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Theoretical study of positron annihilation from F centers of alkali halide crystals*

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The present work is a theoretical study of the two-photon annihilation characteristics of a positron from an F center in alkali halide crystals. It has been experimentally established that positrons can annihilate with F-center electrons in KCl. In the present study, the two-particle problem is solved using several types of trial wave functions and for two choices of the model crystal potentials. The model crystal potentials used are those which have been found useful in theoretical descriptions of F centers. The stability of such systems, the two-photon annihilation lifetime τ and the angular distribution $N(\theta)$ have been calculated in all cases considered; LiX, NaX, KX, and RbX, with X being fluoride, choride, bromide, and iodide ions. A theoretical assessment is given of the prospects of the F-center-electron trapping and annihilating with the positron. Internal trends between the various alkali halides are presented. The lifetimes and angular distribution curves are compared with the experimental data which are available for KCl and NaCl. These calculations lend strong support to the experimental evidence of positron annihilation from F-center electrons, notwithstanding the relative simplicity of the crystal potential employed.

I. INTRODUCTION

The purpose of this study is to calculate the binding energy and the annihilation characteristics of a positron bound to an F center of an alkali-halide crystal. The effect of the positron on the radial distribution of the F-center electron is also investigated. A major objective is to examine the effects of including interparticle correlation in the wave function on the lifetime τ, and two-photon angular distribution $N(\theta)$, of positron annihilation. The present work is part of an investigation to explore the effects of a medium or "environment" on positronium, Ps, and its annihilation characteristics and hence clarify the link to electronic structure. These calculations probe qualitative aspects via model calculations, but also appear of direct use in positron annihilation connected with F centers in alkali-halide crystals.

One stimulus for this work arose from the recent experimental results of Herlach and Heinrich,[1] Dupasquier,[2] Brandt, Waung, and Levy,[3] Mallard and Hsu,[4] and Arefiev and Vorobiev[5] who have studied positron annihilation from alkali-halide crystals with substantial concentrations of F centers. Relative to the pure alkali-halide crystal, usually KCl, a significant change in the angular distribution of two-photon annihilation and a third component in the lifetime spectra is found. Herlach and Heinrich[1] have measured $N(\theta)$ for pure and additively colored KCl (with approximately 5×10^{18} F-centers/cm^3) and Arefiev and Vorobiev[5] have made similar measurements for pure KCl and KCl colored by electron-beam irradiation to produce different concentrations of F centers. Both groups report a new and narrow component to the low-momentum region, i.e., for small angles, of the angular distribution, $N(\theta)$ (see Fig. 4). The significant change in $N(\theta)$ is attributed to annihilation of positrons trapped by F centers, i.e., annihilation with the F-center electron. As is well known the positrons are thermalized before being trapped in *any* defect or forming a complex system. Dupasquier[2] and Mallard and Hsu[4] have measured the lifetime spectra of positron annihilation in KCl single crystals at various F-center concentrations. The data were resolved into three components and the intensity of the longest-lived component ($\tau = 1.0$ nsec) is proportional to the F-center concentration. Bisi, Dupasquier, and Zappa[6] have recently provided useful new data of the magnetic quenching of the long-lived state of the positron in KCl containing F centers. A number of types of defects, e.g., cation vacancies, F_A centers, etc., can presumably contribute characteristic components or modes of annihilation, but these are not explicitly considered in this paper.

Positron annihilation associated with various types of vacancies, especially from lattice vacancies, have been studied very actively in the last three years. The theoretical methods employed by Hodges [7] and Arponen *et al.* [8] to treat positron annihilation from lattice vacancies in metals can also be modified for use in alkali halides. In fact, it would be useful to make such calculations to examine the nature of positron annihilation from cation vacancies in alkali-halide crystals for comparison with other types of defect annihilation, e.g., from F centers. The only previous studies of positron annihilation from F centers involving a detailed calculation known to the authors are due to Berezin and Evarestov in a pair of recent papers,[9,10] which leave many important questions unanswered.

In the present theoretical work, the problem of a positron and an electron in a central model potential is studied. This system is viewed as an *F* center interacting with a positron with both particles trapped in an anion vacancy of the alkali-halide crystal. It should be emphasized that the conclusions presented here are no better than the accuracy of the representation of the potential acting on the electron-positron pair. This work is only a first step in the direction of a more detailed consideration of this difficult problem. In particular, this problem in several ways parallels problems involving excited states of an impurity in a host lattice, e.g., the studies of the spectra of atomic hydrogen trapped in rare-gas crystals clearly indicated that it was necessary to include overlap with the nearest neighbors.[11] Similarly, since the positron charge density shows a very diffuse character (like an excited-electron state), overlap can be expected to be a factor. Obviously we also deal with a rigid lattice.

II. THEORETICAL STATEMENT OF PROBLEM AND METHODS USED

The problem involved is a two-electron system and one expects rather excellent results. However, this depends critically on a realistic and tractable representation of the "effective" potential of the anion vacancy in the crystal. Even the simpler *F*-center problem has resisted rigorous solution in this sense. The system here is a normal *F* center plus a positron, an (Fe^+) center, which can be schematically represented as in Fig. 1. The Schrödinger equation

$$H\Psi(\vec{r}_+, \vec{r}_-) = E\Psi(\vec{r}_+, \vec{r}_-) \tag{1}$$

with the Hamiltonian (in a.u.)

$$H = -\tfrac{1}{2}(\nabla_+^2 + \nabla_-^2) + V(\vec{r}_+) - V(\vec{r}_-) - r_{+-}^{-1} \tag{2}$$

must be solved for the (Fe^+) center. For *S* states, all results depend only on the triangle defined by the center of the anion vacancy and the positions of the electron and positron and not on its orientation. In this case the Hamiltonian has the form

$$\begin{aligned} H = &-\tfrac{1}{2}(\nabla_{r_+}^2 + \nabla_{r_-}^2 + 2\nabla_{r_{+-}}^2) + V(\vec{r}_+) - V(\vec{r}_-) \\ &- \cos\Theta \frac{\partial^2}{\partial r_+ \partial r_{+-}} - \cos\Theta \frac{\partial^2}{\partial r_- \partial r_{+-}} - r_{+-}^{-1}, \end{aligned} \tag{3}$$

with the definition

$$\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right). \tag{4}$$

This expression and the coordinates are as given by Roothaan and Weiss.[12] The potential $V(\vec{r})$ is the effective potential of an anion vacancy of the alkali-halide crystals and we assume the potential acting on the electron, $V(\vec{r}_-)$, and the positron, $V(\vec{r}_+)$, in the anion vacancy have the same functional form. The two potentials, however, can differ. The resulting Schrödinger equation is solved variationally using different model potentials and various trial wave functions.

