Effects of electron-positron correlation on positron annihilation: Self-consistent band-structure calculations in Al

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(Received 14 September 1981)

A formalism has been developed for calculating positron-annihilation characteristics in perfect solids and solids containing defects taking into account the effects of electron-positron correlation self-consistently. The lifetime and two-dimensional angular-correlation spectra have been calculated for positrons annihilating in defect-free aluminum and are in excellent agreement with experiment.

Positron-annihilation spectroscopy has developed into an extremely useful tool for studying the electronic structure of solids. The annihilation characteristics, especially the two-dimensional angular-correlation measurements, provide a wealth of information about the electrons sampled by the positron. In order to interpret the spectra and understand the phenomenon microscopically, a theoretical study of the annihilation process becomes necessary. The problem of a positron in an interacting electron gas has been studied extensively.[1-5] In these calculations the effects of electron-positron correlation are treated accurately, but since details of the electronic structure are ignored, they are expected to give reasonable results only in nearly free-electron-like metals. The alternative approach of band-structure calculations to positron-annihilation studies[6-8] has suffered from the inability to include the effects of electron-positron correlation properly. Enhancement of the lifetime has usually been estimated by the Brandt-Rein-heimer[9] prescription, and there has been some attempt[7] at incorporating momentum-dependent enhancement effects by a generalization of the Kahana theory.[10]

In this Communication, we present a formalism for calculating annihilation characteristics in real metals taking into account the correlation effects self-consistently. The results for positron annihilation in defect-free Al are presented and compared with those from experiment. The formalism is based on the density functional scheme[11] for a two component system. The strong correlation effects enter through the electron-positron correlation energy in the energy functional. Within the local density approximation[11] this is determined by the electron-positron correlation energy for a homogeneous, interacting electron gas, here taken from the results of Arponen and Pajanne.[4]

The energy functional for the electron-positron system is

$$E[n^-,n^+] = \int v^-(\vec{r})n^-(\vec{r})d\vec{r} + \int v^+(\vec{r})n^+(\vec{r})d\vec{r}' + \int \frac{n^-(\vec{r})n^+(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'$$
$$+ \int \frac{n^-(\vec{r})n^-(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}' + \int \frac{n^+(\vec{r})n^+(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}' + G[n^-,n^+] \ , \tag{1}$$

where $v^{-(+)}$ are the ionic potentials, $n^{-(+)}$ the electron and positron densities, and $G[n^-,n^+]$ the kinetic and interaction energy functional.[11] Ideally, in dealing with density-functional theory, one would prefer to ignore the fact that there is only one positron in the system and deal only with densities. However, there is no information available about the variation of electron-positron correlation effects with positron density, and in order to develop a consistent theory it was necessary to treat the positron as a single particle. This necessitates neglect of the positron-positron in-teraction term in Eq. (1) and writing the exchange-correlation energy functional[11] $E_{xc}[n^-,n^+]$ (within the local density approximation) as

$$E_{xc}[n^-,n^+] = \int \epsilon_{xc}^-(n^-(\vec{r}))n^+(\vec{r})d\vec{r}$$
$$+ \int \epsilon_{corr}^{-+}(n^-(\vec{r}))n^+(\vec{r})d\vec{r} \ , \tag{2}$$

where ϵ_{xc}^- is the electron-electron exchange-correlation energy and ϵ_{corr}^{-+} the electron-positron correlation energy in a homogeneous system. Gen-

eralizing the Kohn-Sham scheme[12] leads to the following set of self-consistent equations:

$$[-\nabla^2/2 + v^-(\vec{r}) + V_{\text{Coul}}(\vec{r})$$
$$+\mu_{\text{xc}}(n^-(\vec{r}), n^+(\vec{r}))]\psi_i^-(\vec{r}) = \epsilon_i^- \psi_i^-(\vec{r}) \ ,$$

$$[-\nabla^2/2 + v^+(\vec{r}) - V_{\text{Coul}}(\vec{r}) \tag{3}$$
$$+\epsilon_{\text{corr}}^{-+}(n^-(\vec{r}))]\psi_i^+(\vec{r}) = \epsilon_i^+ \psi_i^+(\vec{r}) \ ,$$

