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Thermalization and diffusion of positrons in solids

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Trapping of thermalized positrons in solids of temperature T by sinks, such as surfaces, vacancies, or voids, can change the mean kinetic positron energy E_+ in the medium so that $(E_+ - 3k_BT/2) \gtrless 0$. The phenomenon of positron heating (>) or cooling (<) of the positron ensemble in a medium with absorbing boundaries arises when microscopic processes of positron scattering and transitions into sink states depend on the positron momentum in the thermal distribution. Positron heating and cooling always reduces the positron trapping rate at sinks, the more so the smaller the volume between absorbing boundaries. The influence of the initial distribution of kinetic positron energies on positron trapping is investigated, and implications for the study of defects in solids with positrons are analyzed.

INTRODUCTION

When positrons from a radioactive source or a beam source enter a solid, they thermalize in times short compared to their mean lifetime with respect to annihilation with electrons into two 0.511-MeV γ rays.[1-6] Through many tries with single positrons in a given experiment, positrons ergotically form a statistical ensemble of noninteracting particles. In this sense, positrons at the time of annihilation have a Boltzmann distribution $\exp(-u)$, where $u \equiv E/k_BT$ is the kinetic positron energy E in terms of the Boltzmann constant k_B and the temperature T of the medium.[7,8] The mean value of u is then $\langle u \rangle_T = E_+/k_BT = \frac{3}{2}$.

The Boltzmann distribution is perturbed if positrons disappear from the volume through trapping at sinks.[9] Surfaces, defects, or impurities can act as positron absorbers.[10] The mean value of the perturbed distribution E_+, corresponding to an effective positron temperature $T_+ \equiv 2E_+/3k_B$, is higher or lower than T depending on the velocity dependence of the disappearance rate from the medium. The disappearance rate from the positron ensemble to sinks is reduced irrespective of whether the microscopic processes leading to trapping cause positron heating ($T_+ > T$) or cooling ($T_+ < T$) in the medium.[9]

The treatment of the phenomena of positron heating and cooling is couched in different terms, but with similar consequences, depending on whether positron trapping proceeds in the diffusion regime or the propagation regime.[12] The trapping rate in the former is limited by the diffusion of particles to the boundaries, whereas in the latter the trapping rate is determined by the matrix element for the transition from an extended thermal positron state in the medium to a localized state in the sink. In general, the trapping rate in either regime depends on the positron momentum. Positrons with the highest trapping rate disappear first from the ensemble, and the mean kinetic energy E_+ of the remaining positrons differs from $3k_BT/2$, giving rise to positron heating or cooling, i.e., $(E_+ - 3k_BT/2) \neq 0$. The interpretation of the rate-determining processes in the diffusion or propagation regimes differ in important ways.[12,13] Still, the symptoms of positron heating and cooling in reducing the mean rates of positron disappearance from finite media and their influence on detectable annihilation parameters are the same. We find it convenient in the following to give our presentation in the language of diffusion theory. When cast in the language of transition probabilities, the results are similar. We address here the question as to the dependence of positron heating and cooling on the initial distribution of positron energies and its observable manifestations. Section I sets the stage by reviewing the slowing-down processes for positrons. The thermalization process is delineated in Sec. II, and the influence of positron heating and cooling on positron lifetime spectra is derived in Sec. III. The results are discussed in Sec. IV in terms of their impact for positron annihilation studies of real solids.

I. POSITRON STOPPING TIMES

In most experiments, positrons are implanted with an exponential depth profile into a material from a radioactive source with kinetic energies ranging up to a maximum source energy E_s that is typically of the order of 1 MeV.[12] Positrons slow down mainly by two mechanisms. The electronic stopping power S_e of the medium is due to ionization and excitation of electrons in the medium. It is shown for aluminum in Fig. 1 as the solid curve. At epithermal energies below some critical value E_c, phonons absorb most of the energy. This can be expressed through a phonon stopping power S_{ph} of the medium. It is indicated as a line of dashes in Fig. 1. In the continuous slowing-down approximation, the time t for a particle of mass m to lose energy in a medium of stopping power S from an initial value E_i to a final value E_f is given by

$$t_S = -\left[\frac{m}{2}\right]^{1/2} \int_{E_i}^{E_f} \frac{dE}{E^{1/2}S} \ . \tag{1}$$

Positron slowing-down times owing to electronic processes have been calculated in various approximations. We find it convenient to consider S_e in two energy ranges relative to the maximum of S_e at $E = E_{\max}$. The stopping power in the range $E_{\max} < E \leq E_s$ is given by the Bethe (B) theory with corrections for the Bhabha positron-electron cross sections and for relativistic effects.[4,14] As given in Ref. 4, the stopping times in this energy range can be estimated accurately with the formula

$$t_B = 7.7 d^{-1}(E_i/mc^2)^{1.2} \tag{2}$$

in units of psec, where the density d of the medium is given in units g/cm^3; $mc^2 = 0.511$ MeV and 1 psec $= 10^{-12}$ sec. Since $E_i/mc^2 \leq E_s/mc^2 \sim 1$, we find that $t_B < 3$ psec in Al and $t_B < 1$ psec in metals like Mo, Pb, and Au.