The spin-averaged annihilation rate for two-γ annihilation, $\Gamma_{2\gamma}$, and the corresponding lifetime, $\tau_{2\gamma}$, can be easily calculated from the normalized wave function via,

$$\begin{aligned} \Gamma_{2\gamma} &= \tau_{2\gamma}^{-1} = \pi\alpha^3\rho \\ &= \pi\alpha^3 \langle \Psi(\vec{r}_+, \vec{r}_-) | \sum_{i=1}^{n} \delta(\vec{r}_+ - \vec{r}_-) | \Psi(\vec{r}_+, \vec{r}_-) \rangle, \end{aligned} \tag{5}$$

where α is the fine-structure constant and ρ is the total electronic charge density at the position of the positron. In our case n is the number of electrons, $n = 1$ and atomic units of time are used. Similarly, from the wave function of the system the angular distribution of the two emitted photons in the long-slit apparatus, $N(\theta)$, can be calculated by the usual equation

$$N(\theta) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\chi(p_x, p_y, p_z = mc\theta)|^2 \, dp_x \, dp_y. \tag{6}$$

In this expression $\vec{p} = (p_x, p_y, p_z)$ is the total momentum of the annihilating pair or the two emitted photons and

$$\chi(\vec{p}) = \int\int e^{-i\vec{p}\cdot\vec{r}_-} \delta(\vec{r}_+ - \vec{r}_-) \Psi(\vec{r}_+, \vec{r}_-) \, d\vec{r}_+ \, d\vec{r}_- \tag{7}$$

is the probability amplitude of finding an electron-positron pair or the two emitted photons in the interval $\vec{p}$ and $\vec{p} + d\vec{p}$.

The angular distribution $N(\theta)$ in Eq. (6) is for two-photon annihilation of one positron and one *F*-

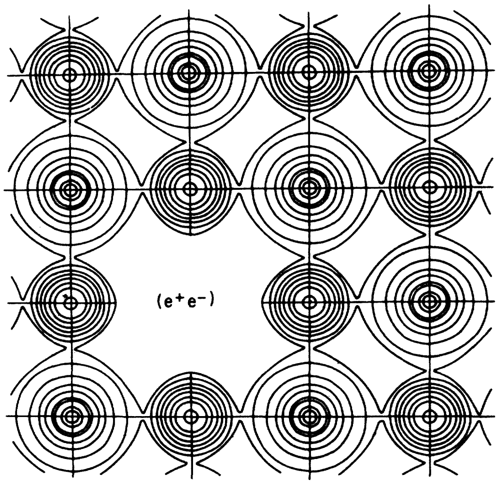

FIG. 1. Model of the (Fe^+) center in NaCl viewed in the (100) plane. Constructed from experimental results of Witte and Wolfel [J. Phys. Chem. 3, 296 (1955)] with no allowance for distortion or polarization effects near anion vacancy.

center electron. In Eqs. (6) and (7), it is assumed that $\Psi(r_+, r_-)$ is normalized to unity. Experimentally, however, an absolute determination of $N(\theta)$ is not usually obtained and $N(\theta)$ is scaled or normalized to facilitate presentation of the results. Accordingly, in this work the values of $N(\theta)$ have been scaled in the following fashion to assist comparison with experimental results. Thus for a group, MX, for a common cation, M, the $N(\theta)$ curve with the largest value at $\theta = 0$ was scaled such that $N(\theta = 0) = 10.0$ and this scale factor ξ is used for remaining members; e.g., for KI, KBr, KCl, and KF the calculated $N_{\text{calc}}(\theta)$ for KI is highest at $\theta = 0$, so we require $N_{\text{calc}}(\theta) = 10.0$ for KI which defines ξ. Then for KBr, KCl, and KF we use $N(\theta) = \xi N_{\text{calc}}(\theta)$. Other normalizations (for example, fixing the area under the curve) are possible, but none are without disadvantages. [In Fig. 5 we also use the alternate normalization to a constant area under the curve, $N(\theta)$, for comparison purposes.]

The radial distribution of the electron has also been calculated both for the F center $D_F(r_-)$, with $\Phi(\vec{r}_-)$ as the F-center wave function,

$$D_F(r_-)dr_- = \int_0^\pi \int_0^{2\pi} |\Phi(\vec{r}_-)|^2 r_-^2 dr_- d\Omega_- \tag{8}$$

and for the (Fe^+) center, $D_{Fe^+}(r_-)$,

$$D_{Fe^+}(r_-)dr_- = \int_0^\pi \int_0^{2\pi} r_-^2 dr_- d\Omega_- \int\int |\Psi(\vec{r}_+, \vec{r}_-)|^2 d\vec{r}_+, \tag{9}$$

where $d\Omega_-$ and $d\Omega_+$ are the angular volume elements and $d\vec{r}_+ = r_+^2 dr_+ d\Omega_+$.

Two types of model potentials have been employed. Both are based on model calculations which are familiar from F-center work. No detailed structure of the potential near the anion vacancy has been included. The potentials used are the following.

(i) *The hydrogenic model potential.* This potential is written simply

$$V(r) = a/r, \tag{10}$$

where the parameter a is empirically determined. The F-center problem is solved using this potential to give $\Delta E_{1s\text{-}2p} = (3a^2/8)$ a.u. and then a is chosen to reproduce the maximum of the experimental F band, presumably due to the $1s\text{-}2p$ transition. Thus

$$a = (8\Delta E_{1s\text{-}2p}/3)^{1/2} \tag{11}$$

and we have used $\Delta E_{1s\text{-}2p}$ from Zahrt and Lin[13] (see Table I).