$$\mu_{\text{xc}}(\rho, \rho') = \rho\left[\frac{d\epsilon_{\text{xc}}^-(\rho)}{d\rho}\right] + \epsilon_{\text{xc}}^-(\rho) + \rho'\left[\frac{d\epsilon_{\text{corr}}^{-+}(\rho)}{d\rho}\right] \ ,$$

$$n^-(\vec{r}) = \sum_i |\psi_i^-(\vec{r})|^2, \quad n^-(\vec{r}) = |\psi^+(\vec{r})|^2 \ ,$$

where $\psi^-(\psi^+)$ are the electron (positron) wave functions and $V_{\text{Coul}}(\vec{r})$ the electrostatic potential due to the electrons. Usual band-structure methods can be employed to solve these equations for the electron and positron eigenstates. In this work we have used the self-consistent pseudopotential formalism with a plane-wave basis set.[13] The ionic potential for the positrons $[v^+(\vec{r})]$ was also replaced by a pseudopotential using a method based on the formalism of Kubica and Stott.[14] According to this, the positron wave function is written as a product of a modified Wigner-Seitz wave function and a positron pseudo-wave function. The positron pseudowave function contains all the information about the crystalline environment and is calculated self-consistently. The modified Wigner-Seitz solution, being fairly insensitive to the environment, is calculated only once.

The positron annihilation rate Λ and the annihilation radiation momentum distribution $R(\vec{p})$ are the two quantities of main interest in positron annihilation spectroscopy. The momentum distribution function is defined as

$$R(\vec{p}) = \sum_{\vec{k}nn'G} \langle 0|d_0^\dagger d_0 c_{\vec{k}n}^\dagger c_{\vec{k}n'}|0\rangle A_{\vec{k}n}^*(\vec{G})$$
$$\times A_{\vec{k}n'}(\vec{G})\delta(\vec{p} - \vec{k} - \vec{G}) \ , \tag{4}$$

where $\vec{k}$ is the wave vector and n the band index for the Bloch states, and where d_0 and $c_{\vec{k}n}$ are the annihilation operators for the states ψ^+ and $\psi_{\vec{k}n}^-$, respectively. The expectation value is taken with respect to the actual ground state of the system. The positron is assumed to be in its ground state at the center of the zone. The momentum matrix element $A_{\vec{k}n}(\vec{G})$ is defined as

$$A_{\vec{k}n}(\vec{G}) = \int d\vec{r}\,\exp[-i(\vec{k}+\vec{G})\cdot\vec{r}]\psi_{\vec{k}n}^-(\vec{r})\psi^+(\vec{r}) \ . \tag{5}$$

To calculate the ground-state expectation value $\langle 0|d_0^\dagger d_0 c_{\vec{k}n}^\dagger c_{\vec{k}n'}|0\rangle$ we have employed a method first

used by Lam and Platzman for Compton scattering.[15] Feynman's theorem implies the relation

$$N_{\vec{k}nn'} \equiv \langle 0|d_0^\dagger d_0 c_{\vec{k}n}^\dagger c_{\vec{k}n'}|0\rangle = \left[\frac{\partial E_{\vec{k}nn'}(\lambda)}{\partial\lambda}\right]_{\lambda=0} \ . \tag{6}$$

Here $E_{\vec{k}nn'}(\lambda)$ is the exact ground-state energy of

$$H_{\vec{k}nn'}(\lambda) \equiv H + \lambda d_0^\dagger d_0 c_{\vec{k}n}^\dagger c_{\vec{k}n'} \ ,$$

where λ is an arbitrary parameter. From the density-functional expression for the ground-state energy [Eq. (1)], it is clear that there are two sources of λ dependence in $E_{\vec{k}nn'}(\lambda)$; (a) an explicit dependence coming from $G[n^-, n^+]$ outside of n^-, n^+, and (b) the dependence contained in n^-, n^+. The second dependence can be neglected because of the stationary property of E with respect to n^-, n^+. The difference between $H_{\vec{k}nn'}(\lambda)$ and H is only in the electron-positron interaction term

