vectors are reduced to be within the first Brillouin zone $(-\pi,\pi)$.

Let U be K or R. Then, the eigenvalue equation (the ground-state energy is taken to be zero)

$$HA\psi_0=\epsilon(m,q)A\psi_0\,, \tag{13}$$

is transformed by U into

$$H\hat{A}\hat{\psi}_0=\epsilon(m,q)\hat{A}\hat{\psi}_0\,, \tag{14}$$

where

$$\hat{A}\equiv UAU^{-1},\quad \hat{\psi}_0\equiv U\psi_0\,. \tag{15}$$

Thus the properties of the new eigenstate $\hat{\psi}\equiv\hat{A}\hat{\psi}_0$ are contained in $\hat{A}$.[5]

Let us first consider the case when m is an odd number. Then n is also odd. By applying the transformation (7a) to (11), we easily see that the state $\hat{\psi}$ is characterized by $-m$ and $-q^r$. Thus by (14) we obtain

$$\epsilon(-m,\,-q^r)=\epsilon(m,q)\,. \tag{16}$$

Similarly the transformation (7b) yields

$$\epsilon(-m,\,q^r)=\epsilon(m,q)\,. \tag{17}$$

Equations (16) and (17) are the main results of the present note. If $\epsilon(m,q)$ is an even function of m as for the des Cloizeaux and Pearson spin waves, we conclude from (16), (17), and (9) that $\epsilon(m,q)$ is an even function of q and has a periodicity of π for odd m. For even m the similar reasoning leads to the relations of the form of (16) and (17) where q^r is replaced by q.

The author wishes to express his sincere gratitude to Professor Irwin Oppenheim for the hospitality extended to the author at MIT and for his continued encouragement.

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[5] Here we assume that the excitation energy $\epsilon(m,q)$ is determined only by m and q and does not depend on the choice of the ground state. This the case if we have a nondegenerate ground state.

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Positron Annihilation in Diatomic Crystals*

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The angular correlation between the two photons created by annihilating positron-electron pairs in lattices with a basis is derived in various approximations. The effects of temperature as introduced through the momentum distribution of the positrons and through lattice vibrations are examined. Self-consistent electron wave functions with exchange are calculated for the LiH crystal in the cell approximation. The resulting x-ray structure factors are in close agreement with the recent extensive experimental data of Calder *et al.* The positron wave function is obtained in the same approximation and the momentum distribution of annihilating positron-electron pairs is calculated. The apparent discrepancy noted by Stewart and March between their angular-correlation data and the electron density distribution in the LiH crystal consistent with the x-ray structure factors can be traced to the phase relations between the wave functions within the unit cell of a lattice with a basis.

INTRODUCTION

FREE thermalized positrons in a crystal annihilate almost exclusively via para-decay with electrons of opposite spin into two photons. Because of momentum conservation, the two photons are emitted in directions 180° apart in the center-of-mass system of the annihilating particles. If the center of mass is in motion relative to the laboratory, an observer sees angles between the photons which deviate from 180°. Therefore two-photon angular-correlation measurements give information on the momentum distribution of the annihilating positron-electron pairs, as was discussed in detail first by De Benedetti *et al.*[1] in 1950. Since then, angular correlation studies have been made by many investigators on a large number of substances.[2]

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† Portions of this article are based on a thesis presented to New York University by Leslie Eder in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] S. De Benedetti, C. E. Cowan, W. R. Konnecker, and H. Primakoff, Phys. Rev. **77**, 205 (1950).

[2] For recent reviews and extensive references, see P. R. Wallace, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 1; M. Deutsch and S. Berko, in *Alpha-, Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1965), Vol. 2, p. 1583.

In early work on diatomic solids, Ferrell[3] discussed the angular distributions observed for alkali halides on the assumption that the thermalized positrons become bound to a negative ion and that the influence of the positive ions can be ignored. He derived angular distributions of alkali halides with widths inversely proportional to the radii of the negative ions. Stewart and Pope[4] made an extensive analysis of the experimental angular distributions of all sodium halides and alkali chlorides, again without including the influence of the positive ions. These authors find that the momentum distributions of the annihilating positron-electron pairs resemble the momentum distributions merely of the valence electrons of the negative ions as calculated from the Hartree-Fock wave functions of the free ions, and therefore they are compatible with the electron-density distribution calculated from x-ray diffraction data.

More recently, Stewart and March[5] reported a new observation in the annihilation of positrons in the diatomic crystals of lithium hydride, LiH, and sodium hydride, NaH. By an analysis similar to that just described they uncovered a significant discrepancy between the momentum distributions of the annihilating positron-electron pairs and that expected from the electron density distributions in these lattices as extracted from x-ray diffraction data.

This observation poses the question as to what aspects are missing in the theory of positron annihilations in diatomic crystals, or, more generally, in crystal lattices with a basis, which do not seem to be important in some crystals as, e.g., in alkali halides, but are important in others as, e.g., in alkali hydrides. It is our purpose to investigate this question.

The annihilation of positrons with free H^- ions has been studied in several papers, and some authors have applied the results to the annihilation in LiH. Most recently, Gol'danskii *et al.*[6] have invoked excited states of the free H^-e^+ system in order to correlate with the lifetime spectrum[7] and the angular correlation data[5] in LiH. Aside from a number of basic reasons to become clear in the following, the mere size of the H^-e^+ system in the excited states so invoked, if compared with the distance between nearest hydrogen neighbors in the LiH lattice, does not recommend this model as a realistic reflection of the general physical situation we are confronted with in describing the positron-electron system in a diatomic crystal.

The positron-electron system in lattices with a basis is treated in Sec. 1, and the angular correlation derived in various approximations. Effects of temperature as introduced through the momentum distribution of the thermal positrons and through lattice vibrations are considered in Sec. 2. The problem of the positron-electron correlation is taken up in Sec. 3 and reduced to that of obtaining an enhancement factor, which we calculate in a statistical approximation. Encouraged by the work of Berko and Plaskett[8] on monoatomic metals, we set up, in Sec. 4, self-consistent calculations in the cell approximation of the electron and positron-electron wave functions in the LiH lattice and uncover the reasons for the discrepancy noted by Stewart and March.