(ii) *The cavity model potential* (*Krumhansl-Schwartz*). This somewhat more flexible potential is

$$\begin{aligned} V(r) &= V_0\,, \quad r < R \\ &= 1/k_0 r, \quad r > R \end{aligned} \tag{12}$$

where R defines the radius of the cavity and k_0 is the static dielectric constant of the crystal. These potential parameters are also from the F-center

TABLE I. Potential parameters describing the interaction of e^+ or e^- with anion vacancy of alkali-halide crystals.

	Cavity model (Krumhansl-Schwartz) as defined by Eq. (12)[a]			Hydrogenlike model [Eq. (10)]	Experimental[b] $(E_{2p} - E_{1s})$
Crystal	R(a.u.)	k_0(a.u.)	V_0(a.u.)	a(a.u.)	(eV)
LiH	3.859	3.61	0.3775	0.485	2.4
LiF	3.794	1.92	0.4152	0.697	4.96
LiCl	4.84	2.75	0.3137	0.562	3.22
LiI	5.67	3.80	0.2616	0.478	2.33
NaF	4.37	1.74	0.3696	0.598	3.65
NaCl	5.317	2.25	0.2947	0.512	2.67
NaBr	5.63	2.62	0.2739	0.475	2.30
NaI	6.11	2.91	0.2507	0.455	2.11
KF	5.03	1.85	0.3202	0.516	2.72
KCl	5.94	2.13	0.2684	0.464	2.20
KBr	6.24	2.33	0.2527	0.439	1.97
KI	6.65	2.69	0.2340	0.421	1.81
RbF	5.33	1.93	0.3016	0.505	2.60
RbCl	6.18	2.19	0.2572	0.441	1.98
RbBr	6.47	2.33	0.2444	0.411	1.72
RbI	6.92	2.63	0.2261	0.396	1.60

[a] The cavity model parameters are the same as used by Zahrt and Lin in their F-center calculations (Ref. 13).

[b] The maxima of the F band were taken from Zahrt and Lin (Ref. 13).

study of Zahrt and Lin.[13] It was originally intended to employ a full point-ion model lattice potential. However, if the ground state is assumed to be an S state and the point-ion potential is expanded into Kubic harmonics one can show that only spherically symmetric terms can contribute to the energy. It is clear that the exact bound state cannot be a *pure* S state since it must contain Kubic harmonic contributions to allow the positron and electron to avoid the ion cores. The spherically symmetric part is found to be very similar in form to the Krumhansl-Schwartz potential except for small oscillations in the region of $r > R$.

The trial wave functions employed are of the form

$$\Psi_u(\vec{r}_+, \vec{r}_-) = \frac{(\alpha\eta)^{3/2}}{\pi} e^{(-\alpha r_+ - \eta r_-)} \quad \text{(uncorrelated)}\,, \tag{13a}$$

$$\Psi_{rc}(\vec{r}_+, \vec{r}_-) = \frac{(2at^2)^{3/2}}{8\pi} e^{-t(2ar_- + r_{+-})/2} \quad \text{(restricted-correlated)}\,, \tag{13b}$$

$$\Psi_c(\vec{r}_+, \vec{r}_-) = \frac{(8\gamma)^{3/2}}{8\pi} e^{(-\beta r_- - \gamma r_{+-})/2} \quad \text{(correlated)}. \tag{13c}$$

The first form (uncorrelated) was taken only for comparison purposes since it was used by Berezin and Evarestov[9] in related calculations. It is very desirable, if possible, that the trial wave functions assume a form which contains as limiting cases wave functions for free Ps and a bound F-center electron. For example, in the correlated wave function (13c) if $\beta \to 0$ (corresponding to the electron *not* bound to the anion vacancy) the wave function goes to that for free Ps after renormalization. Similarly, if $\gamma \to 0$ (corresponding to the electron *not* bound to the positron) the wave function after proper renormalization goes to that of a bound F-center electron and a free positron. The correlated form (13c) thus includes virtual positronium *and* virtual F-center electron as degenerate forms of the wave function. The factor involving $e^{-\alpha r_+}$, used by Berezin and Evarestov,[9,10] has no physical basis since it corresponds to a hydrogenic bound state of the positron to the *anion* vacancy. The positron cannot, however, form a bound state with the anion vacancy which has an effective positive charge (recall that r_+ refers to the distance between the positron and the center of the anion vacancy). It should be noted again that the trial wave functions do not allow for any realistic overlap of the Ps wave function with nearest-neighbor ions.

Using these two model potentials, calculations of the anion vacancy plus an electron and positron were made for 15 alkali-halide and the lithium-hydride crystals following the F-center work of Zahrt and Lin[13] for the same crystals. For certain crystals there are no bound states other than free Ps using the correlated wave functions, i.e., no minimum appears in the energy surface except for Ps. Since the electron-positron correlation seems satisfactory via the $e^{-\gamma r_{+-}/2}$ term, this probably indicates inadequacies of the model potentials which are not realistic representations of all details of the anion vacancy potential in the crystal. The exact wave function must satisfy the cusp conditions[12] for coalesence of electron-positron and electron-anion vacancy (with effective charge of a) pairs. In the correlated wave function used [Eq. (13c)] this requires that $\gamma = 1$ and $\beta = 2a$, respectively. The restricted-correlation wave function is a compromise between satisfying the cusp condition and an accurate representation of the correlation of the electron with the positron and anion vacancy. The restricted trial wave function employed here [Eq. (13b)] is constrained so that (β/γ) is $2a$ as is the case when the exact cusp condition is satisfied. This restricts the general form so that only one variational parameter remains (although correlation is still contained). The electron-positron cusp condition is expected to be of particular importance for the positron lifetime.

III. SUMMARY AND DISCUSSION OF RESULTS

The purpose of this investigation is to explore the dependence of two-γ annihilation parameters on the molecular environment of the (e^+e^-) pair. The weak point in the present study is the simple potentials used to represent a "molecular environment," i.e., the potential at an anion vacancy in an alkali-halide crystal. Our results are probably *qualitatively* reliable, but we will emphasize internal trends rather than absolute values calculated. The six sets of calculations (two model potentials and three trial wave functions) for (Fe^+) centers in 15 alkali-halide crystals and LiH are summarized in Figs. 2–6 and Tables I–III and are briefly discussed below. The F-center calculations by Zahrt and Lin[13] have been used as noted below.