The slowing-down time t_R, in the low-energy range $E < E_F \sim E_{\max}$ can be calculated in terms of the electron-gas theory of conduction electrons with Fermi energy E_F. Following Ritchie[3] (R), S_e for $E < E_F$ is given by

$$S_e = \frac{\pi}{105}\frac{m^2}{\hbar}\left[\frac{2}{m}\right]^{3/2}\frac{E^{5/2}}{E_F} \ , \tag{3}$$

and Eq. (1) yields

$$t_R = \frac{105}{8\pi}\frac{\hbar E_F}{E_f^2} = \frac{186.5}{u_{0f}^2 r_s^2} \tag{4}$$

expressed in psec, where we have introduced $u_{0f} = E_f/k_B T_0$ at $T_0 \equiv 316$ K so that $k_B T_0 = 1.00 \times 10^{-3}$ (a.u.) $= 0.0272$ eV and $E_F = 1.84 r_s^{-2}$ (a.u.) in terms of the one-electron radius r_s (a.u.) defined as $(4\pi/3)r_s^3(\rho a_0^3) = 1$, ρ being the effective conduction-electron density and $a_0 = \hbar^2/me^2 = 0.529$ Å. For epithermal energies E_f of interest here, t_R is always $\gtrsim t_B$. Values of r_s are collated in Table I. We take t_R to represent the electronic stopping time for positrons in the medium.

We note in passing that if positron-phonon interactions were to be unimportant, i.e., if one can set $u_{0f} = 1$, Eq. (4) simplifies to

$$t_R = \frac{186.5}{r_s^2} \ , \tag{5}$$

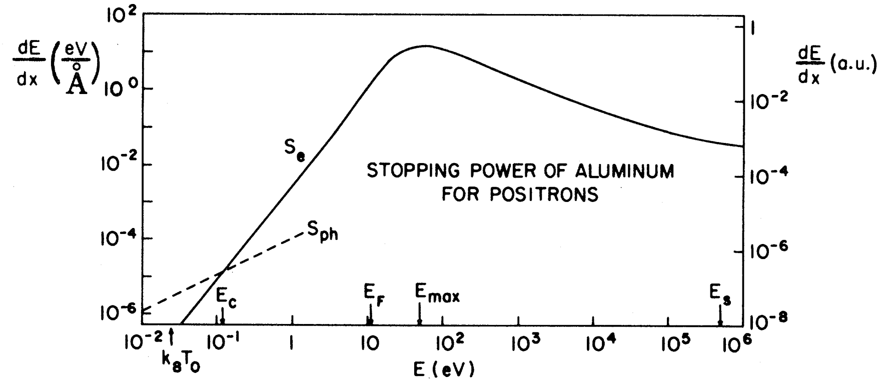

FIG. 1. Stopping of positrons in aluminum. Solid curve: electronic processes from Refs. 3, 4, and 14. Curve of dashes: phonon processes according to Eq. (6). At positron energies below E_c, phonon processes dominate. The arrow at $k_B T_0$ refers to energies at $T_0 = 316$ K.

TABLE I. Critical positron energies E_c, Eq. (7), below which thermalization occurs by phonon scattering. Listed are the density d, the one-electron radius r_s of the conduction electrons[a] in units of a_0, E_c, and the reduced energy parameter $u_{0c} \equiv E_c/k_BT_0 = E_c$ (10^{-3} a.u.), where $T_0 = 316$ K and $k_BT_0 = 27.2 \times 10^{-3}$ eV. The E_c and u_{0c} values are calculated for the deformation potential $W = bE_F$ with $b = 0.575$. Since b falls in the range $\frac{2}{5} \lesssim b \lesssim \frac{2}{3}$, this introduces an uncertainty of ±50% in u_{0c}, as indicated by the horizontal bars in Fig. 3.

Solid	d (g/cm^3)	r_s	E_c (eV)	$u_{0c}=E_c$ (10^{-3} a.u.)	Solid	d (g/cm^3)	r_s	E_c (eV)	$\mu_{0c}=E_c$ (10^{-3} a.u.)
Ag	10.5	1.53	0.22	8.0	Li	0.53	3.21	0.08	3.0
Al	2.7	2.12	0.14	5.3	Mg	1.74	2.70	0.07	2.7
As	5.73	1.76	0.18	6.8	Mo	10.2	1.53	0.22	8.1
Au	19.3	1.49	0.16	5.9	Mn	7.2	1.71	0.18	6.6
B	2.34	1.83	0.29	10.6	Na	0.97	4.24	0.02	0.7
					Ni	8.9	1.80	0.13	4.6
Ba	3.51	3.74	0.01	0.5	Pb	11.3	2.26	0.04	1.6
Be	1.85	1.78	0.38	13.9	Pd	12.0	1.51	0.21	7.7
Bi	9.80	2.17	0.06	2.1	Pt	21.4	1.55	0.13	4.7
C	2.0	1.66	0.47	17.4	P	1.53	5.45	0.01	0.2
Ca	1.54	3.06	0.05	1.8	Sb	6.68	2.06	0.09	3.3
					Se	4.79	1.84	0.18	6.4
Cd	8.64	2.13	0.07	2.4	Si	2.33	1.97	0.21	7.9
Co	8.9	1.91	0.10	3.7	Sn	5.75	2.23	0.07	2.6
Cr	7.2	1.55	0.26	9.7	Sr	2.54	3.32	0.02	0.9
Cs	1.87	5.88	0.003	0.1	Ta	16.6	1.71	0.10	3.8
Cu	8.92	1.83	0.12	4.3					
					Te	6.25	1.91	0.12	4.6
					Ti	4.5	1.93	0.15	5.5
Fe	7.86	2.07	0.08	2.9	Tl	11.9	2.89	0.02	0.6
Ga	5.9	2.26	0.07	2.5	V	5.96	1.68	0.22	8.0
Ge	5.35	2.02	0.11	4.1	W	19.4	1.55	0.14	5.0
In	7.30	2.59	0.03	1.2	Zm	7.14	1.97	0.10	3.8
K	0.86	3.6	0.04	1.4	Zr	6.49	1.88	0.13	4.8

[a] D. Isaacson, Table of r_s values, New York University Radiation and Solid State Laboratory Report, 1972 (unpublished).

still in units of psec. This formula is in excellent agreement with the numerical results calculated in many-body perturbation theory and displayed by Carbotte and collaborators.[5] We estimate that only in a few elements (Ba,Cs,Na,Rb,Sr,Tl; cf. Table I) does electronic stopping dominate the thermalization process all the way down to room temperature.