1. POSITRON ANNIHILATION IN A CRYSTAL LATTICE WITH A BASIS

The lifetime of free positrons in a solid is equal to the reciprocal of the spin-averaged decay rate Γ, which we write as

$$\Gamma=\pi\alpha^3\sum_{n=1}^{N}\int_{\text{crystal}}|\Psi(\mathbf{x}_1,\cdots,\mathbf{x}_n,\cdots,\mathbf{x}_N;\mathbf{x}_+)|^2 \times\delta(\mathbf{x}_n-\mathbf{x}_+)d^3x_1\cdots d^3x_n\cdots d^3x_N d^3x_+. \quad (1)$$

Γ is expressed in the unit of time $\hbar^3/me^4=2.42\times10^{-17}$ sec, α being the fine-structure constant. Equation (1) assumes the annihilation rate to be independent of the relative positron-electron velocities. The summation extends over all N electrons in the crystal. The wave function $\Psi(\mathbf{x}_n;\mathbf{x}_+)$ describes the state of an annihilating positron-electron pair. Since annihilation probes $\Psi(\mathbf{x}_n;\mathbf{x}_+)$ at $\mathbf{x}_n=\mathbf{x}_+$, it is sufficient to consider Ψ to be only a function of $\mathbf{x}_+$, and to write $\Psi_n(\mathbf{x}_+)$; in the following, we shall drop the subscript (+) for brevity. In terms of the Fourier transform of $\Psi_n(\mathbf{x})$, the momentum density becomes

$$|\Phi(\mathbf{p})|^2=\sum_n\left|\int d^3x\;\Psi_n(\mathbf{x})e^{-i\mathbf{p}\cdot\mathbf{x}}\right|^2. \quad (2)$$

We can define an annihilation rate per unit volume in momentum space,

$$\gamma(\mathbf{p})=\pi\alpha^3|\Phi(\mathbf{p})|^2, \quad (3)$$

such that

$$\Gamma=(2\pi)^{-3}\int\gamma(\mathbf{p})d^3p, \quad (4)$$

which follows directly from Eq. (1) by Parseval's theorem.

Most angular-correlation data are recorded relative to some (xyz) coordinate system in the laboratory, in the form

$$I(p_z)=(2\pi)^{-3}\int_0^{2\pi}\int_{p_z}^{\infty}\gamma(\mathbf{p})p\,dp\,d\varphi, \quad (5)$$

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[3] R. A. Ferrell, Rev. Mod. Phys. **28**, 308 (1956).

[4] A. T. Stewart and N. K. Pope, Phys. Rev. **120**, 2033 (1960).

[5] A. T. Stewart and R. H. March, Phys. Rev. **122**, 75 (1961).

[6] V. I. Gol'danskii, A. V. Ivanova, and E. P. Prokop'ev, Zh. Eksperim. i Teor. Fiz. **47**, 659 (1965) [English transl.: Soviet Phys.—JETP **20**, 440 (1965)]. This paper contains references to previous work.

[7] A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. **131**, 1023 (1963).

[8] S. Berko and J. S. Plaskett, Phys. Rev. **112**, 1877 (1958).

where $\rho=(p_x{}^2+p_y{}^2)^{1/2}$, such that

$$\int_{-\infty}^{+\infty} I(p_z)dp_z=\Gamma\,,$$

Eq. (4), except for an unknown scaling factor for $I(p_z)$; in such experiments, $p_z=mc\theta$, where θ is the deviation from π of the angle between the two photons, typically of order milliradians. We can extract from the data the quantity

$$\langle\gamma(p_z)\rangle=-4\pi^2 p_z{}^{-1}(dI/dp_z)\,. \qquad (6)$$

By changing the crystal orientation relative to the laboratory, anisotropies in $\gamma(\mathbf{p})$ can be observed.[2] In some substances, such anisotropies are negligibly small over the experimentally accessible range of p_z and, of course, they are averaged out in polycrystalline materials, where effectively $\gamma(p)=\langle\gamma(p_z)\rangle$.

The theoretical problem then is reduced to deriving $|\Phi(\mathbf{p})|^2$ for the crystal and an injected positron. From it $I(p_z)$ can be calculated, by Eq. (5), and the p dependence compared with angular correlation experiments on a relative scale in $I(p_z)$. The absolute magnitude can be compared separately with experiment by the annihilation rates, as given by Eq. (4).

It follows from the periodicity of the crystal lattice that

$$|\Phi(\mathbf{p})|^2=\sum\nolimits_{\mathbf{k}_+} g(\mathbf{k}_+)\sum\nolimits_{\mathbf{K}} \delta_{\mathbf{p},\mathbf{k}_++\mathbf{k}_-+\mathbf{K}}|\Phi_{\mathbf{k}_++\mathbf{k}_-}{}^c(\mathbf{p})|^2, \quad (7)$$

where $\mathbf{K}$ is a reciprocal lattice vector; $\mathbf{k}_+$ is the wave vector of the positrons with distribution $g(\mathbf{k}_+)$, and $\mathbf{k}_-$ the wave vector of the electrons ranging over all occupied electronic states in the crystal up to some maximum value $(\mathbf{k}_-)_{\max}$. We shall abbreviate $\boldsymbol{\kappa}=\mathbf{k}_++\mathbf{k}_-$ in the following. $\Phi_\kappa{}^c(\mathbf{p})$ denotes the Fourier transform of $\Psi_\kappa(\mathbf{x})$, as in Eq. (2), the integration now extending only over the unit cell. We decompose $\Phi_\kappa{}^c(\mathbf{p})$ by subdividing the unit cell into atomic cells, one centered about each atom in the unit cell. If $\mathbf{d}_j$ is the position of the jth atomic cell in the unit cell, $\Phi_\kappa{}^c(\mathbf{p})$ becomes

$$\Phi_\kappa{}^c(\mathbf{p})=\sum\nolimits_j e^{-i\mathbf{p}\cdot\mathbf{d}_j}\varphi_j(\mathbf{p};\boldsymbol{\kappa})=\sum\nolimits_j e^{-i\mathbf{p}\cdot\mathbf{d}_j} \times\int_{\text{atomic cell } j}\psi_j(\mathbf{x};\boldsymbol{\kappa})e^{-i\mathbf{p}\cdot\mathbf{x}}d^3x\,, \quad (8)$$

where $\varphi_j(\mathbf{p};\boldsymbol{\kappa})$ is the Fourier transform of $\Psi_\kappa(\mathbf{x})$ in the jth atomic cell. The particular form in which Eq. (8) can be employed depends on the approximations chosen for $\Psi_\kappa(\mathbf{x})$ in typical situations, ranging from free electrons in crystals of simple metals to tightly bound electrons in molecular solids. We illustrate this for a lattice with a basis of two atoms 1 and 2. The extension to lattices with arbitrary basis is obvious.

(I) For free particles, $\Psi_\kappa(\mathbf{x})$ is a plane wave and $\varphi_j(\mathbf{p};\boldsymbol{\kappa})$ is nonzero only for $\mathbf{p}=\boldsymbol{\kappa}$; that is, the photons carry away just the momenta of the annihilating particles.

