r}) = \rho_{F^-}(\vec{r};\eta) + \rho_v(\vec{r}) \ . \tag{4}$$

We now list the terms of the point-ion-model Hamiltonian. The kinetic-energy operators for the two defect electrons contribute a term

$$\mathcal{H}_1(\vec{x},\vec{y}) = -(\hbar^2/2m)(\nabla_{\vec{x}}^2 + \nabla_{\vec{y}}^2) \ , \tag{5}$$

where $\nabla_{\vec{x}}^2$ operates on the coordinates of one defect electron and $\nabla_{\vec{y}}^2$ operates on the coordinates of the other defect electron. The mass of electron is m.

We consider the ions as point charges Z_ν, and we write the defect-electron–point-ion interaction operator in the form

$$\mathcal{H}_2(\vec{r}) = Z_F \sum_\nu{}' (Z_\nu/|\vec{r} - \vec{r}_\nu|) \ , \tag{6}$$

where the prime means that the $\nu = 0$ site is not included in the summation; $\vec{r}$ is the position vector for one of the defect electrons, and $\vec{r}_\nu$ is the location of the νth ion. The interaction operator (6) gives the electrostatic potential energy of a defect electron moving in a perfect point-ion lattice which has an ion missing at the $\nu = 0$ site. We define the dimensionless quantity $\alpha_M(F^-)$, which is proportional to the electrostatic potential at an anion site in the perfect point-ion lattice, by the relation

$$\alpha_M(F^-) = \bar{r}_1 [\mathcal{H}_2(\vec{0})/Z_F] \ , \tag{7}$$

where $\bar{r}_1$ is the lattice constant for the CaF_2 structure. The potential energy is invariant under the tetrahedral group, and we may expand it in terms of the Kubic harmonics[11] $Q(\Gamma_i, l, 0)$, e.g.,

$$\begin{aligned}\mathcal{H}_2(\vec{r}) = {} & V_{00}(r)Q(\Gamma_1^e, 0, 0; \theta, \varphi) + V_{30}(r)Q(\Gamma_1^e, 3, 0; \theta, \varphi) \\ & + V_{40}(r)Q(\Gamma_1^e, 4, 0; \theta, \varphi) + \cdots \\ & + V_{n0}(r)Q(\Gamma_1^e, n, 0; \theta, \varphi) + \cdots \ ,\end{aligned} \tag{8}$$

where n is an integer. Because we shall limit the wave functions to functions which belong to the irreducible representations Γ_1^e("1s") and Γ_4^0("2p") and because the following matrix elements vanish,

$$\begin{aligned}&\langle \Gamma_1^e | \, Q(\Gamma_1^e, n, 0; \theta, \varphi) \, | \Gamma_1^e \rangle = 0 \ , \\ &\langle \Gamma_4^0 | \, Q(\Gamma_1^e, n, 0; \theta, \varphi) \, | \Gamma_4^0 \rangle = 0 \ ,\end{aligned} \tag{9}$$

for all $n \geq 3$, we have that

$$\langle \eta | \, \mathcal{H}_2(\vec{r}) \, | \eta \rangle = \langle \eta | \, V_{\text{sph}}(r) \, | \eta \rangle \ ,$$

where the spherically symmetric part of the point-ion-crystal potential is denoted by $V_{\text{sph}}(r) \equiv V_{00}(r)$.

In order to compute V_{sph}, we consider the point ions as distributed on shells centered at the anion vacancy. We denote the radius of shell s by r_s, the number of ions on shell s by S_s, and the charge of the νth ion on shell s by $Q_s = Z_\nu$. We then express the spherically symmetric part of the crystal potential V_{sph} in terms of the above notation, namely,

$$V_{\text{sph}}(r) = \begin{cases} V_0 & \text{for } 0 < r < r_1 \\ V_n + (D_n/r) & \text{for } r_n < r < r_{n+1} \end{cases} \ , \tag{10}$$

where

$$V_0 = Z_v Z_F [\alpha_M(F^-)/\bar{r}_1] \ ,$$

$$V_n = V_0 - Z_v Z_F \sum_{i=1}^{n} (S_i Q_i / r_i) \qquad \text{for } n \geq 1 \ ,$$

and

$$D_n = Z_v Z_F \sum_{i=1}^{n} S_i Q_i \ .$$

The electron–point-ion interaction operator contributes the term

$$\mathcal{H}_2(\vec{r}) = V_{\text{sph}}(r) \ . \tag{11}$$

Because practical considerations limit the number of shells which we may explicitly treat, we will consider the first 21 shells in our computations and use the Coulomb potential for distances beyond the 21st shell:

$$V_{\text{sph}}(r) = (Z_v Z_F/r) \quad \text{for } r > r_{21} \ . \tag{12}$$

The Coulomb interaction between the two defect electrons contributes the term

$$\mathcal{H}_C(\vec{x},\vec{y}) = (Z_F^2/|\vec{x} - \vec{y}|) \ . \tag{13}$$

Combining the terms (5), (11), and (13), we write the total F^--center Hamiltonian for the point-ion model as the sum of one-body and two-body operators:

$$\begin{aligned}\mathcal{H}_T(\vec{x},\vec{y}) &= -(\hbar^2/2m)(\nabla_{\vec{x}}^2 + \nabla_{\vec{y}}^2) + V_{\text{sph}}(\vec{x}) \\ &\quad + V_{\text{sph}}(\vec{y}) + (Z_F^2/|\vec{x} - \vec{y}|) \\ &= \mathcal{H}_0(\vec{x}) + \mathcal{H}_0(\vec{y}) + \mathcal{H}_C(\vec{x},\vec{y}) \ ,\end{aligned} \tag{14}$$

where

$$\mathcal{H}_0(\vec{x}) = -(\hbar^2/2m)\nabla_{\vec{x}}^2 + V_{\text{sph}}(\vec{x}) \ .$$

Because all the terms of the model Hamiltonian are real, we may choose the electronic wave functions $\Psi_\eta(x, y)$ to be real. They are also normalized to the crystal volume:

$$\int dx \int dy \, \Psi_\eta^*(x,y)\Psi_\eta(x,y) = 1 \ , \tag{15}$$

where the integrations over dx and dy are interpreted to include integration over the entire crystal volume and summation over the spin coordinates.

III. HFS EQUATIONS

We define now for computational convenience the quantities with which we shall compute the total energy of the F^- center. When the author listed the F^--center states, he has assumed implicitly that the central-field approximation is reasonable for the low-lying states with angular momentum quantum number $l \leq 2$ in a tetrahedral potential. The most general central-field representation for the one-electron wave functions u is

$$u_{nlms}(x) = R_{nlms}(r) Y_{lm}(\theta, \varphi) \alpha_s ,$$

where $R(r)$ is the radial function, Y_{lm} is a spherical harmonic function, and α_s is the spin function. The principal, orbital, magnetic, and spin quantum numbers are, respectively, n, l, m, and s. We shall use, however, the more restrictive representation

$$u_{nlms}(x) = R_{nl}(r) Y_{lm}(\theta, \varphi) \alpha_s .$$

We define the radial functions $P_{nl}(r) = rR_{nl}(r)$, and normalize them to the crystal volume, $\int P_{nl}^2(r) dr = 1$.

We express the spherically averaged total electronic charge density for both spins in terms of the radial functions

$$\rho_{av}(r) = -e[\sigma(r)/4\pi r^2] ,$$

where the spherical density $\sigma(r)$ is

$$\sigma(r) = \sum_{nl} \omega_{nl} P_{nl}^2(r) ,$$

and the occupation number of the spatial orbital for both spins in ω_{nl}. The summation $\sum_{nl} \omega_{nl}$ equals 2 for the F^- center.

It is now convenient to introduce the abbreviations which will appear in the HFS equations for the one-electron wave functions u_1 and u_2. The electronic wave function for the F^- center will be constructed from these two functions:

$$I_{12} = I_{21} = \int dx\, u_1(x) u_2(x) , \tag{16}$$

$$H_{ij} = H_{ji} = \int dx\, u_i(x) \mathcal{H}_0(\vec{x}) u_j(x) , \tag{17}$$

and

$$\mathcal{G}_{ij}(\vec{r}) = \int dx\, u_i(x) \mathcal{H}_C(\vec{x}, \vec{r}) u_j(x) . \tag{18}$$

The Schrödinger equations for the F^--center wave functions are obtained by performing the variation of the expectation value of the total Hamiltonian,

$$\langle \mathcal{H}_T \rangle = \frac{\int dx \int dy\, \Psi_\eta^*(x, y) \mathcal{H}_T(\vec{x}, \vec{y}) \Psi_\eta(x, y)}{\int dx \int dy\, \Psi_\eta^*(x, y) \Psi_\eta(x, y)} , \tag{19}$$

with respect to the wave functions $\Psi_\eta(x, y)$ subject to the normalization constraint. The variation gives the equation

$$\int dx \int dy\, \delta\Psi_\eta^*(x, y) [\mathcal{H}_T(\vec{x}, \vec{y}) - E] \Psi_\eta(x, y) = 0 . \tag{20}$$

Equation (20) is to be valid for any arbitrary variation of the function $\Psi_\eta^*(x, y)$. Hence, we obtain the Schrödinger equation

$$\mathcal{H}_T(\vec{x}, \vec{y}) \Psi_\eta(x, y) = E \Psi_\eta(x, y) \tag{21}$$

for each of the orbitals with symmetry η.