Usually, then, as positron energies approach $\frac{3}{2}k_BT$, phonon processes dominate the energy loss, with a stopping power given by

$$S_{\mathrm{ph}} = \frac{2}{\pi}\frac{m^3W^2}{\hbar^4 d}E \tag{6}$$

in terms of the lattice deformation potential W. In metals, one may set $W = bE_F$, where $\frac{2}{5} \lesssim b \lesssim \frac{2}{3}$.[15,16] The electronic stopping power falls below the phonon stopping power at energies $E \le E_c$ where the critical energy E_c is at the demarkation $S_{\mathrm{ph}} = S_e$ (cf. Fig. 1). In terms of Eqs. (3) and (6), we obtain

$$E_c^{3/2} = \frac{105b^2}{2^{1/2}\pi^2}\frac{m^{5/2}}{\hbar^3}\frac{E_F^3}{d} . \tag{7}$$

For definiteness we set $b = 0.575$ and find for $u_{0c} \equiv E_c/k_BT_0$ the values 5.3 (for Al), 5.9 (Au), 8.1 (Mo), and 1.6 (Pb). Other values are given in Table I.

We insert Eq. (6) into Eq. (1) and integrate over the interval $(E_c - 3k_BT/2) > 0$ with the result

$$t_{\mathrm{ph}}=\frac{\pi\hbar^4 d}{3^{1/2}m^{5/2}b^2E_F^2(k_BT)^{1/2}}\left[1-\left(\frac{3k_BT}{2E_c}\right)^{1/2}\right]. \tag{8}$$

Comparison of the phonon thermalization time with the electronic stopping time t_R [from Eq. (4) with $E_f=E_c$],

$$t_{\mathrm{ph}}=4\left[(\tfrac{3}{2}u_{0c})^{1/2}\left(\frac{T_0}{T}\right)^{1/2}-1\right]t_R\ , \tag{9}$$

shows that for most metals listed in Table I the phonon thermalization times are larger than the electronic stopping time and decrease slowly with increasing temperature of the medium.

In summary, we estimate the total stopping time,

$$t_S=t_B+t_R+t_{\mathrm{ph}}\ ,$$

in terms of Eqs. (2), (4), and (8) at room temperature to be 13 psec in Al and 45 psec in Pb. More detailed treatments[5] do not change these results significantly with regard to the present context. The stopping times are short compared to the annihilation time in metals, ~200 psec.[17–19] We find them to be comparable to the thermal relaxation times symptomatic of positron heating and cooling.[9]

II. THERMAL RELAXATION

The results of the preceding section suggest the following picture. Positrons in penetrating into a metal slow down very rapidly, in tens of picoseconds or less, to energies E comparable to E_c far below the Fermi energy E_F of the conduction electrons. From then on, positron-phonon interaction controls the final thermalization process. Under laboratory conditions, there is never more than one positron present in the medium. Positron behavior is described in the ergodic sense by a time-dependent distribution function $\hat{f}$ of noninteracting particles in velocity and space. The approach to thermal equilibrium is then prescribed by the Fokker-Planck equation that we can write in the form

$$\frac{\partial\hat{f}}{\partial t}+\gamma_B\hat{f}=\nabla_{\vec{\mathrm{v}}}(D_v\nabla_{\vec{\mathrm{v}}}\vec{\mathrm{f}}+\gamma_E\vec{\mathrm{v}}\hat{f})\ , \tag{10}$$

where $\vec{\mathrm{v}}$ is the velocity of a positron of energy $E=\frac{1}{2}mv^2<E_c$, D_v the diffusion constant in velocity space, and γ_E the thermalization rate. The positron annihilation rate γ_B in the metal bulk in this energy range is known to be independent of E.[20] If also D_v and γ_E are constants and related as $D_v=(k_BT/m)\gamma_E$, the solution of Eq. (10) for a particle of initial velocity $\vec{\mathrm{v}}_i$ is[21]

$$\hat{f}(\vec{\mathrm{v}},t;\vec{\mathrm{v}}_i)=\left[\frac{2\pi k_BT}{m}(1-e^{-2\gamma_Et})\right]^{-3/2}\times\exp\left[-\frac{m\,|\vec{\mathrm{v}}-\vec{\mathrm{v}}_ie^{-\gamma_Et}|^2}{2k_BT(1-e^{-2\gamma_Et})}-\gamma_Bt\right]. \tag{11}$$