A. Energy values and binding energies

We are interested in the total energy of the (Fe^+) center, $E(Fe^+)$, and trends within the sequence of alkali halides. The variationally determined energy values are summarized in Tables II and III. For comparative purposes the energy of free positronium (−6.80 eV) and especially the energies of the F center using both potentials for all crystals are significant here. It should be noted that using the same potentials, the F-center energy values also correspond to an "anti-F-center," i.e., a positron trapped in a cation vacancy.

The relative energy values for the F center (or anti-F-center), the (Fe^+) center, and Ps are particularly important here and we define the binding energy of a positron to an F center : $E_B(e^+)=E(F)-E(Fe^+)$; and the binding energy of Ps to a cation (or anion) vacancy : $E_B(\mathrm{Ps})=E(\mathrm{Ps})-E(Fe^+)$.

These results suggest that the positron can be bound to an F-center electron, i.e., to an S-state F center. For both potentials the wave functions with electron-positron correlation show binding energies, $E_B(e^+)$, from 1.0 to 2.0 eV greater than the result where correlation is neglected. The greatest binding energy occurs for the hydrogenic potential using a correlated wave function—the Krumhansl-Schwartz (KS) potential gives smaller, but still sizeable binding energies. The binding energy of a positron to an F center is, however, substantially less than the binding energy of a positron to a cation (M^+) vacancy which varies from 4.0 to 6.0 eV for the KS potential. In only a few cases do these results suggest (on an energy basis) that Ps can be trapped in a crystal vacancy (cation or anion) or bound by the potential used. This is academic since we do not have a realistic possibility of Ps being *trapped* in a vacancy, although Ps can energetically be *formed* with an F-center electron in all cases. In the latter case the barrier to escape the vacancy is substantial and annihilation occurs before tunneling of Ps. These simple energy results support the contention that a positron can easily be trapped at either an F center or a cation vacancy. The annihilation characteristics of alkali halides with defects should show a lifetime spectra associated with at least these two modes of annihilation.[4]

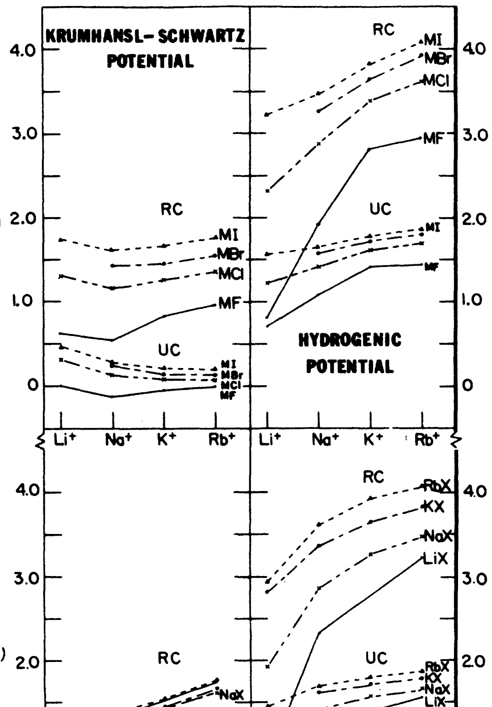

FIG. 2. Binding energy of a positron to an F-center electron in alkali-halide crystals using Krumhansl-Schwartz and hydrogenic potentials. Results for uncorrelated (UC) and restricted-correlated (RC) wave functions of (e^+e^-) system.

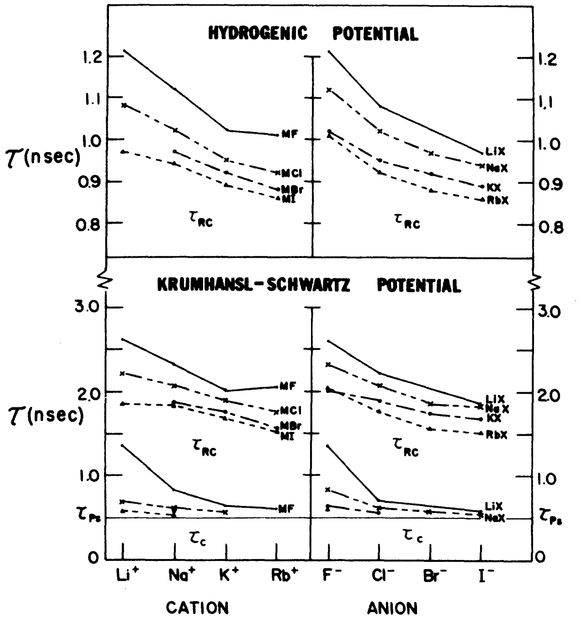

FIG. 3. Two-photon positron annihilation lifetimes τ for alkali-halide crystals with an F center using Krumhansl-Schwartz and hydrogenic potentials. Results for restricted-correlated (RC) and correlated (C) wave functions of (e^+e^-) system.

The strength of binding of the positron to the F center depends sensitively on the inclusion of (e^-e^+) correlation in the wave function and the crystal considered. There is also a dependence on the form of the "crystal" potential used. For a given potential the energy of the (Fe^+) center is lower than that for the analogous F center (same potential) when an uncorrelated wave function is used except for NaF, KF, and RbF using KS potential. The fluorides (including LiF) are characterized by the smallest k_0, largest V_0, and the smallest cavity radius by the KS potential which indicates the weakest potential for the positron. This is consistent with earlier results,[9,10] but as soon as correlation effects are added all (Fe^+)-center energy levels drop by 1.0–2.0 eV. While it is true that the uncorrelated result is not the fully independent-particle result, the main conclusions cannot be escaped. Namely, that *any* meaningful treatment of Ps trapped in a medium must adequately include electron-positron correlation, i.e., the virtual Ps wave-function form must provide a major component of the trial wave function. This was a major flaw in the qualitative study of Berezin and Evarestov[9,10] and is probably relatively independent of the potential used. While explicit inclusion of the electron-positron correlation does not pose great practical problems for Ps in a medium, this implies that if *another* path of annihilation is formation of an (X^-e^+) system, then a full treatment of positron-valence electron correlation seems advisable.[14]