Because the Schrödinger equation (21) cannot be solved exactly even by numerical methods, we shall use the self-consistent-field method [Hartree-Fock (HF)] to calculate the wave functions of the stationary states of the F^- center. Each of the two defect electrons moves in the average field of the other defect electron. Even though the model Hamiltonian (14) is spin independent, we shall include the symmetry effects of the spins of the two defect electrons in accordance with the Pauli exclusion principle. That is, we approximate the wave function $\Psi_\eta(x, y)$ by the HF wave function:

$$\Psi_\eta(x, y) \approx \Psi_\eta(x, y; \mathrm{HF}) = 2^{-1/2} [u_1(x) u_2(y) - u_1(y) u_2(x)] . \tag{22}$$

The functions u_1 and u_2 are normalized to the crystal volume and the spin space

$$\int dx\, u^*(x) u(x) = 1 .$$

We obtain a set of coupled intergrodifferential equations for the functions u_1 and u_2 by substituting Eq. (22) into Eq. (21), by carrying out the variation with respect to u_1 and u_2 separately, and by equating to zero the coefficients of δu_1 and δu_2 which appear in the integrand. Using Eqs. (16) to (18), we have two coupled equations for u_1 and u_2 [12]:

$$[\mathcal{H}_0(\vec{r}) - E + H_{22} + \mathcal{G}_{22}(\vec{r})] u_1(r) = \{I_{12} [\mathcal{H}_0(\vec{r}) - E] + H_{12} + \mathcal{G}_{12}(\vec{r})\} u_2(r) , \tag{23}$$

$$[\mathcal{H}_0(\vec{r}) - E + H_{11} + \mathcal{G}_{11}(\vec{r})] u_2(r) = \{I_{12} [\mathcal{H}_0(\vec{r}) - E] + H_{12} + \mathcal{G}_{12}(\vec{r})\} u_1(r) . \tag{24}$$

Since the bracketed operators in Eqs. (23) and (24) are different functions of r, their solutions $u_1(x)$ and $u_2(x)$ are not, in general, orthogonal to one another. However, the structure of the self-consistent field equations (23) and (24), which arises from the antisymmetric properties of the wave function $\Psi_\eta(x, y; \mathrm{HF})$, permits us to regard the spin orbitals u_1 and u_2 as orthogonal functions [12]:

$$\int dx\, u_i^*(x) u_j(x) = \delta_{ij} . \tag{25}$$

The HF variational equations (23) and (24) may be solved in principle by numerical iterative techniques. Such a procedure requires an excessive amount of computer time. To reduce the computa-

tion time, we introduce Slater's simplified version of these HF equations.[9] His simplification is based upon a free-electron exchange approximation for the exchange terms which occur in Eqs. (23) and (24) when the two defect electrons are in a triplet configuration ($S=1$). Following Slater's suggestion, we assume that the averaged exchange potential for the F^- center at the point r is equal to the exchange potential which a free-electron gas would have if its total electron charge density for both spins were equal to that of the nonuniform system (the two F^--center defect electrons), namely,

$$V_{\text{exch}}(\vec{r}) = -3e^2[(3/8\pi)e^{-1}|\rho(\vec{r})|]^{1/3} . \quad (26)$$

Equation (26) means that the averaged exchange potential for the two F^--center electrons depends only on the local electronic charge density $\rho(\vec{r}) = \rho_{F^-}(r, \eta)$. Thus the problem of calculating the exchange integrals g_{ij} when $i \neq j$ for the triplet states is circumvented.

Keeping the above assumptions in mind, we write the HFS variational equations for the F^- center when the electrons are in a triplet state:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + V_{\text{shp}}(r) + V_C(r) + V_e(r)\right)P_{nl}(r) = E_{nl}P_{nl}(r) , \quad (27)$$

where the Coulomb potential $V_C(r)$ has the form

$$V_C(r) = (e^2/r)\int_0^r \sigma(t)\,dt + e^2\int_r^\infty [\sigma(t)/t]\,dt ,$$

and the exchange potential $V_e(r)$ has the form

$$V_e(r) = -3e^2[(3/8\pi)e^{-1}|\rho_{\text{av}}(r)|]^{1/3} .$$

Let us define $V_s(r) = V_C(r) + V_e(r)$ for future use. The HF variational equations for the central-field approximation of the F^- center in a singlet state become

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + V_{\text{sph}}(r) + V_C(r)\right)P_{nl}(r) = E_{nl}P_{nl}(r) . \quad (28)$$

The Slater free-electron exchange approximation stresses the similarities between the exchange hole for a free-electron gas and for an atomiclike system such as the F^- center. We now mention some difficulties. The above exchange hole in the atomiclike F^- center is not, in general, spherically symmetric and does not attain its maximum value at the position of the electron as the exchange hole for the free-electron gas does. As the electrons move away from the vacancy, the exchange hole lags behind. This lag is slight for spatially compact states, but it becomes important for spatially diffuse states. Hence, Eq. (26) becomes suspect at large values of r.