From the initial distribution $\hat{f}\to\delta(\vec{\mathrm{v}}-\vec{\mathrm{v}}_i)$ when $\gamma_Et\ll1$, Eq. (11) approaches the Boltzmann distribution

$$\hat{f}=\left(\frac{m}{2\pi k_BT}\right)^{3/2}e^{-E/k_BT}e^{-\gamma_Bt} \tag{12}$$

as thermal equilibrium is reached in the limit $\gamma_Et\gg1$. The spatial distribution spreads concommitantly as governed by a mean spatial diffusion coefficient D, from $\delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}_i)$ at the initial site $\vec{\mathrm{r}}_i$ to

$$\sim(4\pi Dt)^{-3/2}e^{-|\vec{\mathrm{r}}-\vec{\mathrm{r}}_i|^2/4Dt}\ . \tag{13}$$

The thermal history of a positron is uncertain at least to the extent that $\delta\vec{\mathrm{v}}_i\delta\vec{\mathrm{r}}_i>\hbar/m$ in compliance with the Heisenberg relation. That is, Eqs. (11) and (13) describe positrons only for times

$$t>\hbar/(4D\gamma_Emk_BT)^{1/2}\sim1\ . \tag{14}$$

expressed in psec. Epithermal positron wave packets begin to evolve in times comparable to electronic stopping times, Eq. (4), and the thermal history is largely unaffected by the way in which positrons arrive at the initial epithermal phase-space point $(\vec{\mathrm{r}}_i,\vec{\mathrm{v}}_i)$ with energy $E\le E_c$.

When absorbing boundaries impose conditions on the distribution function $\hat{f}$ and the spatial diffusion coefficient D depends on the positron velocity v, Eq. (10) has to be modified. The Boltzmann equation for the isotropic part $\hat{f}_0$ of the velocity distribution, in terms of the energy variable $u=E/k_BT$, becomes[9]

$$\frac{\partial\hat{f}_0}{\partial t}+\gamma_B\hat{f}_0=\frac{\gamma_E}{u^{1/2}}\frac{\partial}{\partial u}\left[u^{3/2}\omega^*\left(\hat{f}_0+\frac{\partial\hat{f}_0}{\partial u}\right)\right]+\gamma_E\frac{u}{\omega^*}\nabla_{\vec{\rho}}^2\hat{f}_0\ . \tag{15}$$

The first term on the right-hand side of Eq. (15) corresponds to Eq. (10). The second term describes the spatial behavior of $\hat{f}_0$ as a function of the reduced space variable $\vec{\rho}\equiv\vec{\mathrm{r}}/\Lambda_E$, where Λ_E is the thermalization length related to the thermal relaxation rate γ_E or to the thermal relaxation time $\tau_E \equiv \gamma_E^{-1}$ as $\Lambda_E = (2D\tau_E)^{1/2}$. The velocity-dependent spatial diffusion coefficient has the form

$$D(v) = \frac{1}{3}\frac{v^2}{\omega} \tag{16}$$

in terms of the positron-phonon scattering frequency ω. Equation (15) contains the reduced scattering frequency $\omega^* \equiv \omega/\omega_0$ in terms of the frequency ω_0 at $E = k_B T$ or $u = 1$.

The general solution of Eq. (15) can be expanded in the form

$$\hat{f}_0 = e^{-\gamma_B t} \sum_{\nu\zeta} A_{\nu\zeta} R_\nu(\vec{\rho}) F_{\nu\zeta}(u) e^{-\kappa_{\nu\zeta} t} . \tag{17}$$

The coefficients $A_{\nu\zeta}$ are fixed by the initial conditions. The function $R_\nu(\vec{\rho})$ is the νth eigenfunction of the equation

$$\nabla_{\vec{\rho}}^2 R(\vec{\rho}) = -q^2 R(\vec{\rho}) . \tag{18}$$

It imposes spatial boundary conditions on $\hat{f}_0$. In particular, one has $\hat{f}_0 = 0$ at positron-absorbing walls. This sharp boundary may not be fulfilled near vacancies and could lead to an overestimate of the diffusion heating or cooling effect. To each $R_\nu(\vec{\rho})$, $\nu = 1, 2, \ldots,$ belongs an eigenvalue q_ν which appears in the rate $\kappa_{\nu\zeta}$ and in the function $F_{\nu\zeta}(u)$ which determines the energy distribution of the positrons in the presence of absorbing walls. The general form of $F_{\nu\zeta}(u)$ is given in Eq. (19) of Ref. 9.

The functions R_ν and $F_{\nu\zeta}$ were analyzed for models of ω^* by setting $\omega^* = u^{1+\alpha}$, where α is a parameter that depends on the scattering process in an average way and is assumed here to be independent of u. Scattering such that $\alpha > 0$ results in diffusion heating ($E_+ > \frac{3}{2} k_B T$), and $\alpha < 0$ in diffusion cooling ($E_+ < \frac{3}{2} k_B T$). Only for $\alpha = 0$ is Eq. (12) the exact solution of Eq. (15) and $E_+ = \frac{3}{2} k_B T$, irrespective of constraints.[9] As summarized in Table I of Ref. 9, α varies from $\alpha \sim 1$ for positron-electron scattering to $\alpha \sim -\frac{1}{2}$ for positron-phonon scattering and $\alpha \sim -\frac{2}{3}$ for positron-defect scattering. In the following, we emphasize the model $\alpha = -1$, because it falls within the range of α values of interest for epithermal processes, namely positron-phonon ($\alpha = -\frac{1}{2}$), positron-impurity ($\alpha = -1$), and positron-defect ($\alpha = -\frac{3}{2}$) scattering.[9] For this value of α, moreover, the Boltzmann equation can be solved exactly.