The cell approximation implies that the wave function in the unit cell can be written in the form $\psi_c(\mathbf{x};\boldsymbol{\kappa})=\psi_1(\mathbf{x};\boldsymbol{\kappa})+\psi_2(\mathbf{x};\boldsymbol{\kappa})\exp(i\boldsymbol{\kappa}\cdot\mathbf{d}_{12})$, where $\psi_j(\mathbf{x};\boldsymbol{\kappa})=u_j(\mathbf{x};\boldsymbol{\kappa})\exp(i\boldsymbol{\kappa}\cdot\mathbf{x})$, the function $u_j(\mathbf{x};\boldsymbol{\kappa})$ being the periodic part of the wave function in the jth atomic cell. In the original form of the cell approximation, one sets $u_j(\mathbf{x};\boldsymbol{\kappa})\simeq u_j(\mathbf{x};0)$ and obtains

$$|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\boldsymbol{\kappa}=\mathbf{K}}=|u_1(\mathbf{K})|^2+|u_2(\mathbf{K})|^2+2|u_1(\mathbf{K})|\,|u_2(\mathbf{K})|\cos(\mathbf{K}\cdot\mathbf{d}_{12})\,, \quad (9)$$

where $u_j(\mathbf{K})$ is the Fourier transform of $u_j(\mathbf{x};0)$ with regard to $(\mathbf{p}-\boldsymbol{\kappa})=\mathbf{K}$. Writing $\mathbf{K}$ in terms of the unit reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$,

$$\mathbf{K}=2\pi\{h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3\}\,,\quad h,\,k,\,l=0,\,\pm1,\,\pm2,\cdots,$$

we have specifically in lattices with NaCl structure that

$$|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\boldsymbol{\kappa}=\mathbf{K}}=|u_1(\mathbf{K})\pm u_2(\mathbf{K})|^2, \quad (10)$$

where the plus sign applies for $(h+k+l)=$ even integer, the minus sign otherwise.

In the general case, where the $\boldsymbol{\kappa}$ dependence of $u_j(\mathbf{x};\boldsymbol{\kappa})$ is taken into account, forms similar to Eq. (9) obtain, but $u_j(\mathbf{K})$ will then not depend merely on the difference $(\mathbf{p}-\boldsymbol{\kappa})$, but on both arguments $(\mathbf{p},\boldsymbol{\kappa})$ separately.

One might expect that Approximation (I) applies whenever an itinerant electron model offers an adequate description of the properties of the crystal (metals, intermetallic compounds, covalent and ionic crystals).

(II) If we use tight-binding approximations for each atomic cell, in the sense that the wave function in the unit cell is represented by $\psi_c(\mathbf{x};\boldsymbol{\kappa})=\psi_1(\mathbf{x})+\psi_2(\mathbf{x})\times\exp(i\boldsymbol{\kappa}\cdot\mathbf{d}_{12})$, we obtain instead of Eq. (9)

$$|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\boldsymbol{\kappa}=\mathbf{K}}=|\varphi_1(\mathbf{p})|^2+|\varphi_2(\mathbf{p})|^2+2|\varphi_1(\mathbf{p})|\,|\varphi_2(\mathbf{p})|\cos(\mathbf{K}\cdot\mathbf{d}_{12})\,. \quad (11)$$

Specifically in lattices with NaCl structure,

$$|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\boldsymbol{\kappa}=\mathbf{K}}=|\varphi_1(\mathbf{p})\pm\varphi_2(\mathbf{p})|^2. \quad (12)$$

For a more general admixture of atomic states, as it appears in solving the degeneracy problem between atoms 1 and 2, the interference term again will not depend only on the difference $(\mathbf{p}-\boldsymbol{\kappa})$ but on both $(\mathbf{p},\boldsymbol{\kappa})$ separately.

Approximation (II) should apply if the states in one atomic cell are almost degenerate with the states in the atomic cells of the same kind in all surrounding unit cells of the lattice (semiconductors, insulators).

(III) In certain solids, it suffices to choose a tight-binding approximation for the entire unit cell of the form $\psi_c(\mathbf{x};\boldsymbol{\kappa})=\psi_1(\mathbf{x})+\psi_2(\mathbf{x})$, in which case,

$$|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\boldsymbol{\kappa}=\mathbf{K}}=|\varphi_1(\mathbf{p})|^2+|\varphi_2(\mathbf{p})|^2+2|\varphi_1(\mathbf{p})|\,|\varphi_2(\mathbf{p})|\cos(\mathbf{p}\cdot\mathbf{d}_{12})\,. \quad (13)$$

This form should describe substances like condensed

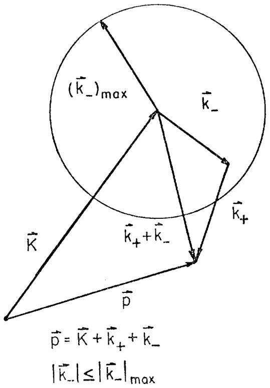

FIG. 1. Restrictions imposed on the summation leading to Eq. (19).

diatomic molecules interacting by van der Waals forces (molecular crystals).

(IV) In extreme tight-binding situations within each atomic cell, no phase relations exist within and between the unit cells, and

$$|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\kappa=\mathbf{K}} = |\varphi_1(\mathbf{p})|^2 + |\varphi_2(\mathbf{p})|^2. \qquad (14)$$

This approximation should be good, e.g., for highly ionic crystals, diatomic van der Waals crystals, and ion cores.

We note from these examples that, in the majority of cases, a cross term appears which depends on the geometrical structure of the unit cell. Such terms have not been included heretofore in calculations of the positron annihilation in lattices with a basis. Specifically in the previous work on ionic crystals referred to in the Introduction, Approximation (IV) had been adopted with the additional assumption of an affinity between the positrons and the negative ions so strong that $|\varphi_{\text{pos.ion}}(\mathbf{p})|^2 = 0$. But as our example LiH demonstrates, such cross terms can play an important role in the angular correlation of the two gamma quanta created by the annihilation of positrons in crystals.

2. TEMPERATURE EFFECTS

Equation (7) had been derived for an adiabatically rigid lattice and an unspecified distribution of positron momenta $g(\mathbf{k}_+)$. If at the time of annihilation the positrons are in thermal equilibrium with the lattice of temperature T,

$$g(\mathbf{k}_+,T) = (\pi^{1/2}\zeta)^{-3} \exp(-k_+{}^2/\zeta^2), \qquad (15)$$

where

$$\zeta(T) = (2m_+{}^* k_B T)^{1/2}. \qquad (16)$$

The effective positron mass is denoted by $m_+{}^*$, and k_B stands for Boltzmann's constant.