The self-Coulomb-energy part of the total electronic Coulomb energy cancels exactly in the conventional HF method a corresponding energy in the total exchange energy. This cancellation does not occur in the HFS equation at large r. Following Latter,[13] we alter the sum $V_s(r)$ so that it has the correct asymptotic behavior at large r. We define

$$V(r) = V_C(r) + V_e(r) \quad \text{for} \quad r < r_0$$

and

$$V(r) = e^2\left(\sum_{nl}\omega_{nl} - 1\right)\Big/r \quad \text{for} \quad r \geq r_0.$$

The radius r_0 is that value for r at which

$$V_s(r_0) = e^2\left(\sum_{nl}\omega_{nl} - 1\right)\Big/r_0 .$$

Thus, we use approximation (26) for the region $r < r_0$ in which the exchange hole follows the motion of the electron fairly well, and we use the correct asymptotic form $e^2(\sum_{nl}\omega_{nl} - 1)/r$ for the region $r \geq r_0$.

IV. CORRELATION ENERGY AND TOTAL F^--CENTER ENERGY

The HF method does not include the spatial correlation in the motion of the two defect electrons produced by their instantaneous Coulomb repulsion $\mathcal{H}_C(\vec{x}, \vec{y})$. But even though the Coulomb correlation is neglected, the HF method does introduce a statistical (exchange) correlation in the motion of electron pairs with the same spin through the antisymmetric (determinantal) wave function. Since Coulomb correlation is most important when the electrons are close together and since the statistical correlation tends to keep electrons with the same spin far apart, neglect of the Coulomb correlation in the HF equations for the triplet states of the F^- center is tolerable. But, the HF equations for the singlet states of the F^- center contain no exchange terms and, hence, no statistical correlations.

Since the Coulomb correlation is much more important for the singlet states of the F^- center than it is for the triplet states, we shall follow the procedure of Milter[8] which estimates the Coulomb correlation energy for atomiclike systems. The approximate HF wave function (22) is the source of the Coulomb correlation problem. It arises from that fact that $\Psi_\eta(x, y; \text{HF})$ does not depend upon the norm $|\vec{x} - \vec{y}|$ and that $\Psi_\eta(x, y; \text{HF})$ contains products of one-electron wave functions. We define the correlation energy by

$$E_C = \langle \Psi_\eta(x, y)|\,\mathcal{H}_T\,|\Psi_\eta(x, y)\rangle$$

$$-\langle \Psi_\eta(x,y;\mathrm{HF})|\,\mathcal{H}_T\,|\Psi_\eta(x,y;\mathrm{HF})\rangle\ . \qquad (29)$$

Let us assume also that a correlation operator $\mathcal{E}_C(|\vec{x}-\vec{y}|)$ exists such that its expectation value in the approximate representation $\Psi_\eta(x,y;\mathrm{HF})$ is the correlation energy

$$E_C=\langle \Psi_\eta(x,y;\mathrm{HF})|\,\mathcal{E}_c(|\vec{x}-\vec{y}|)\,|\Psi_\eta(x,y;\mathrm{HF})\rangle\ . \qquad (30)$$

We may introduce, then, the correlation potential $W_c(\vec{r})$ by the following operation:

$$W_c(\vec{r})=\int d^3x\,\Psi_\eta(x,y;\mathrm{HF})\,\mathcal{E}_c(|\vec{x}-\vec{r}|)\Psi_\eta(x,r;\mathrm{HF})\ . \qquad (31)$$

Mitler[8] and Wigner[14] introduce in the HF equations an additional central "correlation" potential $W(r)$ to which pairs of electrons with opposite spin are subject. The approximate correlation potential $W(r)$ has the form[14]

$$W(r)=-e^2\,0.288/[5.1a_0+r_s(r)]\ , \qquad (32)$$

where a_0 is the Bohr radius and the local density of electrons is

$$e^{-1}|\rho(r)|=[(4\pi/3)r_s^3(r)]^{-1}\ .$$

We expect that expression (32) is a good estimate for the correlation potential $W_c(\vec{r})$; that is, $W(r)\approx W_c(\vec{r})$. Our prescription is, then, to replace $V_C(r)$ in the singlet HF variational equations (28) with $V_C(r)+W(r)$. Because the inequality,

$$0\le W(r_s)/V_{\mathrm{exch}}(r_s)\le 0.314r_s/(5.1a_0+r_s)\le 0.314r_s\ ,$$

is obtained, we do not include the Coulomb correlation potential in the triplet HF variational equations (27).