To begin with, we describe the thermalization of positrons in an infinite medium. The last term in Eq. (15) and q in Eq. (18) vanish and, setting $R_\nu(\vec{\rho})\,|_{\nu=1} = 1$, Eq. (17) becomes

$$\hat{f}_0 = e^{-\gamma_B t} \sum_{\zeta=1}^{\infty} A_\zeta F_\zeta(u) e^{-\kappa_\zeta t} . \tag{19}$$

Specifically for $\alpha = -1$, we have[9]

$$F_\zeta = u^{-1/2} e^{-u} H_{2\zeta-1}(u^{1/2}) \tag{20}$$

with the thermalization rates

$$\kappa_\zeta = (\zeta - 1)\gamma_E , \tag{21}$$

where H_m is the Hermite polynomial of order m. If the positrons have an initial distribution $g(u, u_c)$ with regard to the characteristic value

$$u_c = E_c / k_B T = u_{0c}(T_0/T) ,$$

where u_{0c} is listed in Table I and $T_0 = 316$ K, then

$$\hat{f}_0\,|_{t=0} = \sum_\zeta A_\zeta F_\zeta(u) = g(u, u_c) \tag{22}$$

with the normalization condition

$$\frac{2}{\pi^{1/2}} \int_0^\infty g(u, u_c) u^{1/2} du = 1 . \tag{23}$$

The coefficients are given by the orthogonality relations of Hermite polynomials as

$$A_\zeta = [2^{2\zeta-1}(2\zeta-1)!\pi^{1/2}]^{-1} \times \int_0^\infty H_{2\zeta-1}(u^{1/2}) g(u, u_c) du . \tag{24}$$

Noting that $H_1(x) = 2x$, we find that $A_1 = \frac{1}{2}$ independent of $g(u, u_c)$, and Eq. (19) becomes

$$\hat{f}_0 e^{-\gamma_B t} e^{-u}[1 + A_2 u^{-1/2} H_3(u^{1/2}) e^{-\gamma_E t} + A_3 u^{-1/2} H_5(u^{1/2}) e^{-2\gamma_E t} + \cdots] . \tag{25}$$

Equation (25) describes the fact that at $t = 0$ exactly one positron resides in the intial velocity distribution, according to Eqs. (22) and (23), and that $\hat{f}_0$ in an infinite medium always tends to the Boltzmann distribution $\exp(-u)$ in times larger than $\tau_E = \gamma_E^{-1}$.

In restricted media, $q > 0$ in Eq. (18), the thermalization process changes and $\hat{f}_0$ in general approaches Eq. (17), and not the distribution $\exp(-u)$ with mean value $\langle u \rangle_T = \frac{3}{2}$. Positron heating and cooling imparts deviations from this value that grow, through q of Eq. (18), with the spatial constraints imposed on the medium by positron sinks. Inasmuch as positrons trapped in sinks annihilate in discernibly different ways from positrons that annihilate in the bulk of the medium, annihilation measurements are affected by positron diffusion heating and cooling. In the following we discuss as an example the extent to which such effects reveal something about the initial positron distribution in positron lifetime spectra.

III. POSITRON LIFETIME SPECTRA

Positrons in a homogeneous medium have only one annihilation rate γ_B. It is given by the overlap between the extended positron wave function and the electron wave function of the medium. It is independent of u at epithermal energies.[20] Integration of Eq. (25) yields the probability $p_B(t)$ that the positrons survive in the bulk at time t,

$$p_B(t)=\frac{2}{\pi^{1/2}}\int_0^\infty u^{1/2}\hat{f}_0(u,t)du=e^{-\gamma_B t} . \quad (26)$$

Great care has been given over the years to the preparation of samples so uniform that the measured positron annihilation probabilities can be described by Eq. (26) and positron lifetimes γ_B^{-1} can be extracted that are basic material constants.[10,17,18]

The interest in media with positron traps arises from the fact that positrons have proven to be very sensitive probes for the exploration of surfaces and defects of solids. The positron lifetime spectrum reflects alternate modes of annihilation in traps. As we pointed out recently,[9] the trapping process affects the energy distribution in the bulk in such a manner that the rate of diffusion to the traps becomes smaller the smaller the solid or the larger the trap concentration.

We wish to study the effect of the initial distribution $g(u,u_c)$ on this phenomenon, and chose the useful example of $\alpha=-1$ and spherical traps (vacancies or voids) of radius r_V. We assume that the traps are uniformly distributed throughout the medium. Each is placed in the center of a Wigner-Seitz sphere of radius R_V, at low trap density $3/4\pi R_V^3$ such that $R_V \gg r_V$. Equation (18) has the solution

$$R(\vec{\rho})=(q\rho)^{-1}\sin(q\rho-\phi) , \quad (27)$$

where $\phi=qr_V/\Lambda_E$. The first eigenvalue of interest here is

$$q=\left[\frac{3r_V}{R_V}\right]^{1/2}\frac{\Lambda_E}{R_V} . \quad (28)$$

Since the experiment does not view the space dependence of $\hat{f}_0$, we integrate Eq. (17) over all space and obtain

$$\hat{f}_0(u,t)=e^{-\gamma_B t}\sum_{\zeta=1}^{\infty}A_\zeta F_\zeta(u)e^{-\kappa_\zeta t} . \quad (29)$$

This has the same appearance as Eq. (19) except that now

$$F_\zeta(u)=u^{-1/2}e^{-u(\beta+1/2)}H_{2\zeta-1}[(2\beta u)^{1/2}] , \quad (30)$$

$$\kappa_\zeta=[(2\zeta-\tfrac{1}{2})\beta-\tfrac{3}{4}]\gamma_E , \quad (31)$$

where

$$\beta(q)\equiv(q^2+\tfrac{1}{4})^{1/2} . \quad (32)$$

For $q=0$ (no boundaries) and thus $\beta=\frac{1}{2}$, we retrieve Eq. (25) and the bulk lifetime spectrum equation (26).

