Positron trapping model for point defects and grain boundaries in polycrystalline materials

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The exact solution of a diffusion-reaction model for the trapping and annihilation of positrons in grain boundaries of polycrystalline materials with competitive trapping at intragranular point defects is presented. Closed-form expressions are obtained for the mean positron lifetime and for the intensities of the positron lifetime components associated with trapping at grain boundaries and at intragranular point defects. The closed-form solutions allow direct insight in the physical details of the positron annihilation characteristics and can be conveniently applied for the analysis of experimental data. It turns out that the model is not only essential for positron annihilation studies which aim at issues of grain-boundary physics or nanoscaled material but is also of relevance for studies of point defects in polycrystalline materials when grain sizes are in the micrometer range.

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I. INTRODUCTION

Positron annihilation represents a versatile probe technique for the study of atom-scale-sized free volumes in condensed matter.[1–3] The increase in the lifetime of positrons (e^+) associated with e^+ trapping at free volumes allows us to detect and characterize free-volume-type defects. A focus of application is on the study of lattice vacancies and vacancy agglomerates in crystals, but the method is being employed increasingly in the study of grain boundaries and interfaces of polycrystalline materials and nanophase materials.[4–11] The quantitative description of the annihilation characteristics in grain boundaries and interfaces is more complex compared to point defects since the diffusion limitation of the trapping process has to be taken into account whereas trapping at point defects can be reasonably well described by rate theory. The situation becomes even more complex when e^+ trapping both at grain boundaries and at point defects occurs.

This paper presents a model for a quantitative description of diffusion-reaction-controlled e^+ trapping at grain boundaries and concomitant trapping at point defects in the grains. The relevance of this model is not restricted to e^+ annihilation studies which aim at issues of grain-boundary physics or nanoscaled material but applies also to studies of point defects in polycrystalline materials when grain sizes are in the micrometer range.

Positron trapping in grain boundaries[12,13] was originally analyzed by means of the rate equations of the standard two-state trapping model.[14,15] However, it turned out that for two-dimensionally extended defects, such as surfaces[16,17] or grain boundaries, the specific trapping rates are high so that the conditions for reaction-controlled trapping and for the applicability of rate theories are not fulfilled. The opposite limit of an entirely diffusion-controlled process where the boundary acts as ideal sinks for e^+ (Refs. 18 and 19) (i.e., Smoluchowski-type boundary condition) is not applicable either.

Therefore, a fully satisfactory description of e^+ trapping at grain boundaries can only be achieved within the framework of a more general diffusion-reaction theory. Such a theory was worked out by Dupasquier *et al.*,[20] by Würschum and Seeger,[21] and by Kögel[22] for e^+ trapping at grain boundaries and similarly also for e^+ trapping at flat surfaces and interfaces.[23,22] A model which, in addition to diffusion-reaction-limited e^+ trapping at grain boundaries, takes into account transition-limited e^+ trapping at intragranular point defects, was developed at first by Cizek *et al.*[10] based on the work of Dupasquier *et al.*[20] In this model, solutions obtained of the e^+ annihilations characteristics were given in form of infinite series.[10] In contrast to that, the present treatment based on the mathematical approach of[21] yields *closed-form expressions* of the major e^+ annihilation parameters for this application relevant case of competitive e^+ trapping in grain boundaries and point defects. These closed-form expressions allow deeper insight in the physical details of e^+ annihilation characteristics and can be conveniently applied for the analysis of experimental data.

II. MODEL

The model describes the positron annihilation characteristics in polycrystalline materials where positrons are trapped and annihilated both in vacancy-type point defects inside the grains and free-volume-type defects in grain boundaries. Trapping at point defects inside the grains can be well described by a transition-limited trapping process, whereas for e^+ trapping at grain boundaries both the e^+ diffusion and the transition reaction at the grain boundary has to be taken into account (so-called diffusion-reaction-controlled trapping process).

The behavior of the positrons is described by their bulk (free) lifetime τ_f, by their lifetime (τ_v) in the vacancy-type point defects inside the grains, by their lifetime (τ_b) in the grain boundaries, and by their bulk diffusivity D. Trapping at the point defects and the grain boundaries are characterized by the specific e^+ trapping rate σ_v and α, respectively.