The capacity of an F center or a cation (M^+) vacancy to bind a positron is sensitive to the potential provided by the host crystal. The explicit form of the potential is also important and affects the internal trends expected. In Fig. 2 calculations including correlation and the hydrogenic potential show substantial variation in the binding energy of the positron to an F center with $E_B(e^+)$ increasing with anion and cation size (i.e., for MX, $= \mathrm{I}^- > \mathrm{Br}^- > \mathrm{Cl}^- > \mathrm{F}^-$ and for MX, $M = \mathrm{Rb}^+ > \mathrm{K}^+ > \mathrm{Na}^+ > \mathrm{Li}^+$). Even though the hydrogenic potential is simpler than the KS potential, it has been effectively scaled by using experimental results and may be more reliable than the KS potential whose parameters come entirely from sources outside the F-center problem. The uncorrelated result for the hydrogenic potential shows much less system dependence. If the hydrogenic potential results are reliable, we can expect that large cation–large anion systems offer the best possibilities for binding a positron to an F-center electron. This is quite reasonable since as we see the binding energy of the F-center electron is least for these systems. Concerning the competition between the cation vacancy and the F center for binding a positron, the situation always favors the cation vacancy except for large anion–large cation cases. Experimental information in this regard would be most helpful.

The KS potential certainly is preferred to describe the F-center system (see Zahrt and Lin[13] and Ziman[15]) and allows greater flexibility to describe the potential of the crystal. The KS potential closely approaches the actual point-charge model as has been pointed out on several occasions. Our results using the KS potential show several unusual features. First of all, we note in Fig. 2 that the correlated results using the KS potential suggest that the positron binding energy is not very sensitive to the cation for a given anion, e.g., for bromides, $E_B(e^+) = 1.43(\mathrm{Na}^+)$, $1.45(\mathrm{K}^+)$, $1.54(\mathrm{Rb}^+)$. The $(1s\text{-}2p)$ F-center transition trend shows the trend $\Delta E(\text{expt.}) = 2.30$ (NaBr), 1.97 (KBr), and 1.72 (RbBr) and it would appear that binding a positron would show at least as much variation as excitation. The KS potential employs a cavity of radius R and we find that when the radius exceeds 6.18 a.u. (as in KBr, KI, RbCl, RbBr, and RbI) the fully correlated calculation gives only 6.80 eV for the total energy, i.e., the energy of free positronium. The wave function also goes to the free positronium wave function in these cases. In the KS potential calculations the wave function is joined at the boundary of the cavity which suggests that for these crystals the cavity is large enough to contain essentially unperturbed Ps with the associated

TABLE II. Results of the calculation of (Fe^+) center using hydrogenic model potential.

	Uncorrelated wave function					Restricted correlated wave function				
Crystal	α (a.u.)	η (a.u.)	$-E(\mathrm{Fe}^+)$ (eV)	$E_B(e^+)$ (eV)	τ (nsec)	β (a.u.)	γ (a.u.)	$-E(\mathrm{Fe}^+)$ (eV)	$E_B(e^+)$ (eV)	τ (nsec)
LiH	0.210	0.551	4.734	1.533	17.7	0.773	0.797	6.354	3.154	0.98
LiF	0.155	0.717	7.315	0.705	30.1	1.037	0.744	7.426	0.816	1.21
LiCl	0.192	0.607	5.523	1.225	20.1	0.868	0.772	6.621	2.324	1.08
LiI	0.211	0.546	4.668	1.560	17.7	0.764	0.800	6.337	3.228	0.97
NaF	0.183	0.635	5.951	1.085	21.7	0.913	0.763	6.793	1.928	1.12
NaCl	0.204	0.570	4.989	1.422	18.3	0.807	0.788	6.432	2.865	1.02
NaBr	0.212	0.544	4.640	1.570	17.5	0.761	0.801	6.330	3.260	0.97
NaI	0.216	0.531	4.464	1.647	17.2	0.736	0.809	6.287	3.471	0.94
KF	0.203	0.574	5.037	1.415	18.5	0.811	0.786	6.445	2.823	1.20
KCl	0.214	0.537	4.547	1.618	17.4	0.747	0.805	6.305	3.376	0.95
KBr	0.219	0.520	4.335	1.713	17.0	0.716	0.815	6.260	3.638	0.92
KI	0.223	0.508	4.189	1.778	16.7	0.693	0.823	6.236	3.825	0.89
RbF	0.205	0.565	4.923	1.453	18.3	0.798	0.790	6.410	2.941	1.01
RbCl	0.219	0.521	4.344	1.698	17.0	0.718	0.814	6.263	3.617	0.92
RbBr	0.225	0.501	4.108	1.809	16.6	0.680	0.827	6.226	3.928	0.88
RbI	0.227	0.492	4.001	1.867	16.6	0.661	0.834	6.215	4.081	0.86

energy, lifetime, and angular correlation. The interesting prospect then arises that essentially free Ps can exist in large cation alkali halides. It is more likely, however, that this merely reflects that the *R* used is not suitable for this problem. The uncorrelated and restricted-correlated results do not show this behavior for the KS potential and presumedly this is because the electron-positron correlation, and hence average separation, is underestimated so that the pair is sensitive to a larger radius (also these forms cannot go to free Ps).

These energy results do not permit very confident conclusions to be drawn. Both potentials are quantitatively lacking. The binding of a positron to a cation vacancy has recently been considered by Varisov and Prokop'ev[16] who include limited details of the cation neighbor interactions (i.e., X^- ions). The possibility and features of positron annihilation in a cation vacancy should be explored in detail.

B. Positron lifetime and angular correlations, $N(\theta)$

The positron lifetime spectra has been studied by several authors and our interest focuses particularly on the lifetime spectra from alkali-halide crystals with high *F*-center concentrations. Data are published only for the lifetimes and angular correlation of KCl crystals. In a detailed study to relate the lifetime spectra to the various defects possible in a KCl crystal, Mallard and Hsu[4] conclude that the τ_3 component of the lifetime spectra is due to several competing processes—mainly cation vacancies and *F* centers. Measurements of lifetime spectra have also been studied by Tumosa, Nicholas, and Ache[17] in NaCl crystals with defects induced by several means. There is need for measurements for other alkali-halide crystals with various types of controlled defects to give a clearer picture of the processes contributing to the lifetime spectra.