The lifetime spectrum due to annihilation in the bulk in the presence of sinks follows from integration of Eq. (29),

$$p_B(t)=e^{-\gamma_B t}\sum_{\zeta=1}^{\infty}n_\zeta(q)e^{-\kappa_\zeta(q)t} , \quad (33)$$

where $n_\zeta(q)\equiv A_\zeta(q)P_\zeta(q)$ depends on u_c and on q through $\beta(q)$ as

$$A_\zeta=\frac{(2\beta)^{1/2}2^{-2\zeta}}{(2\zeta-1)!}\frac{2}{\pi^{1/2}} \times\int_0^\infty e^{-(\beta-1/2)u}H_{2\zeta-1}[(2\beta u)^{1/2}]g(u,u_c)du \quad (34)$$

and

$$P_\zeta=\frac{2}{\pi^{1/2}}\int_0^\infty u^{1/2}F_\zeta(u)du =\frac{(2\zeta-1)!}{(\zeta-1)!}\left[\frac{2\beta-1}{2\beta+1}\right]^{\zeta-1}\frac{2^3\beta^{1/2}}{(2\beta+1)^{3/2}} . \quad (35)$$

The total lifetime spectrum of positrons in the bulk (B) and trapped by the absorbing walls (W) becomes, with

$$p_B(0)=\sum_{\zeta=1}^{\infty}n_\zeta(q)=1 ,$$

$$p(t)=p_B(t)+p_W(t) =\sum_{\zeta=1}^{\infty}[n_\zeta(1-\Phi_\zeta)e^{-(\gamma_B+\kappa_\zeta)t}+\Phi_\zeta e^{-\gamma_W t}] , \quad (36)$$

where

$$\Phi_\zeta=\kappa_\zeta/(\gamma_B+\kappa_\zeta-\gamma_W) . \quad (37)$$

Similarly, the fractions F_B and F_W of all positrons that annihilate in the bulk and the walls, respectively, are given by

$$F_B = 1 - F_W = \int_0^\infty \gamma_B p_B(t)\,dt = \sum_{\zeta=1}^{\infty} \frac{n_\zeta}{1+\kappa_\zeta \tau_B} \tag{38}$$

as can be detected in angular-correlation or Doppler-shift measurements. Up to this point, our development is exact.

We restrict the further discussion to the first component $\zeta = 1$ in Eq. (33)ff. All higher terms decay so fast that they remain unresolved by typical instrumental resolutions of annihilation channels. That is, we write Eq. (36) in the form

$$p(t) \simeq I_1 e^{-\Gamma_1 t} + I_2 e^{-\Gamma_2 t} , \tag{39}$$

where the intensities

$$I_1 = 1 - I_2 = n(\gamma_B - \Gamma_2)/(\Gamma_1 - \Gamma_2) \tag{40}$$

and the disappearance rates

$$\Gamma_1 = \gamma_B + \kappa, \quad \Gamma_2 = \gamma_W \tag{41}$$

are related to q and u_c through $n(q) \equiv n_1(q)$ and $\kappa(q) \equiv \kappa_1(q)$.

We evaluate Eqs. (34) and (35) for $\zeta = 1$, and drop the ζ subscript in the following, i.e., we calculate

$$\begin{aligned} n(q) &\equiv n_1(q) \equiv A_1(q,u_c)P_1(q) \\ &= \left[\frac{4\beta}{2\beta+1} \right]^{3/2} \frac{2}{\pi^{1/2}} \\ &\quad \times \int_0^\infty e^{-(\beta-1/2)u} g(u,u_c) u^{1/2}\,du , \end{aligned} \tag{42}$$

for three different initial epithermal positron-energy distributions $g(u,u_c)$ subject to the normalization condition, Eq. (23).

1. Exponential distribution:

$$g_0 = u_c^{-3/2} e^{-u/u_c} . \tag{43}$$

Equation (42) yields

$$n_0(q) = \left[\frac{4\beta}{2\beta+1} \right]^{3/2} \frac{1}{[1+(\beta-\frac{1}{2})u_c]^{3/2}} . \tag{44}$$

Note that for $u_c = 1$, Eq. (43) becomes the Boltzmann distribution

$$g_1 = e^{-u} , \tag{45}$$

and Eq. (44) reduces to the result given for $\alpha = -1$ in Table III of Ref. 9,

$$n_1 = \left[\frac{2^{3/2}\beta^{1/2}}{2\beta+1} \right]^3 , \tag{46}$$

where now the subscripts on n refer to the initial distribution.

2. Uniform distribution:

$$g_2 = \frac{3}{4\pi} \left[\frac{\pi}{u_c} \right]^{3/2} \Theta(u - u_c) , \tag{47}$$

where $\Theta(x)$ is the step function. One obtains

$$n_2(q) = \frac{3\pi^{1/2}}{4} \left[\frac{2\beta}{q^2 u_c} \right]^{3/2} \left[\operatorname{erf} y - \frac{2y}{\pi^{1/2}} e^{-y^2} \right] , \tag{48}$$

where $y \equiv [(\beta - \frac{1}{2})u_c]^{1/2}$.