Hence, the HFS equations (which include the exchange energy and correlation energy and from which we numerically compute the radial wave functions) become

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_{\mathrm{sph}}(r)+V(r)\right)P_{nl}(r)=E_{nl}P_{nl}(r) \qquad (33)$$

for the triplet F^--center states and

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_{\mathrm{sph}}(r)+V_C(r)+W(r)\right)P_{nl}(r)=E_{nl}P_{nl}(r) \qquad (34)$$

for the singlet F^--center states.

The author does not compute here the total energy of the F^- center by summing the eigenvalues of the HF variational equations and subtracting one-half times the expectation values of those two-body operators which are estimated in the self-consistent-field method by effective one-body potentials. The numerical results from Ref. 15, Chap. I suggest that the HF wave functions are less sensitive to modifications in effective potentials than are the eigenvalues. For this reason, the author expects that the more accurate way to compute the total energy of the F^- center is to compute the total energy directly from the original Hamiltonian (14) by using the HF wave functions which obtain from Eqs. (33) and (34). The triplet state has a total energy given by

$$E_T[\eta(nl\uparrow;n'l'\uparrow)]=\int d^3x\,u_{nl}(x)\mathcal{H}_0(\vec{x})u_{nl}(x)+\int d^3y\,u_{n'l'}(y)\mathcal{H}_0(\vec{y})u_{n'l'}(y)+\int d^3x\int d^3y\,u_{nl}(x)u_{n'l'}(y)\mathcal{H}_C(\vec{x},\vec{y})u_{nl}(x)u_{n'l'}(y)-\int d^3x\int d^3y\,u_{nl}(x)u_{n'l'}(y)\mathcal{H}_C(\vec{x},\vec{y})u_{nl}(y)u_{n'l'}(x)\ . \qquad (35)$$

Similarly, the singlet state has a total energy given by

$$E_T[\eta(nl\uparrow;n'l'\downarrow)=\int d^3x\,u_{nl}(x)\mathcal{H}_0(\vec{x})u_{nl}(x)+\int d^3y\,u_{n'l'}(y)\mathcal{H}_0(\vec{y})u_{n'l'}(y)+\int d^3x\int d^3y\,u_{nl}(x)u_{n'l'}(y)\mathcal{H}_C(\vec{x},\vec{y})u_{nl}(x)u_{n'l'}(y)+\tfrac{1}{2}\left[\int d^3x u_{nl}(x)W(\vec{x})u_{nl}(x)+\int d^3y\,u_{n'l'}(y)W(\vec{y})u_{n'l'}(y)\right]\ . \qquad (36)$$

The terms containing the correlation potential $W(r)$ must be included in order to obtain Eq. (34) by a variation of the functions u_{nl} and $u_{n'l'}$ which appear in the expectation value of the Hamiltonian $\mathcal{H}_T$.

V. SPATIAL PROPERTIES

The expectation value of a given power of the radial coordinate r gives us information on the

spatial extent of the two defect electron wave functions. As a measure of the spatial extent, we have chosen to consider the first and third powers of r for each of the orbitals, namely,

$$r_{nl}[s,\eta(nl;n'l')] = r_1^{-s}\int R_{nl}(r) r^s R_{nl}(r) 4\pi r^2\, dr\ , \tag{37}$$

$$r_{n'l'}[s,\eta(nl;n'l')] = r_1^{-s}\int R_{n'l'}(r) r^s R_{n'l'}(r) 4\pi r^2\, dr\ , \tag{38}$$

where $s=1$ or 3 and r_1 is the nearest-neighbor distance of the perfect lattice. The ratio

$$r_e(nl) = [r_{nl}(s=3)/r_1^2 r_{nl}(s=1)]\ ,$$

also indicates to what extent the radial functions have extended tails. Values of $r_e < 1$ indicate compact states and values of $r_e > 1$ indicate diffuse states. The author has chosen to present the wave-function data in this manner and not to present many numerical tables of the wave functions as functions of the radial coordinate.

VI. RESULTS AND CONCLUSIONS

This section contains the results predicted by the preceding point-ion model for the F^- center with estimates for the exchange energy and the Coulomb correlation energy included. Table I lists the values of the input data which have been used.