The positron-lifetime calculations reported here (see Tables II and III) display the expected large dependence on inclusion of electron-positron correlation. As obvious from Eq. (5), τ is inversely proportional to the expectation value of $\delta(\vec{r}_+ - \vec{r}_-)$ so that insufficient attention to instantaneous electron-positron positions will give an underestimate of $\langle | \delta(\vec{r}_+ - \vec{r}_-) | \rangle$ and hence a lifetime larger than experiment. The uncorrelated wave function for both the hydrogenic and KS potential gives rather large lifetimes, e.g., 50–250 nsec for KS potential and 20–30 nsec for the hydrogenic potential. The uncorrelated wave function is obviously very poor as $r_{+-} \to 0$ and generally the positron sees much less electron density with which to annihilate. Once electron-positron correlation is introduced,

TABLE III. Results of the calculation of (Fe⁺) center using Krumhansl-Schwartz potential.

	Uncorrelated wave function					Restricted correlated wave function					Correlated wave function				
Crystal	α (a.u.)	η (a.u.)	$-E(\mathrm{Fe}^+)$ (eV)	$E_B(e^+)$ (eV)	τ (nsec)	β (a.u.)	γ (a.u.)	$-E(\mathrm{Fe}^+)$ (eV)	$E_B(e^+)$ (eV)	τ (nsec)	β (a.u.)	γ (a.u.)	$-E(\mathrm{Fe}^+)$ (eV)	$E_B(e^+)$ (eV)	τ (nsec)
LiH	0.135	0.475	6.105	0.675	54	0.715	0.737	7.060	1.630	1.24	0.707	0.748	7.060	1.630	1.19
LiF	0.108	0.470	6.463	0.007	92	0.803	0.576	7.077	0.621	2.61	0.716	0.714	7.110	0.654	1.37
LiCl	0.107	0.409	5.583	0.319	102	0.685	0.609	6.577	1.313	2.21	0.464	0.898	6.839	1.575	0.69
LiI	0.102	0.372	5.078	0.469	121	0.616	0.644	6.356	1.747	1.86	0.336	0.952	6.779	2.170	0.58
NaF	0.091	0.428	6.117	−0.124	147	0.716	0.599	6.785	0.544	2.32	0.546	0.844	6.925	0.684	0.83
NaCl	0.092	0.382	5.377	0.132	153	0.637	0.622	6.418	1.173	2.07	0.375	0.936	6.800	1.555	0.61
NaBr	0.094	0.370	5.169	0.239	148	0.613	0.645	6.362	1.432	1.86	0.333	0.952	6.784	1.854	0.58
NaI	0.091	0.352	4.916	0.291	165	0.589	0.647	6.236	1.611	1.84	0.259	0.974	6.771	2.146	0.54
KF	0.086	0.393	5.637	−0.054	177	0.649	0.629	6.531	0.840	2.00	0.415	0.918	6.825	1.134	0.64
KCl[a]	0.082	0.355	5.083	0.082	211	0.595	0.641	6.262	1.261	1.89	0.283	0.967	6.778	1.777	0.56
KBr	0.083	0.344	4.906	0.140	208	0.578	0.658	6.219	1.453	1.75		free positronium			
KI	0.083	0.332	4.698	0.223	213	0.562	0.667	6.149	1.674	1.68		free positronium			
RbF	0.085	0.379	5.447	−0.002	186	0.631	0.625	6.421	0.972	2.04	0.370	0.938	6.803	1.354	0.60
RbCl	0.081	0.346	4.951	0.087	220	0.579	0.657	6.230	1.366	1.76		free positronium			
RbBr	0.080	0.336	4.804	0.127	231	0.561	0.682	6.221	1.544	1.57		free positronium			
RbI	0.079	0.322	4.591	0.203	244	0.546	0.689	6.147	1.759	1.52		free positronium			

[a] The only experimental results are for KCl; τ is 0.95 nsec (Duspaquier, Ref. 2) and 1.1 nsec (Arefiev and Vorobiev, Ref. 5).

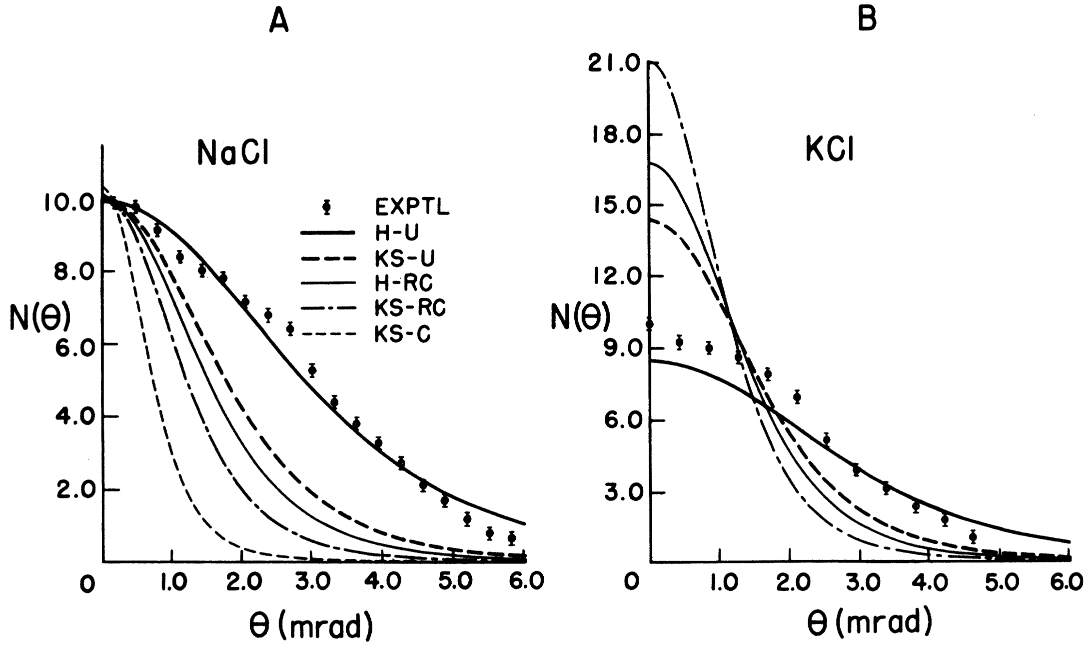

FIG. 4. Angular distribution for two-photon positron annihilation $N(\theta)$ from F centers in alkali-halide crystals. Theory for various approximate wave functions (lines) and experiment (unconnected points). Experimental results are from Herlach and Oggenfuss [Ref. 18). (A) Sodium chloride with normalization of $N(\theta)=10.0$ at $\theta=0$. (B) Potassium chloride with normalization of $N(\theta)$ such that area under all curves the same.