3. Delta distribution:

$$g_3 = \frac{1}{2} \left[\frac{\pi}{u_c} \right]^{1/2} \delta(u - u_c) , \tag{49}$$

which gives

$$n_3(q) = \left[\frac{4\beta}{1+2\beta} \right]^{3/2} e^{-(\beta-1/2)u_c} . \tag{50}$$

The differences in the relations between n and q through $\beta(q)$, Eq. (32), constitute the effect of the initial positron distribution on positron annihilation characteristics in solids with traps. In this treatment, both n, Eq. (40), and the trapping rate κ, Eq. (41), depend on the parameter q which increases with trap concentration. Figure 2 illustrates n_1, n_2, and n_3 for various values of u_c. The point where $n(q_{1/2}) = \frac{1}{2}$ is of particular interest, because it can be determined with reasonable accuracy from experiments. For example, one can plot the mean annihilation rate $\Gamma = I_1\Gamma_1 + I_2\Gamma_2$ in the form

$$n = \frac{\Gamma - \gamma_W}{\gamma_B - \gamma_W} \tag{51}$$

as a function of the sample treatment that produces positron traps. Weak trapping implies $n = 1$ and $\Gamma = \gamma_B$. When positron heating and cooling is strong, one finds $\Gamma < \gamma_B$, and at $\Gamma_{1/2} = (\gamma_B + \gamma_W)/2$, conditions corresponding to $q_{1/2}$ are reached. Figure 3 demonstrates that $q_{1/2}$ values of typical metals are significantly smaller for g_2 or g_3 than for g_1. Ignorance of the initial epithermal distribution limits access to accurate empirical values of τ_E and affects analysis near surfaces and at defect concentrations near saturation of positron trapping where the role of divacancies, defect clusters, etc., be-

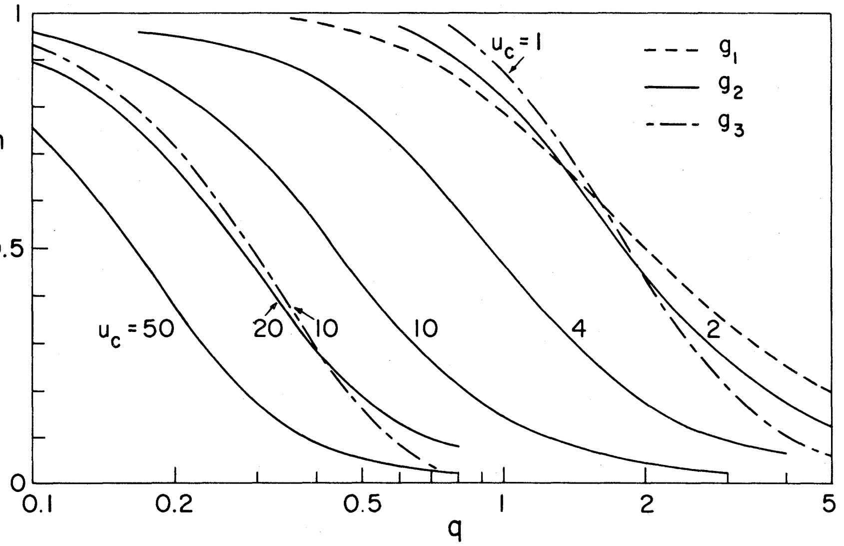

FIG. 2. Relation (for the model $\alpha=-1$) between $n(q)$ extracted from data by Eqs. (39) and (51) and the parameter $q\sim\Lambda_E/L$ which measures the ratio between the positron thermalization length Λ_E and the spacing L between positron-absorbing walls or traps. If the initial positron distribution is the Boltzmann distribution g_1 (curve of dashes), n drops to the value $n(q_{1/2})=\frac{1}{2}$ when $q_{1/2}=2$, irrespective of $u_c=E_c/k_BT$; for the definition of E_c, cf. Fig. 1 and Eq. (7). The parameter $q_{1/2}$ becomes smaller than 2 with increasing u_c if the initial distribution resembles a uniform distribution g_2 (solid curves) or a distribution g_3 that is peaked near E_c (curves of dashes and dots).

comes interesting. It is important, moreover, to ascertain whether the experiment can provide information about $g(u,u_c)$ itself.

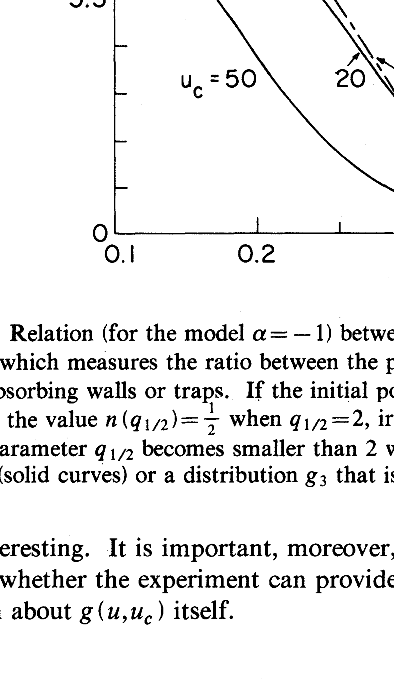

FIG. 3. Determination of $q_{1/2}$ from experiment, e.g., via Eq. (51) and Fig. 2, combined with the u_c values of solids (Table I) can give information about the initial positron energy distribution below E_c. If it is the Boltzmann distribution g_1, $q_{1/2}=2$ irrespective of u_c; if it is a uniform distribution g_2 or a peaked distribution g_3, the $q_{1/2}$ of most metals should be significantly smaller than 2. The upper marks indicate u_c values at $T=316$ K (Table I). The bars indicate the uncertainty of the choice of deformation potentials in calculating u_c values and apply to both curves marked g_2 and g_3.