The author computed the low-lying state of the helium atom to check his F^--center computer programs. He obtains, when the Coulomb correlation energy is included, a ground-state energy of -2.881 a.u. and a $^1S(1s,1s)$ to $^1P(1s,2p)$ transition energy of 0.73 a.u. These numbers compare favorably with the respective experimental values of -2.904 and 0.78 a.u. The numerical procedures selected by the author give the energy eigenvalues to an accuracy of $|\Delta E|/E \approx 0.001$. They also give the self-consistent potential appearing in the HF equation to an accuracy of $|\Delta V|/V \approx 0.01$. The quantities ΔE and ΔV are, respectively, the changes in the trial eigenvalue and the self-consistent potential which occur between two successive iterations in the numerical integration procedure. Solving the F^--center problem to greater accuracy requires an excessive amount of computer time. The author does not feel that the rather simple model given in this paper warrants greater numerical accuracy in the solution of the HF equations.

The two-electron F^--center calculations for crystals with monovalent anions are not as straightforward as the two-electron F-center calculations for crystals with divalent anions. The present theoretical study indicates that the F^- center in the alkaline-earth fluorides is expected to have very few bound states. It also suggests that it may have only one bound state, the ground state. In fact, the above model gives no firm evidence that it has at least one bound excited state.

The numerical integration of the singlet HFS Eq. (34) for $1s$ orbitals of the ground state $^1S(1s,1s)$ converges very slowly. After 10 min of computation on a digital computer, the self-consistent-potential criterion $|\Delta V|/V \leq 0.01$ is not met. The numerical

TABLE I. Input data for the point-ion model of the F^- center with exchange energy and correlation energy. The quantity $\alpha_M(F^-)$ is proportional to the electrostatic potential at the anion site. The quantity $\bar{r}_1$ is the lattice constant for the calcium fluoride structures. The quantity $\alpha_M(F^-)$ is dimensionless and the lattice constant is expressed in terms of atomic units (1 a.u. of length = 0.0529 nm).

	CaF_2	SrF_2	BaF_2
$\alpha_M(F^-)$	4.071	4.071	4.071
$\bar{r}_1$	10.32[a]	10.95[a]	11.71[a]

[a]G. C. Benson and E. Dempsey, Proc. Roy. Soc. (London) A266, 344 (1962).

TABLE II. Ground-state energy $^1S(1s,\ 1s)$ of the two-electron F^- center CaF_2, SrF_2, and BaF_2. The ground-state energy $E_T(F^-)$ is computed by substituting the orbital $(n=1,\ l=0)$, which is obtained from Eq. (33), into Eq. (36). The spatial extent quantities $r_{1s}(1)$, $r_{1s}(3)$, and $r_e(1s)$ are defined in the text and are dimensionless. The binding energy E_B is given by Eq. (39). The energies are expressed in terms of atomic units (1 a.u. of energy = 27.2 eV).

	CaF_2	SrF_2	BaF_2
$E_T(F^-)$	-0.318	-0.307	-0.296
$r_{1s}(1)$	0.986	0.965	0.943
$r_{1s}(3)$	2.03	1.85	1.66
$r_e(1s)$	2.06	1.92	1.76
E_B	0.048	0.048	0.049

TABLE III. Ground state $^1S(1s,\ 1s)$ of the two-electron F^- center in CaF_2, SrF_2, and BaF_2. The ground-state energy $E_T(F^-)$ is computed by substituting the orbital $(n=1,\ l=0)$, which is obtained from Eq. (33) modified by the addition of the Coulomb correlation potential $W(r)$ to the potential $V(r)$, into Eq. (36). The spatial extent quantities $r_{1s}(1)$, $r_{1s}(3)$, and $r_e(1s)$ are defined in the text and are dimensionless. The binding energy E_B is given in Eq. (39). The energies are expressed in terms of atomic units (1 a.u. of energy = 27.2 eV).

	CaF_2	SrF_2	BaF_2
$E_T(F^-)$	-0.319	-0.309	-0.297
$r_{1s}(1)$	0.908	0.889	0.870
$r_{1s}(3)$	1.42	1.29	1.16
$r_e(1s)$	1.56	1.45	1.34
E_B	0.049	0.050	0.050

TABLE IV. Ground state and the lowest-lying excited state of the one-electron F center in CaF_2, SrF_2, and BaF_2. The ground-state energy $E_T(F, 1s)$ is computed by substituting the orbital ($n=1$, $l=0$), which is obtained from Eq. (34) with $W(r)=0$ and with $V_C(r)=0$, into Eq. (40). The lowest-lying-excited-state energy $E_T(F, 2p)$ is computed by substituting the orbital ($n=2$, $l=1$), which is obtained from Eq. (34) with $W(r)=0$ and with $V_C(r)=0$, into Eq. (40). The theoretical transition energy between the ground state and lowest-lying excited state is $E_T(1s\text{-}2p)$. The experimental value for the optical absorption energy of the F center at 4 K is E_e. The spatial extent quantities $r_{1s}(1)$, $r_{1s}(3)$, and $r_e(1s)$ are defined in the text and are dimensionless. The energies are expressed in terms of atomic units (1 a.u. = 27.2 eV).