the lifetime drops to around 1 nsec for both potentials—the only experimental value ascribed to *F*-center annihilation gives 0.95 (Ref. 2) and 1.3 nsec (Ref. 5) whereas we calculate 0.95 (hydrogenic potential), 1.89 (KS restricted correlated), and 0.56 (KS fully correlated) nsec. Details are not confidently clear from these results, but the general aspect of the importance of including the electron-positron correlation seems established. Again referring only to the KCl result, the simpler hydrogenic model potential seems superior, reinforcing appreciation that this result is scaled via the *F*-center spectra. It would be overly optimistic to suggest that the lifetimes in Table II are probably good estimates, but for internal trends we are more confident of their reliability. The trends in lifetimes are summarized in Fig. 3 which show a maximum variation from about 20% using hydrogenic potentials to about 30% for the KS potential in going through the alkali halides. The actual range of variation is from 0.97 to 1.21 nsec for the hydrogenic potential–restricted correlated result which is close to the experimental limits of resolution.

The internal trends of lifetimes with fixed cation or anion show very regular behavior. The only exception seems to be the points for KF which are not on a smooth curve. However, plots of the corresponding potential parameters (e.g., *a* of the hydrogenic potential) *also* show KF out of line with the others. The KS results predict lifetimes about twice as long as those for the hydrogenic potentials, but the absolute changes with system are not large and both potentials suggest a gradual decrease in lifetime as anion or cation (or both) increase in size. The longest lifetime would be for LiF. The calculation with a fully correlated wave function and the KS potentials again demonstrates that as the cavity becomes larger, the behavior becomes identical with that of free Ps. In both trends (with anion and cation) one approaches the free positronium lifetime.

It would be desirable to compare the best lifetimes calculated (e.g., the hydrogenic potential and restricted correlated wave function case) with those for lifetimes from cation vacancies of the same crystals. The predictions of the lifetimes from the cation vacancies have not been calculated here although the methods used elsewhere by Arponen *et al.*[8] and Varisov and Prokop'ev[16] are applicable.

The angular correlation of the two-photon annihilation is a sensitive probe of the momentum distribution of the electronic charge with which the positron annihilates. We are interested in how accurately the angular distribution is calculated using the model potentials employed here, how important is electron-positron correlation on $N(\theta)$, and what is the connection between $N(\theta)$ and alkali-halide crystals? The conclusions we have reached

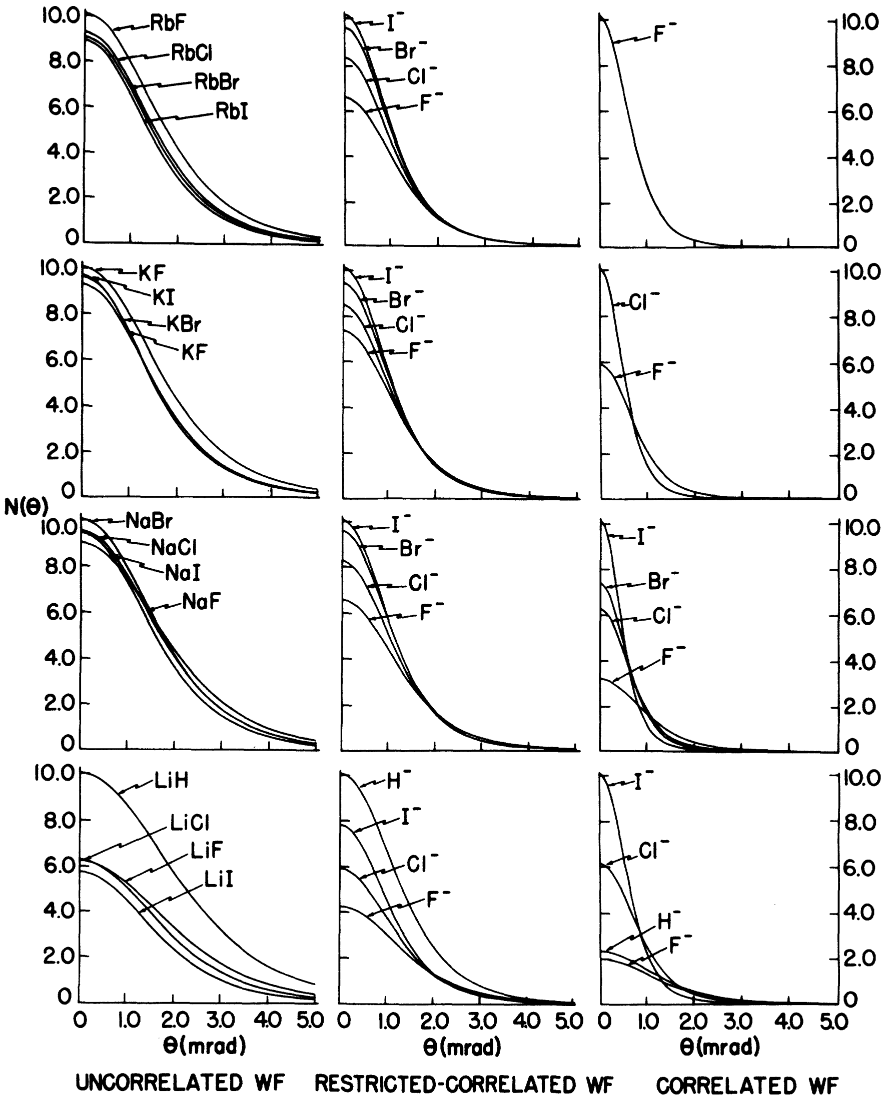

FIG. 5. Angular distribution for two-phonon positron annihilation $N(\theta)$ from F centers in alkali-halide crystals. Dependence on alkali-halide and wave function quality. All results for Krumhansl-Schwartz potential. Fluorides □, chlorides ○, bromides △, and iodides +.