IV. DISCUSSION

The previous sections have demonstrated, first of all, that in most metals the electronic stopping of positrons to kinetic energies E_c, where phonons take over, is fast compared to epithermal processes. This allows us to treat positrons as if their velocity distribution in a medium of temperature T evolves from an initial distribution $g(u,u_c)$, at energies less than $u_c=E_c/k_BT$, to a final distribution in times comparable to a material-characteristic relaxation time τ_E. The final distribution is the Boltzmann distribution $\exp(-u)$ if the medium is uniform over distances large compared to the mean free path for thermal relaxation Λ_E. It is related to τ_E as $\Lambda_E=(2D\tau_E)^{1/2}$ where D is a positron diffusion constant. The mean kinetic positron energy is then $\frac{3}{2}k_BT$. If the medium is finite compared to Λ_E, positrons diffuse from the volume to the absorbing "walls" of the medium before the Boltzmann distribution is sampled. Since this escape from the medium occurs first for the fastest diffusing particles, the mean kinetic particle energy E_+ now differs from $\frac{3}{2}k_BT$. We refer to this difference as the particle diffusion heating or cooling. The net result is that trapping by the walls occurs according to a mean rate that is reduced relative to the trapping rate for the thermal Maxwell-Boltzmann distribution, and that this reduction is stronger the smaller the medium. We would normally think, for example, of the trapping rate by vacancies in a metal per unit vacancy density as a constant volume capture rate.[12] Positron diffusion heating and cooling in fact reduces the volume rate when the spacing of the traps becomes comparable or smaller than the material-characteristic length Λ_E and, thus, makes the volume rate dependent on the vacancy concentration itself.

The crucial parameter for this effect is q which is a measure of Λ_E divided by the spacing between sinks. Internal consistency requires that we deduce the same q value for a given material from all types of experiments. To illustrate, in Ref. 9 we estimated from experimental data[22] of the mean lifetime and the mean annihilation rate in Al, at conditions such that $n=\frac{1}{2}$, the thermal relaxation time $\tau_E \simeq 60$ psec. From the experimental quantity $I_2(\Gamma_1-\Gamma_2)$ [Ref. 9, Table II(c)] at $n=\frac{1}{2}$ follows the trapping rate

$$\kappa_{1/2}=I_2(\Gamma_1-\Gamma_2)-\tfrac{1}{2}(\gamma_B-\gamma_W)\ , \qquad (52)$$

from which we extract for $\alpha=-1$ (Ref. 9, Table III)

$$q_{1/2}=\tfrac{1}{2}[(\tfrac{4}{3}\kappa_{1/2}\tau_E+1)^2-1]^{1/2}\ . \qquad (53)$$

With $(\gamma_B-\gamma_W)\simeq 2\times 10^{-3}$ psec^{-1} and $I_2(\Gamma_1-\Gamma_2)$ $\cong 8\times 10^{-3}$ psec^{-1} at $T\sim 650$ K we obtain $\kappa_{1/2}=7\times 10^{-3}$ psec^{-1}. The "experimental" value of $q_{1/2}$ becomes $q_{1/2}\simeq 0.6$. Figure 3 shows that this is decidedly smaller than the value $q_{1/2}=2$ predicted for all solids for an initial Boltzmann distribution g_1. In fact at u_c(650 K Al)$\simeq 2.6$ and $q_{1/2}=0.6$, the measurements are consistent with g_2 or g_3, i.e., an initial positron energy distribution that is uniform or peaked near $E_c=0.14$ eV. There are theoretical arguments in favor of such initial distributions. Analysis of data in terms of vacancy formation enthalpies is unaffected by positron heating or cooling if the experimental conditions are restricted to low vacancy concentrations where $\Gamma\simeq\gamma_B$.

A new analysis of the data for the diffusion of positrons in small metal grains of radius R,[23] for which $q=\pi\Lambda_E/R$, reveals an effect of positron heating and cooling on $D=D_{\text{eff}}q^2/\kappa\tau_E$ which, however, is only minor in the R range investigated.

We conclude that high concentrations of positron traps, or surfaces of small solids, can cause positron diffusion heating or, considering the important epithermal scattering processes, more likely diffusion cooling. Positron heating or cooling comes about if the trapping process is velocity dependent so that parts of the thermal positron distribution are trapped before others. In consequence, the remaining positron ensemble has a mean kinetic energy E_+ different from $3k_BT/2$, and the mean trapping rate from the volume is then always lower than one would observe if all positrons were to be trapped with equal probability. The trapping-rate reduction is more pronounced the smaller the volume of the medium between the positron-absorbing walls. Analysis of experimental data reveals symptoms of positron cooling. They permit estimates of positron thermalization times and give indications of the initial epithermal energy distribution of positrons in the phonon-dominated regime from which the thermal distribution evolves. We find evidence on one set of data for Al that positrons are deposited into the phonon-dominated energy range with a distribution that is uniform or somewhat peaked toward the upper limit of the phonon range. Positron heating and cooling interferes with the linear analysis of positron trapping by defect clusters at high defect concentrations. It limits the defect concentrations or the layers below surfaces where positron trapping is a simple marker of bulk properties. Its manifestations open new channels for the exploration of the statistical dynamics of positrons in matter.

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