$$H_{\text{int}} = \sum_{\vec{k}n\,\vec{k}'n'} V_{\vec{k}n,\,\vec{k}'n'} c_{\vec{k}n}^\dagger c_{\vec{k}'n'} d_0^\dagger d_0 \ , \tag{7}$$

where $V_{\vec{k}n,\,\vec{k}'n'}$ is the matrix element of $V(r-r')$, the interaction potential. The local-density approximation [Eq. (2)] then implies that Eq. (6) can be written as

$$N_{\vec{k}nn'} = \int \frac{\partial\epsilon_{\text{corr}}^{-+}(n^-(\vec{r}))}{\partial V_{\vec{k}nn'}} n^+(\vec{r})d\vec{r} \ . \tag{8}$$

In an electron gas there is no analog of an interband interaction and the term on the right-hand side of Eq. (8) is not defined for $n \neq n'$. Only $N_{\vec{k}nn}$ can therefore be calculated from local density theory. In this case the derivative in Eq. (8) is the distribution function in a homogeneous system. Consequently, we have to make an additional assumption of neglecting interband annihilation processes involving an electron in state $\vec{k}n$ and a hole in state $\vec{k}n'$. Since these are second-order processes, their contribution is expected to be small compared to purely intraband annihilation events.

The momentum distribution [Eq. (4)] can then be expressed as

$$R(\vec{p}) = \sum_{\vec{k}n\,\vec{G}} N(\epsilon_{\vec{k}n})|A_{\vec{k}n}(\vec{G})|^2\delta(\vec{p} - \vec{k} - \vec{G}) \ ,$$
$$N(\epsilon) = \int N^0(\epsilon, n^-(\vec{r}))n^+(\vec{r})d\vec{r} \ , \tag{9}$$

where $N^0(\epsilon, n^-(\vec{r}))$ is the momentum distribution function in a homogeneous interacting electron gas expressed as a function of the energy, $\epsilon = p^2/2m$. The function $N(\epsilon)$ differs from the Fermi distribution function in two respects; (a) it is enhanced near the Fermi energy (ϵ_F) and (b) it has a long-range tail

beyond ϵ_F due to transitions caused by correlation effects.[5] Hence, the summation in Eq. (9) is not restricted to bands below ϵ_F as in independent-particle-model (IPM) calculations.[6] The electron-positron correlations also affect $A_{kn}(\vec{G})$, but to a lesser extent for nearly constant densities, $n^{-(+)}$. The annihilation rate Λ can similarly be expressed in terms of the corresponding quantity Λ^0 for the homogenous system

$$\Lambda = \int \Lambda^0(n^-(\vec{r}))\, n^+(\vec{r})\, d\vec{r} \ . \tag{10}$$

The values for Λ^0 and $N^0(\epsilon)$ were obtained from the work of Arponen and Pajanne.[4,5]