Each lattice point executes thermal vibrations about its equilibrium position, of mean-square amplitude $\langle U^2(T)\rangle$, and Debye-Waller factors appear modifying $|\Phi_\kappa{}^c(\mathbf{p})|^2$. The result is written conveniently in the form

$$|\Phi_\kappa{}^c(\mathbf{p},T)|^2{}_{\mathbf{p}-\kappa=\mathbf{K}} = |\textstyle\sum_j e^{-i\mathbf{p}\cdot\mathbf{d}_j}\varphi_j(\mathbf{p};\boldsymbol{\kappa})e^{-W_j(\mathbf{K},T)}|^2$$
$$+\text{small damping terms}, \qquad (17)$$

where

$$2W_j(\mathbf{K},T) = K^2\langle U_{\mathbf{K}}{}^2(T)\rangle_j. \qquad (18)$$

$\langle U_{\mathbf{K}}{}^2(T)\rangle_j$ denotes the mean-square amplitude of the jth atom in the unit cell along the direction of $\mathbf{K}$. Unlike in x-ray diffraction, the momenta $\mathbf{p}$ resolved by angular-correlation measurements do not extend far enough to probe the range where the contributions from $\mathbf{K}>0$ become dominant, and normally the effect of the Debye-Waller factors can be neglected.

Observing the restrictions imposed by the δ function, cf. Fig. 1, we integrate Eq. (7) with Eq. (15) for a spherically symmetric $(\mathbf{k}_-)_{\max}$. Abbreviating $\beta(T) \equiv \zeta(T)/|\mathbf{k}_-|_{\max}$, we obtain

$$|\Phi(\mathbf{p},T)|^2 = \textstyle\sum_{\mathbf{K}} \mathfrak{B}(|\mathbf{K}-\mathbf{p}|/$$
$$|\mathbf{k}_-|_{\max},\beta(T))\,|\Phi_\kappa{}^c(\mathbf{p})|^2{}_{\mathbf{p}-\kappa=\mathbf{K}}, \qquad (19)$$

where

$$\mathfrak{B}(y,\beta)$$
$$= \frac{1}{2}\left\{1+\operatorname{erf}[(1-y)/\beta] - \frac{\beta}{\pi^{1/2}y}\exp[-(1-y)^2/\beta^2]\right\}$$
$$-\frac{1}{2}\left\{1-\operatorname{erf}[(1+y)/\beta] - \frac{\beta}{\pi^{1/2}y}\exp[-(1+y)^2/\beta^2]\right\}. \qquad (20)$$

In the experimentally important ranges of $y \sim 1$ and $\beta \sim 0.1$, the second bracket vanishes. Figure 2 shows the function $\mathfrak{B}(y,\beta)$ for different $\beta(T)$ of interest. At low temperatures, $\beta \to 0$, and we retrieve Eq. (7) with

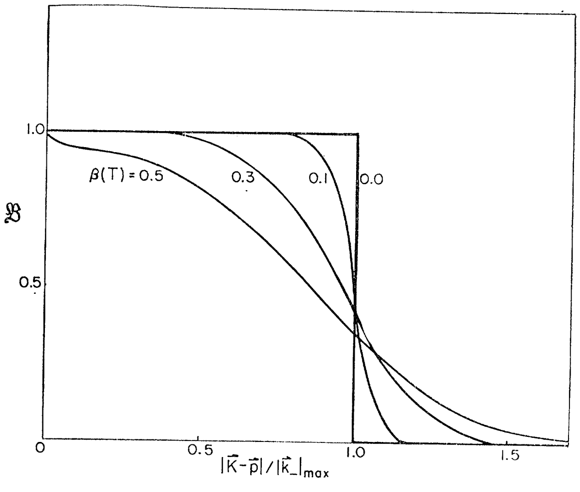

FIG. 2. The temperature function $\mathfrak{B}(|\mathbf{K}-\mathbf{p}|/|\mathbf{k}_-|_{\max}, \beta(T))$, Eq. (20), for representative values of $\beta(T) = \zeta(T)/|\mathbf{k}_-|_{\max}$.

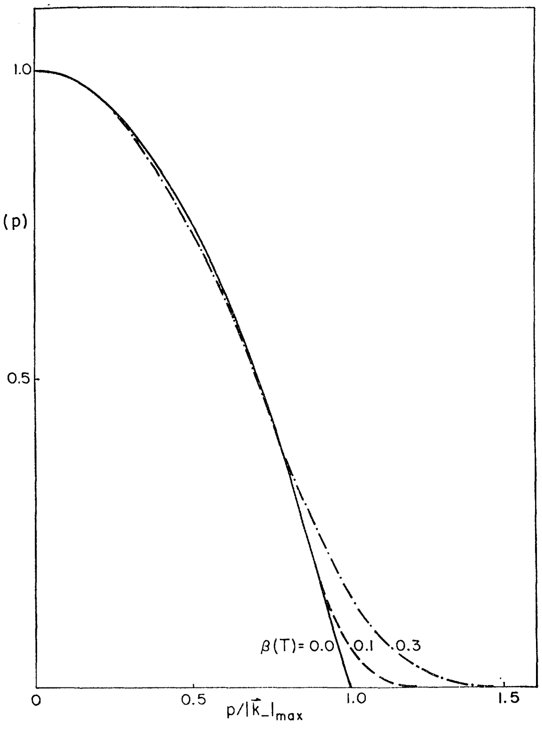

FIG. 3. Effect of temperature on the angular correlation function $I(p)$, Eq. (5), normalized to unity at $p=0$.

$g(\mathbf{k}_+)=\delta_{\mathbf{k}_+,0}$, since

$$\lim_{\beta\to 0}\mathfrak{B}\left(\frac{|\mathbf{K}-\mathbf{p}|}{|\mathbf{k}_-|_{\max}},\beta\right)=\delta_{\mathbf{p},\mathbf{k}_-+\mathbf{K}}. \tag{21}$$

This temperature effect is incorporated into the angular correlation function $I(p)$ by inserting Eq. (19) into Eq. (5) and integrating. On further integration, we retrieve the Γ of Eq. (4) which is independent of β. As illustrated in Fig. 3, the thermal distribution of the positron momenta smears the distribution near $|\mathbf{k}_-|_{\max}$. Here and in the following $I(p)$ is always taken to be normalized to unity at $|\mathbf{p}|=0$. If applied to simple metals for example, $|\mathbf{k}_-|_{\max}$ is to be identified with the maximum momentum k_F of the Fermi distribution of the conduction electrons. Even at the highest experimentally accessible temperatures, the effect of the lifting of the degeneracy of the Fermi distribution is negligibly small compared to the smearing of $I(p)$ by $g(\mathbf{k}_+,T)$.