	CaF_2	SrF_2	BaF_2
$E_T(F, 1s)$	−0.270	−0.259	−0.247
$r_{1s}(1)$	0.741	0.732	0.722
$r_{1s}(3)$	0.623	0.595	0.567
$r_e(1s)$	0.840	0.813	0.785
$E_T(F, 2p)$	−0.153	−0.153	−0.152
$r_{2p}(1)$	0.995	0.963	0.934
$r_{2p}(3)$	1.49	1.32	1.17
$r_e(2p)$	1.50	1.37	1.25
$E_T(1s-2p)$	0.116	0.106	0.096
E_e	0.121[a]	0.105[a]	0.075[a]

[a]B. C. Cavenett *et al.*, Solid State Commun. 5, 653 (1967).

integration of the triplet HFS Eq. (33) converges much faster than that for the singlet HFS Eq. (34). Also, the numerical integration of the triplet HFS Eq. (33) with the Coulomb correlation potential $W(r)$ added to the potential $V(r)$ converges in a reasonable time. We consider the $1s$ orbitals which are obtained from the triplet HFS Eq. (33) and from the triplet HFS Eq. (33) with $V(r)$ replaced with $V(r)+W(r)$ as good approximations to the $1s$ orbital which would be obtained from the singlet HFS Eq. (34) if computer time were not a limitation. Inserting these $1s$ orbitals into the Eq. (36) for the singlet state gives an estimate of the ground state $^1S(1s, 1s)$ energy of the F^- center.

Tables II and III contain the numerical estimates of the ground state for the point-ion lattice with no distortion. The author has not discussed in this paper the results when the nearest neighbors move to accommodate the two defect electrons. The inward motion of the neighboring ions becomes very large ($\approx 0.23(\sqrt{3}/4)\bar{r}_1$) and the classical ionic-lattice model from which the change in lattice energy is computed may be incorrect for such large distortions. The F^--center binding energy E_B is the difference in energy between the ground-state one-electron F-center energy $E_T[F, 1s]$ and the ground-state F^--center energy $E_T[F^-, {}^1S(1s, 1s)]$:

$$E_B = E_T[F, 1s] - E_T[F^-, {}^1S(1s, 1s)] . \quad (39)$$

The F-center energy for the ground state is given by the expression

$$E_T[F, 1s] = \int d^3r\, u_{1s}(r)\, \mathcal{H}_0(\vec{r})\, u_{1s}(r) ,$$

where the "$1s$" F-center wave function is the $u_{1s}(r)$ solution to the HFS Eq. (34) with $V_C(r)=0$ and $W(r)=0$.

The contents of Tables II and III demonstrate that the ground-state energy of the F^- center is rather insensitive to the details of the $1s$ orbital used in Eq. (36). In fact, substituting the F-center $1s$ function given in Table IV into Eq. (36) yields, respectively, for CaF_2, SrF_2, and BaF_2, values for the F^--center energy $E_T(F^-)$ of −0.299, −0.290, and −0.279 a.u. These lead, respectively, for CaF_2, SrF_2, and BaF_2, to the values for the F^--center binding energy E_B of 0.029, 0.031, and 0.032 a.u.

The results of this paper indicate that the point-ion–lattice model given above for the F^- center in the alkaline-earth fluorides (CaF_2, SrF_2, and BaF_2) has one state (the ground state) for which the two electron orbitals may be both bound. The nature of possible excited states remains uncertain. The binding energies in Tables II and III and the binding energies mentioned in the previous paragraph suggest that if the F^- center were to exist in the alkaline-earth fluorides, then it probably would exhibit an absorption band which attains a maximum value on the long-wavelength side of the M band. The author feels that any stronger statements are not justified by a model as simple as the present model. More theoretical and experimental research is required before definitive statements may be made. We expect that the effects of electronic and ionic polarizations are much more important for F^- centers at monovalent anion sites than they are for F centers at divalent anion sites.

ACKNOWLEDGMENTS

The author thanks Dr. A. D. Franklin, Dr. A. H. Kahn, and Dr. H. Raveche for helpful discussions.

[1]E. Sonder and W. A. Sibley (unpublished). The notation for color centers proposed by these authors is used in this paper.