are summarized in Figs. 4 and 5. In Fig. 4 we have compared the angular distribution which we obtain for various kinds of variational wave functions and for two-model potentials with the experimental results for KCl and NaCl kindly provided by Herlach and Oggenfuss.[18] In Fig. 4(A) each angular distribution for NaCl is normalized to give $N(\theta = 0) = 10.00$ as is the experimental custom since absolute measurements are not available. The general trend is the same for both KCl and NaCl. One notes that for a given potential (KS or hydrogenic) that introducing correlation into the wave function sharpens the angular distribution curve. This sharpening is most pronounced for the KS potential. In contrast to this we have presented in Fig. 4(B) the two-γ angular distributions for KCl in which the area under all curves is the same value. Both comparisons indicate that when electron-positron correlation is introduced into the wave function the angular distribution becomes sharp and begins to approach that of free positronium (which would be a δ function in these plots). The important result, however, is that the *uncorrelated* wave functions appear to give the best agreement with experiment in both cases. The best agreement is the uncorrelated wave function with the hydrogenic potential and this is not affected significantly by varying the manner of normalizing the $N(\theta)$ curves. The implication is that the electron momentum distribution in the F center plus positron in the actual crystal defect is not nearly as peaked around the low momenta as the correlated wave function results indicate. The F-center electrons in our calculations seem to be too loosely bound in the system with the model potentials used. But no possibility of explicit participation of the nearest-neighbors of the de-

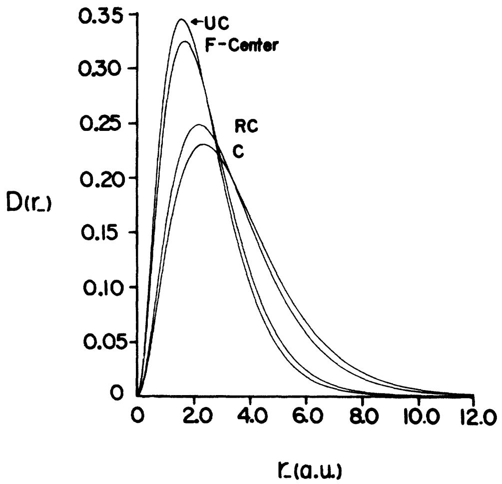

FIG. 6. Radial distribution function $D(r_-)$ of an electron in an *F* center compared to the situation in the (Fe^+) center. Results given for uncorrelated (UC), restricted correlated (RC), and correlated (C) wave functions. The system is NaF.

fect in the annihilation process is allowed and this could be a correction which must be made. We feel, however, that the more sophisticated wave function is insufficient if a more realistic model potential is not available.

The detailed insets of Fig. 5 show the internal trends in angular distribution curves for the alkali halides for the KS potential (the parallel curves for the hydrogenic potential are similar in most respects). If we assume that the restricted-correlated wave function results correctly give the order within the sequence *M*I, *M*Br, *M*Cl, and *M*F, then the KS and hydrogenic model-potential calculations agree. Both indicate that the angular distribution curves become progressively sharper with the size of the halide ion with $I^- > Br^- > Cl^- > F^-$. This is consistent with the simple notion and results that the region of low momenta is increasingly more important as the halide ion and vacancy increases in size. In the one set of calculations successful for correlated wave functions, e.g., those for Na*X*, the same trend of halide angular distribution curves is observed. However, for the uncorrelated wave functions the KS and hydrogenic results are not in agreement and the order is fully reversed for the KS potential in the case of the rubidium halides. The hydrogenic potential results do predict the correct order although the curves do not differ greatly. Finally we may note that for the fully correlated wave functions and the KS potential that the angular distribution curves become progressively more peaked around $\theta = 0$ and finally vanish from Fig. 5. For example, in Na*X* all four systems are shown, for K*X* only KCl and KF are shown, and for Rb*X*, only RbF survives. This is clearly related to the situation where free positronium becomes possible in the larger cavities and with the wave function flexibility to approach free positronium. This is a property of the model potential, but does again suggest that one may find almost free positronium annihilation from *F* centers in alkali-halide crystals with large anions and cations. The same situation also is obtained in the case of the hydrogenic model potential except now the curves are less steep and fewer systems survive.

C. Electron radial distributions

In Eqs. (8) and (9) we have defined the radial distribution for the electron for the *F* center and for the system of positron electron in a anion vacancy. In Fig. 6 the radial distribution for the electron is given for NaF with a hydrogenic potential and all three levels of approximate wave function. The calculations with some correlation included show a definite expansion of the electron charge distribution relative to that for an *F* center electron. This is as expected and arises from competition between the anion vacancy and the positron for the electron. Note the close similarity between the uncorrelated wave function result and the *F*-center charge distribution. The uncorrelated wave function does not permit appreciable expansion of the electron radial distribution.

IV. CONCLUSIONS

The present calculations strongly support the concept of annihilation of positrons from *F*-center electrons in alkali-halide crystals. The *F* center is certainly energetically capable of capturing a positron. We see evidence that electron-positron correlation is important and must be taken into account to obtain reasonable lifetimes and binding energies. However, the correlated results give an unsatisfactory account of the angular correlation for two-γ annihilation and we attribute this to either an inadequate model potential or the need to include a more detailed interaction (or overlap) with nearest neighbors. Further calculations with more detailed account of the lattice potential at the anion vacancy are desirable.

The internal trends of positron binding energies, lifetimes, and angular correlation for the alkali halides are consistent with the simple ideas associated with the expected size of the cavity and the corresponding momentum distribution of the *F*-center electron in the presence of a positron. In particular, large anion–large cation systems can show nearly-free-Ps behavior.

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[18] The plots in Figs. 4A and 4B were made using experimental data kindly furnished by Dr. Dierk Herlach (for KCl) and Albert Oggenfuss (for NaCl) of the Laboratorium F. Festforperphysik, ETH, Zurich. The details of the KCl measurements are contained in the thesis of Herlach [(ETH, Zurich, 1973) (unpublished)]. The NaCl results plotted in Fig. 4A are unpublished results of Albert Oggenfuss. The measurements of the angular distribution, $N(\theta)$, for NaCl starts at $\theta = 0.16$ mrad so we actually set $N(\theta = 0.16) = 10.00$ to define ξ.