Stewart and Shand[9] apparently interpreted the temperature smearing of their angular correlation data on Na in a similar manner, and found it to be consistent with an average effective positron mass of $(1.9\pm0.3)m_0$, where m_0 denotes the free-electron rest mass.

Before such analysis, it is advantageous to subtract out the normally temperature-insensitive parts of the angular distribution, such as contributions from core annihilations and experimental background. This suggests the study of the difference function

$$\Delta I=I(T_2)-I(T_1), \tag{22}$$

which primarily retains the $\mathbf{K}=0$ part of the distribution. This function has a conspicuous maximum ΔI_M at some $p=p_M$, as illustrated for different temperatures T_1, T_2 in Fig. 4. Under favorable conditions, the quantities $(\Delta I_M,p_M)$ can be measured accurately. To third-order terms the maximum is given by

$$\begin{aligned}\Delta I_M(T_1,T_2)=\tfrac{1}{4}\Delta\beta_M+(\pi^{-1/2}-\tfrac{1}{4})\\ \times[\Delta\beta_M-\Delta\beta_M{}^2+(2/\pi^{1/2})\Delta\beta_M{}^3],\end{aligned} \tag{23}$$

with the abbreviations

$$\beta_{1,2M}=\zeta(T_{1,2})/p_M$$

and

$$\Delta\beta_M{}^n=\beta_{2M}{}^n-\beta_{1M}{}^n.$$

Given $(\Delta I_M,p_M)$, the effective positron mass can be extracted by Eq. (23), and $|\mathbf{k}_-|_{\max}$ by Eq. (24).

$$|\mathbf{k}_-|_{\max}=[1-(\pi^{-1/2}-\tfrac{1}{6})\beta_{1M}\beta_{2M}]p_M. \tag{24}$$

Although the condition $|\mathbf{k}_-+\mathbf{k}_+|=|\mathbf{k}_-|_{\max}$ implies that positrons with all momenta $0\leq|\mathbf{k}_+|\leq|\mathbf{k}_-|_{\max}$ are being probed here, the exponential form of $g(\mathbf{k}_+,T)$, Eq. (15), insures that merely positrons with $\mathbf{k}_+\simeq0$ contribute significantly. Conversely only electrons with $|\mathbf{k}_-|$ very close to $|\mathbf{k}_-|_{\max}$ participate. In this sense, the experimental determination of the position of the maximum, at p_M, and its height ΔI_M amounts to a measurement of the effective mass $m_+{}^*$ of positrons with $\mathbf{k}_+\simeq0$. Moreover for metals, the measured $|\mathbf{k}_-|_{\max}$, if compared with the free-electron k_F, determines an

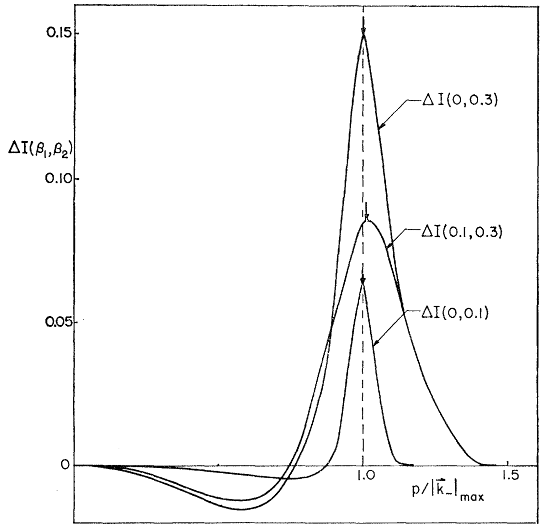

FIG. 4. Examples of the p dependence of the difference function $\Delta I(\beta_1,\beta_2)$ for normalized angular correlation functions at representative values of $\beta(T)$. The positions of the maxima, ΔI_M, are indicated by arrows.

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[9] A. T. Stewart and J. B. Shand, Bull. Am. Phys. Soc. **10**, 21 (1965).

effective mass m_-^* of the electrons at the Fermi surface. For example from the graphs of data on Na,[9] taking its Fermi surface to be spherical, we read that $m_+^*(\mathbf{k}_+\simeq 0) = 1.7\ m_0$ and $m_-^*(k_F) = 0.9\ m_0$, approximately.

On approaching the melting point the contributions from the high-$\mathbf{K}$ components to the angular distribution are suppressed such that relatively more annihilations appear in the $\mathbf{K}=0$ domain. Because of our normalization convention, ΔI_M will then be smaller than it would have been for the perfectly ordered crystal of the same temperatures. That is, the effective positron mass as determined by Eq. (23) will appear to decrease in the melting range of the crystal, the reduction being a measure of the loss of long-range order in the lattice. To exploit this method further, it may be possible to study the anisotropies of $\beta(m_+^*)$ and of $|\mathbf{k}_-|_{\max}$ along different crystal axes by performing experiments like those of Berko and Plaskett[8] at various temperatures.

3. ENHANCEMENT

Since Bloch wave functions govern the positrons in a crystal lattice, the positron-electron Coulomb interaction term in the Schrödinger equation for the electrons in a unit cell is of order L^{-1}, where L is the number of unit cells in the crystal; i.e., the positron-electron interaction has no appreciable effect on any particular electron. Still, the accumulative polarization effect on all the N electrons in the lattice can be appreciable in the proximity of the positron. This is confirmed by the positron lifetimes in metals, for example, which in many instances signify electron densities at the site of the positron several times higher than the mean. The large effective positron mass in Na just discussed indicates that the positrons carry the burden of a polarized electron cloud. However on scaling $I(\mathbf{p})$, the measured angular distributions follow very nearly the distributions calculated on the basis of unenhanced electron wave functions. If we integrate the latter as indicated in conjunction with Eq. (5), we obtain unenhanced lifetimes which are at variance with experiment. This observation suggests that enhancement is insensitive to $\mathbf{p}$; it manifests itself primarily in the absolute values of $I(\mathbf{p})$ and thus remains hidden in the arbitrary scale of the experimental angular distributions. Because of this circumstance, to be amplified further in the following, we could present the preceding discussions without direct reference to positron-electron correlation, except in an average way by introducing an effective m_+^* in $g(\mathbf{k}_+)$. In preparation for the calculations to be reported in Sec. 4, we now must consider enhancement explicitly. The problem of enhancement in the uniform electron gas has been studied extensively by Ferrell[3] and Kahana.[10] For our purposes, we need to develop ways of handling enhancement in nonuniform electron distributions, at least in an approximate manner.