[2]H. W. den Hartog, thesis (University of Groningen, The Netherlands, 1969) (unpublished).

[3]B. W. Faughman *et al.* (unpublished).

[4]Quantities with dimensions of energy and length also are expressed here in terms of atomic units; 1 a.u. = 27.2 eV for energy and 1 a.u. = 0.0529 nm for length.

[5]Z. J. Kiss, Phys. Today 23 (No. 1), 42 (1970).

[6]J. Arends, Phys. Status Solidi 7, 805 (1964).

[7]B. C. Cavenett *et al.*, Solid State Commun. 5, 653

(1967).
[8]H. Mitler, Phys. Rev. 99, 1835 (1955).
[9]J. C. Slater, Phys. Rev. 81, 385 (1951).
[10]H. S. Bennett, Phys. Rev. B 1, 1702 (1970).
[11]F. C. Van der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947); B. S. Gourary and F. J. Adrian, *ibid.* 105, 1180 (1957).
[12]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957), p. 140.
[13]R. Latter, Phys. Rev. 99, 510 (1955).
[14]E. Wigner, Trans. Faraday Soc. 34, 678 (1938); Phys. Rev. 46, 1002 (1934).
[15]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963), Chap. I.

PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

Exciton Emission and Donor-Acceptor Association in Thallium Bromide

Ludwig Grabner
National Bureau of Standards, Washington, D. C. 20234
(Received 3 May 1971)

Free- and bound-exciton emission with longitudinal optical (LO) phonon cooperation is reported in undoped TlBr. The binding energies of the bound excitons with respect to the free exciton are 4 and 7 meV, respectively. A photocurrent peak at the energy of the free exciton at 4 K is interpreted as due to an Auger process at the bound-exciton complexes. Extrinsic photocurrent is reported. The temperature dependence of its excitation spectrum is anomalous from the point of view of the conventional Riehl-Schön recombination model and is shown to be consistent with a model involving donor-acceptor pairs.

INTRODUCTION

Strong exciton absorption in TlBr in the region of the fundamental edge was first observed by Pleil,[1] although it was not initially recognized as such. Nikitine and Reiss[2] first attributed this absorption to an exciton. This was confirmed by Tutihasi,[3] Lefkowitz *et al.*,[4] and more recently by the extensive work of Bachrach and Brown[5] on strain-free films. The latter, in addition, interpret a peak at slightly larger energy than the exciton peak, and separated from it by somewhat less than the energy of a longitudinal optical (LO) phonon, as an exciton-phonon bound state. This is a new quasiparticle proposed by Toyozawa and Hermanson[6] to explain an anomaly in phonon cooperation in exciton emission and absorption, respectively. The anomaly consists of the observation that, in some materials, the position of the lines due to cooperating phonons is not symmetrical with respect to the no-phonon exciton line. In particular, in optical absorption, the separation of the exciton peak from a higher energy companion is less than the energy of the LO phonon. In emission, on the other hand, this separation is equal to the LO phonon. The idea of the exciton-phonon bound state has recently been elaborated on by Toyozawa[7] and Sak.[8] In addition, Bachrach and Brown[5] determined the exciton effective mass from the Faraday-rotation pattern of the exciton line and the binding energy of the exciton (6.5 meV) from the oscillatory magnetoabsorption.

In this paper we shall demonstrate radiative recombination via free and bound excitons as well as an Auger process, a competing radiationless process, for bound excitons in which the bound-exciton energy appears as kinetic energy of one of the particles by ejection into its respective conduction band. Finally, nominally pure TlBr, just as TlCl,[9-11] will be shown to exhibit marked extrinsic photoconductivity. The spectrum of extrinsic photocurrent will be shown to exhibit an anomalous temperature dependence and suggest donor-acceptor pairing instead of isolated defects.

CRYSTALS AND EXPERIMENTAL TECHNIQUES

TlBr is cubic and has CsCl structure. It is distinguished by an unusually large static dielectric constant[12] 30.4 (290 K), which increases to 35.1 (1.5 K). Its band gap at 4 K is 3.016 eV and the binding energy of the free exciton is 6.5 meV.[5] The change of band gap with temperature is anomalous, increasing as the temperature increases. This was noticed early by Fesefeldt[13] and confirmed by other workers[5] and is a property shared by TlCl.[14] Some of the physical properties of TlBr have been tabulated in Ref. 5.

The nominally undoped single crystals of TlBr used in this work were obtained from two commercial sources. After cutting and polishing, the samples were annealed for 12 h at 250 °C as suggested by Smakula.[15] Without annealing, the linewidths of the exciton emission to be reported below were much wider. The electrodes used in the