This formalism was applied to calculate Λ and $R(\vec{p})$ for defect-free aluminum. Contributions from core electrons and core orthogonalization effects were not taken into account. The norm-conserving[16] pseudopotential used for the electrons was calculated by Pickett.[17] The value obtained for Λ is 6.05 ns^{-1}, giving a positron lifetime of 165 ps, which is in excellent agreement with the experimental value[18] (appropriately extrapolated to 0 K) 161 ±1 ps. The contribution from core annihilations is expected to increase Λ by a small amount of the order of 6%.[8] The function $R(\vec{p})$, for $\vec{p}$ along [100], is compared in Fig. 1 with the results obtained from (a) IPM calculation, all correlation effects neglected in Eq. (9), and (b) the Kahana[10] theory. The Kahana enhancement is seen to differ significantly from the prediction of Eq. (9). The two-dimensional angular-correlation spectrum $N(p_z,p_y) = \int dp_x R(\vec{p})$ is shown in Fig. 2(a). The agreement with experiment[19] is very good except for the magnitude of the high-momentum components (HMC).[20] The effects of electron-positron correlation are evident on comparing this spectrum with previous band-structure results.[6,21] Near the Fermi momentum the IPM results fall below the experimental curves showing a more spherical shape[21] whereas the experimental (cf. Fig. 2, Ref. 19) and present theoretical results [Fig. 2(a)] show a more cylindrical shape. Other than the difference in shape, the structure seen in Fig. 2(a), resulting from band-structure effects, is very similar to that obtained by Wakoh (cf. Fig. 21, Ref. 6). The structure in the experimental spectrum (Fig. 2, Ref. 19) is less sharply defined because of the finite experimental resolution.[21,22] A particular cross section of Fig. 2(a), $N(p_z,p_y=0)$, was examined after folding in the experimental resolution; the structure in the resulting spectrum was indistinguishable from the experimental results. The complete two-dimensional spectrum was not smoothed by the resolution function, since the main purpose of this work is to examine many-body effects by comparing the present results with those of previous band-structure calculations. The
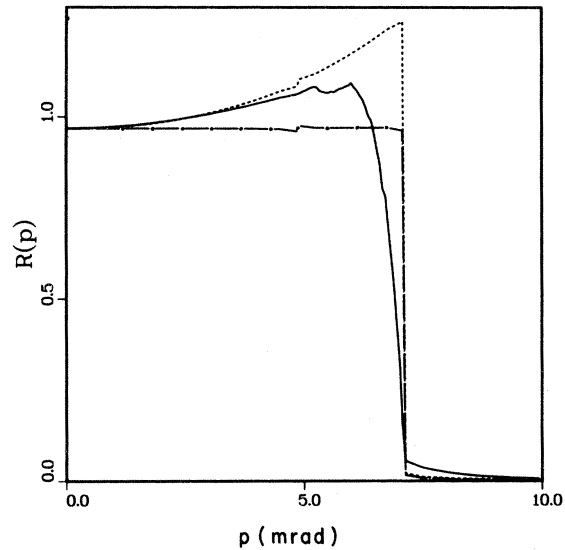

FIG. 1. Momentum distribution along the [100] direction [1 mrad$\equiv mc\,(10^{-3})$] obtained from Eq. (10) (solid curve), Kahana theory (dotted curve), and independent-particle model (chain-dotted curve).

HMC of $N(p_z,p_y)$ are shown in Fig. 2(b) (a vertical enlargement of the complete spectrum). The most obvious many-body effects are seen in the p_z and p_y directions, where there is a clear enhancement of the distribution over the IPM predictions in good agreement with the experimental results of Berko et al. (cf.
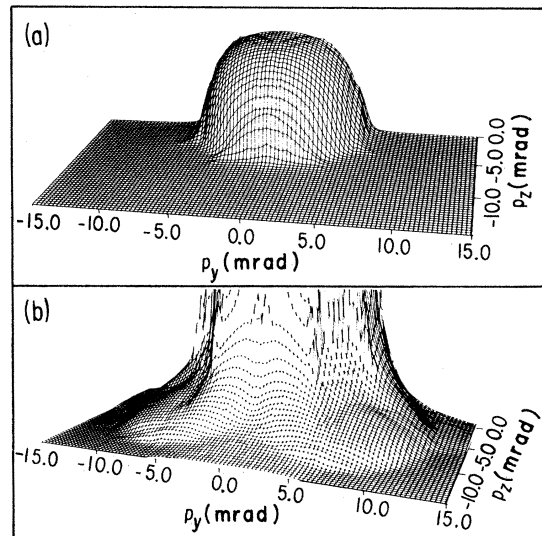

FIG. 2. (a) Two-dimensional angular-correlation surface in Al. The integration direction p_x is along [100]. Experimental two-dimensional resolution [e.g., nearly Gaussian cross sections of 0.6 m rad by 1.65 mrad full width at half maximum (Ref. 21)] was not taken into account. (b) High-momentum region of the two-dimensional angular-correlation surface shown in Fig. 1(a). The amplification factor is 10.

Fig. 5, Ref. 22). The overall structure of the HMC is in much better agreement with experiment than results of IPM calculations.[20]

In conclusion, a formalism has been developed for incorporating electron-positron correlation effects into band-structure calculations. The application of this method to defect-free Al has yielded results in excellent agreement with experiment. The method is of general applicability and is easily applied to perfect solids, solids with defects, or solid surfaces by generalization of existing self-consistency schemes.

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