Formally, a wave function enhancement factor can be derived as follows. As did Krisement[11] for the electron gas, we construct the wave function, in Eq. (1), of the interacting positron-electron system by introducing a pair correlation function G_{+-}.

$$\Psi(\mathbf{x}_1,\cdots,\mathbf{x}_n,\cdots,\mathbf{x}_N;\mathbf{x}_+)=\Psi_0(\mathbf{x}_1,\cdots,\mathbf{x}_n,\cdots,\mathbf{x}_N)\times G_{+-}(|\mathbf{x}_1-\mathbf{x}_+|,\cdots,|\mathbf{x}_n-\mathbf{x}_+|,\cdots,|\mathbf{x}_N-\mathbf{x}_+|)\chi_+(\mathbf{x}_+)\,, \tag{25}$$

where χ_+ is the wave function of the noninteracting positron. Ψ_0 is the wave function of the electron system taken to be unaffected by the presence of the positron, by virtue of what has been said above. The ansatz

$$G_{+-}=G_+G_- \tag{26}$$

splits G_{+-} into a part G_+ which affects only the positron, and a part G_- affecting only the electrons. We identify $G_+\chi_+$ with the positron wave function ψ_+ in the lattice characterized by Ψ_0, and obtain for the wave function in Eq. (2)

$$\Psi_n(\mathbf{x})=\psi_+(\mathbf{x})\xi_n(\mathbf{x})\Psi_{0n}(\mathbf{x})\,, \tag{27}$$

where

$$\xi_n(\mathbf{x})=\Psi_{0n}^{-1}(\mathbf{x})\int\Psi_0(\mathbf{x}_1,\cdots,\mathbf{x}_n,\cdots,\mathbf{x}_N)\times G_-(|\mathbf{x}_1-\mathbf{x}|,\cdots,|\mathbf{x}_n-\mathbf{x}|,\cdots,|\mathbf{x}_N-\mathbf{x}|)\times\delta(\mathbf{x}_n-\mathbf{x})d^3x_1\cdots d^3x_n\cdots d^3x_N \tag{28}$$

is the enhancement factor.

For our purposes, it suffices to estimate $\xi(\mathbf{x})$ by the statistical method. The electrons, of total density $\rho_0(\mathbf{x})$, if treated as free and on equal footing, form a local Fermi surface corresponding to a Fermi momentum $k_F(\mathbf{x})$. Denoting the density matrix elements by $\rho(\mathbf{x},\mathbf{x}')$ and

$$\Xi(\mathbf{x},\mathbf{x}')=\xi(\mathbf{x})\xi^*(\mathbf{x}')\,,$$

Eq. (2) with Eq. (27) becomes

$$|\Phi(\mathbf{p})|^2=\int d^3xd^3x'\rho_+(\mathbf{x},\mathbf{x}')\Xi(\mathbf{x},\mathbf{x}')\rho_0(\mathbf{x},\mathbf{x}')e^{-i\mathbf{p}\cdot(\mathbf{x}-\mathbf{x}')}\,, \tag{29}$$

where now

$$\rho_0(\mathbf{x},\mathbf{x}')=\frac{2}{(2\pi)^3}\int_{k'\leq k_F(\mathbf{x})}e^{i\mathbf{k}'\cdot(\mathbf{x}-\mathbf{x}')}d^3k'\,. \tag{30}$$

Taking $\psi_+(\mathbf{x})$ to vary slowly over the distance $|\mathbf{x}-\mathbf{x}'|$ in which $\rho_0(\mathbf{x},\mathbf{x}')$ vanishes, we can average over a δ function and obtain

$$|\Phi(\mathbf{p})|^2=2\int d^3x\rho_+(\mathbf{x})\Xi(\mathbf{x})\Theta(p-k_F(\mathbf{x}))\,, \tag{31}$$

where $\Theta(x)=(1/2)[1-(x/|x|)]$ is the step function. At finite temperatures the step function is to be replaced by $\mathfrak{B}(p/k_F(\mathbf{x});\zeta(T)/k_F(\mathbf{x}))$. After integration we

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[10] S. Kahana, Phys. Rev. **117**, 123 (1960); **129**, 1622 (1963).

[11] O. Krisement, Phil. Mag. **2**, 245 (1957).

obtain the angular-correlation function in the statistical approximation

$$I(p)=\frac{\alpha^3}{4\pi}\int d^3x\rho_+(\mathbf{x})\Xi(\mathbf{x})\Theta(p-k_F(\mathbf{x}))(k_F{}^2(\mathbf{x})-p^2)\,, \quad (32)$$

and with

$$k_F{}^3(\mathbf{x})=3\pi^2\rho_0(\mathbf{x})\,,$$

the corresponding annihilation rate

$$\Gamma=\pi\alpha^3\int d^3x\rho_+(\mathbf{x})\Xi(\mathbf{x})\rho_0(\mathbf{x})\,. \quad (33)$$

Equation (32) bears out the fact that the dependence of $I(p)$ on p is affected only weakly by the enhancement.

In linear-response theory, the enhancement factor is given by

$$\Xi(\mathbf{x})=1+(2\pi)^{-3}\rho_0{}^{-1}(\mathbf{x})\times\int d^3q[\epsilon^{-1}(\mathbf{q},\omega;\rho_0(\mathbf{x}))-1]_{\omega=0}\,, \quad (34)$$

where ϵ is the wave number and frequency-dependent dielectric constant of an electron gas of density $\rho_0(\mathbf{x})$. We have evaluated Eq. (34) with Lindhard's quantum-mechanical dielectric constant of the electron gas.[12] It applies to the weak interaction case, i.e., as long as the parameter $\chi^2(\mathbf{x})=(3\pi^5\rho_0(\mathbf{x}))^{-1/3}<1$, which holds over the range of $\rho_0(\mathbf{x})$ encountered in the solids of interest here. In this range, the approximate relation

$$\Xi(\mathbf{x})=1+1.153\rho_0{}^{-1/4}(\mathbf{x}) \quad (35)$$

represents the exact function to better than 0.3%.

We conclude that for the problems at hand it should be a good approximation to simplify Eq. (27) by setting $\Psi_n(\mathbf{x})=\psi_+(\mathbf{x})\Xi^{1/2}(\mathbf{x})\Psi_{0n}(\mathbf{x})$, since in crystals generally the positron wave function is large only in domains where the electron density varies slowly. It is small in domains where the electron density may vary rapidly but in any case is high, and the errors made in still using this approximation should be unimportant.

4. AN EXAMPLE: LiH

The lithium hydride crystal has attracted theoretical interest for many years because of its simple electronic configuration. The first investigation, by the cell method, into the electronic structure was made by Ewing and Seitz.[13] More recently, Lundqvist[14] has calculated the electron-density distribution by the molecular-orbital method. In light of the observation of Stewart and March,[5] namely, that the angular correlation data appeared to be in disagreement with the x-ray scattering data, it became important to calculate the electron wave functions and the positron wave function in the LiH crystal on the same footing. This would enable one to calculate in a consistent way the x-ray structure factors and the angular correlation function for positron annihilations. Comparison with experiment should then show whether the two sets of data are, in fact, intrinsically consistent with one another, or whether some basic elements are missing in the theoretical interpretation of either.

In pursuing this program, we consider the unit cell in the face-centered cubic lattice of the LiH crystal to be made up of two equal atomic cells centered about the Li and the H atom. We approximate the atomic cells by Wigner-Seitz spheres of equal volume and impose the conditions of continuity on the electron and positron wave functions across the sphere boundaries. The two K-shell electrons are taken to be part of the Li core and are represented by screened hydrogenic wave functions. For the two valence electrons, we construct the potential in each atomic cell in the manner summarized in Eq. (36). Atomic units are used throughout.

$$V=V^{\text{Coulomb}}+V^{\text{exchange}}+V^{\text{correlation}}+V^{\text{Madelung}}\,, \quad (36)$$

with the following definitions:

$$V^{\text{Coulomb}}(r)=-\frac{Z}{r}+\sum_j\int_{\text{cell}}\frac{\rho_j(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}d^3x'\,. \quad (37)$$

The first term is due to the nucleus in the cell, of atomic number Z, the second to all electrons in the cell.

$$V^{\text{exchange}}(r)=-[(3/\pi)\rho_{\text{valence}}(r)]^{1/3}\,, \quad (38)$$

the Dirac approximation of the exchange energy, assumes that locally the electrons behave as a uniform electron gas of density $\rho_{\text{valence}}(r)$:

$$V^{\text{correlation}}(r)=-\frac{(1-\ln 2)}{\pi^2}\times\ln\left[1+\left(\frac{3}{\pi}\rho_{\text{valence}}(r)\right)^{1/3}\frac{(0.89\pi\eta-1)}{(1-\ln 2)}\right], \quad (39)$$

where $\eta=(4/9\pi)^{1/3}$. This correlation potential is based on an interpolation formula first given by Lewis.[15,16]

$$V^{\text{Madelung}}(r)=\frac{Mq_{\text{eff}}}{R}-\frac{(1-q_{\text{valence}}/s)}{R}\,, \quad (40)$$

where M is the Madelung constant, R the nearest-neighbor distance in the crystal, s the number of

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[12] J. Reinheimer and W. Brandt, Bull. Am. Phys. Soc. **9**, 354 (1964). The results for the free-electron gas are identical to those of J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1959), obtained by a different technique.

[13] D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936).

[14] S. O. Lundqvist, Arkiv Fys. **8**, 177 (1954).

[15] H. W. Lewis, Phys. Rev. **111**, 1554 (1958).

[16] D. F. Du Bois and M. G. Kivelson, Phys. Rev. **127**, 1182 (1962).

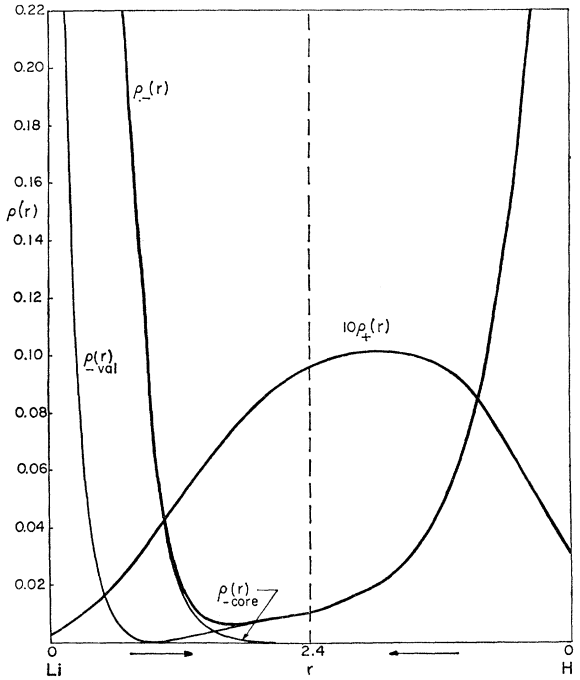

FIG. 5. The positron and electron densities, $\rho_+(r)$ and $\rho_-(r)$, in the unit cell of the LiH crystal along the line connecting the atomic Li and H cells across the cell boundary at $r=2.4$ atomic units.

valence electrons per unit cell,

$$q_{\text{eff}}=Z-\int_{\text{cell}}\rho_{\text{total}}(\mathbf{x})d^3x\,,$$

and

$$q_{\text{valence}}=\int_{\text{cell}}\rho_{\text{valence}}(\mathbf{x})d^3x\,.$$

Equation (40) represents the potential set up in the reference cell by the other atomic cells in the crystal. The second term is a correction to the Madelung potential which arises if one assumes that the exchange hole is distributed throughout the cell with the same density as a valence electron.

In order that the valence electron wave functions be orthogonal to the core wave functions a pseudopotential, $V^{\text{pseudo}}(r)$, was constructed following the Schmidt orthogonalization method.[17]

With this potential self-consistent wave functions for the valence electrons in the LiH crystal were calculated in the cell approximation. We used the IBM 7094 computer of the New York University Computing Center. The positron wave function was calculated in the same approximation, after appropriate modifications of $V(r)$, which amount to omitting $V^{\text{exchange}}(r)$, $V^{\text{pseudo}}(r)$ and the second term in Eq. (40). In Fig. 5, the resulting densities along the line connecting neighboring Li and H cells are shown. The rapid rise of the electron density toward the origin of the Li cell derives mainly from the K-shell electrons. In the H cell, the electron density rises more slowly in such a manner that the minimum falls within the Li cell. As a consequence, the maximum of the positron density falls inside the H cell. We note that the positron density has finite values at the nuclei. It rises with the slope $(d\rho_+(r)/dr)_{r=0}=2Z\rho_+(0)$.

From the electron density distribution we calculated the x-ray structure factors as a function of $(\sin\theta)/\lambda$ in the standard manner.[18] In the range of the detectable Bragg reflections, results from the cell method agree with those obtained by the molecular orbital method.[19] By fortunate coincidence Calder *et al.*[20] published 21 structure factors of LiH, covering a very large range of $(\sin\theta)/\lambda$, just after this investigation was begun. Before the theoretical values can be compared with these data, allowance must be made for the finite temperature by appropriate Debye-Waller factors. We fitted the theoretical curves to the experimental data by taking separate values of B for the Li and H atoms in the relation $W=B[(\sin\theta)/\lambda]^2$, with the result that $B_{\text{Li}}=1.12$ Å^2, and $B_{\text{H}}=1.80$ Å^2; this is to be compared

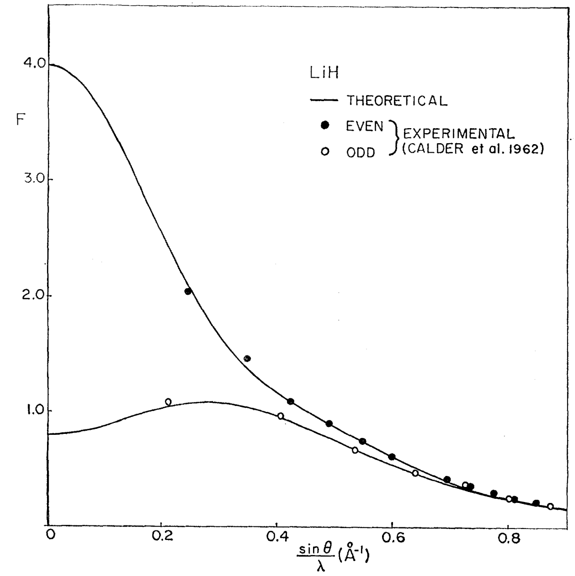

FIG. 6. Temperature corrected theoretical structure factors of LiH compared with the experimental points obtained by Calder *et al.* (Ref. 20).

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[17] See, e.g., J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[18] See, e.g., R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, Ltd., London, 1948).

[19] I. Waller and S. O. Lundqvist, Arkiv Fys. **7**, 121 (1953). The even and odd form factors in their paper begin to coalesce at somewhat lower values of $(\sin\theta)/\lambda$ than the ones calculated here and the experimental data. This slight discrepancy can be traced quantitatively to the inaccuracy near the hydrogen nucleus of the screened hydrogenic wave function employed in their paper. We benefitted from an enlightening discussion with Professor Waller on this point.

[20] R. S. Calder, W. Cochran, D. Griffiths, and R. D. Lowde, J. Phys. Chem. Solids **23**, 621 (1962).

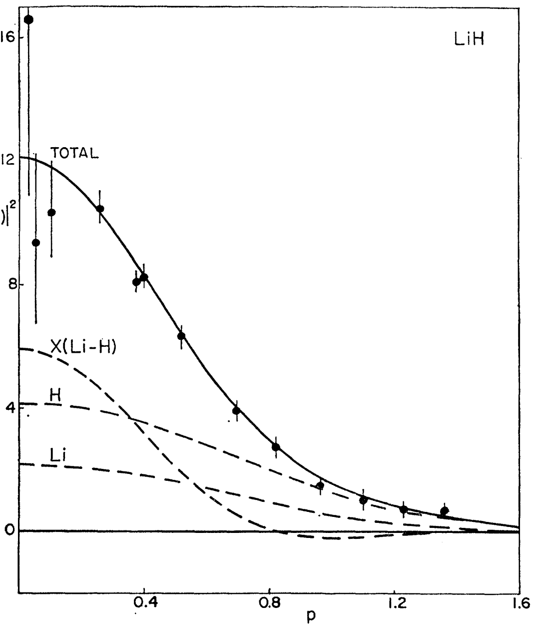

FIG. 7. Comparison of the theoretical momentum density of annihilating positron-electron pairs in LiH (solid curve) with the experimental points of Stewart and March (Ref. 5). The dashed curves (Li and H) derive from the separate atomic cells, and X from the cross term.

with the values $B_{\mathrm{Li}}=1.22\pm0.10$ Å^2 and $B_{\mathrm{H}}=1.80\pm0.03$ Å^2 derived from neutron diffraction data.[20] As Fig. 6 shows, we find agreement over the entire range of $(\sin\theta)/\lambda$. The intercept of the even reflection curve with the ordinate is equal to the total number of electrons in the unit cell, four in LiH, by the sum rule. The intercept of the odd reflection curve with the ordinate is equal to the difference between the electron charge attributed to the Li atomic cell and that attributed to the H atomic cell. Writing symbolically $\mathrm{Li}^{+a}\mathrm{H}^{-a}$ to emphasize the degree of ionic character in the unit cell, our self-consistent density distribution yields $a=0.60$. Table II summarizes the corresponding values quoted by other investigators.

TABLE I. The effective charge per atomic cell of $\mathrm{Li}^{+a}\mathrm{H}^{-a}$ (in units of the electronic charge).

	a	Reference
Theoretical	0.35	Ewing and Seitz[a] (1936)
	0.30	Lundqvist[b] (1954)
	0.60	This paper (1965)
Experimental	0.25 ± 0.25	Ahmed[c] (1951)
	0.46 ± 0.01	Cochran[d] (1958)
	0.52 ± 0.007	Calder, Cochran, Griffiths, and Lowde[e] (1962)

[a] Reference 13.
[b] Reference 14.
[c] M. S. Ahmed, Phil. Mag. 42, 997 (1951).
[d] W. Cochran, Rev. Mod. Phys. 51, 47 (1958).
[e] Reference 20.

We conclude that the burden for the discrepancy observed by Stewart and March must be placed on the interpretation of the angular correlation data. In Fig. 7 we indicate the various contributions to the total $|\Phi(p)|^2$ calculated in the cell approximation, including enhancement as described in Sec. 3. The momentum densities of the positron-electron pairs annihilating in the Li cells and in the H cells decline monotonically with increasing p. The curve denoted by X accounts for the redistribution caused by the interference between the two atoms in the unit cell. This term sharpens the distribution as compared to what would have been obtained by merely taking Approximation (IV). The total distribution is in close agreement, over the entire range of momenta, with the experimental data prepared according to Eq. (6).

Without enhancement, we calculate a $|\Phi(p)|^2$ which differs in magnitude but, if normalized to the same value of the ordinate, lies undiscernibly close to the solid curve on the scale of Fig. 7. This confirms for our system the essential point brought out by Eq. (31), namely, that the enhancement has only a small effect on the p dependence of the angular correlation. But if integrated in the sense of Eq. (4), the resulting lifetime is four times as long as that obtained from the $|\Phi(p)|^2$ with enhancement.

As a global check, we integrate over this theoretical curve and, by Eq. (4), obtain a positron lifetime in LiH equal to 2.44×10^{-10} sec. The measured dominant lifetime is $(2.1\pm0.3)\times10^{-10}$ sec.[7]

In summary, the angular correlation data reported by Stewart and March[5] are consistent with our conclusions about the role played by the phase relations of the positron-electron wave function within the unit cell of a diatomic lattice: They sharpen the angular correlation function of the LiH crystal.

ACKNOWLEDGMENT

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