The temporal and spatial evolution of the density ρ_g of free positrons within the grains is governed by

$$\frac{\partial \rho_g}{\partial t} = D\nabla^2 \rho_g - \rho_g \left(\frac{1}{\tau_f} + \sigma_v C_v \right), \tag{1}$$

where C_v denotes the concentration of vacancy-type point defects in the grains. The grain structure is modeled by as-

suming spherical grains of radius r_0. The e^+ trapped in the grain boundaries are described in terms of a planar density ρ_b obeying the rate equation

$$\frac{d\rho_b}{dt} = \alpha\rho_g(r_0,t) - \frac{1}{\tau_b}\rho_b. \tag{2}$$

The temporal evolution of the number of e^+ trapped in the point defects inside the grain is given by

$$\frac{dN_v}{dt} = -\frac{1}{\tau_v}N_v + \sigma_v C_v N_f, \tag{3}$$

where the number N_f of positrons in the free state follows from integration of ρ_g,

$$N_f = \int \rho_g dV. \tag{4}$$

The continuity of the e^+ flux at the "boundary" between the grain interior and the grain boundary is expressed by

$$D\,\nabla\,\rho_g|_{r=r_0} + \alpha\rho_g(r_0,t) = 0. \tag{5}$$

As initial condition we adopt the picture that at $t=0$ all thermalized positrons are in the free state and homogeneously distributed in the grains, i.e., initial density $\rho_g=\rho_g(0)$. Under this initial condition the solution of Eq. (1) exhibits spherical symmetry. The time dependence is handled by the Laplace transforms

$$\tilde{\rho}_{g,b}(r,p) = \int_0^\infty \exp(-pt)\rho_{g,b}(r,t)dt,$$

$$\tilde{N}_{v,f}(p) = \int_0^\infty \exp(-pt)N_{v,f}(t)dt, \tag{6}$$

which leads to the basic equations

$$\frac{d^2\tilde{\rho}_g}{dr^2} + \frac{2}{r}\frac{d\tilde{\rho}_g}{dr} - \gamma^2\tilde{\rho}_g = -\frac{\rho_g(0)}{D}, \tag{7}$$

with

$$\gamma^2 = \gamma^2(p) := \frac{\tau_f^{-1} + \sigma_v C_v + p}{D},$$

and

$$\tilde{\rho}_b = \frac{\alpha\tilde{\rho}_g(r_0,p)}{\tau_b^{-1} + p}, \tag{8}$$

$$\tilde{N}_v = \frac{\sigma_v C_v}{\tau_v^{-1} + p}\tilde{N}_f, \tag{9}$$

with the boundary condition

$$D\left.\frac{d\tilde{\rho}_g}{dr}\right|_{r=r_0} + \alpha\tilde{\rho}_g(r_0,p) = 0. \tag{10}$$

The solution of differential Eq. (7) satisfying Eq. (10) can be written as

$$\tilde{\rho}_g(r,p) = Ai_0(\gamma r) + \frac{\rho_g(0)}{\tau_f^{-1} + \sigma_v C_v + p}, \tag{11}$$

$$A := \frac{-\alpha\rho_g(0)(\tau_f^{-1} + \sigma_v C_v + p)^{-1}}{(\tau_f^{-1} + \sigma_v C_v + p)\gamma^{-1}i_1(\gamma r_0) + \alpha i_0(\gamma r_0)}, \tag{12}$$

with i_0 and i_1 as the modified spherical Bessel functions of order n,[24]

$$i_n(z) := \left(\frac{\pi}{2z}\right)^{1/2} I_{n+1/2}(z),$$

$$i_0 = \frac{\sinh z}{z}, \quad i_1 = \frac{\cosh z}{z} - \frac{\sinh z}{z^2}, \tag{13}$$

where $I_{n+1/2}(z)$ represents the Bessel function.

In a positron annihilation experiment we are interested in the total probability $n(t)$ that a e^+ implanted at $t=0$ has not yet been annihilated at time t. $n(t)$ is given by the number density of e^+ per grain at time t as follows:

$$n(t) = \frac{1}{\frac{4}{3}\pi r_0^3\rho_g(0)}\left\{\int_0^{r_0} 4\pi r^2\rho_g(r,t)dr + 4\pi r_0^2\rho_b(t) + N_v(t)\right\}. \tag{14}$$

The Laplace transform of $n(t)$ can be calculated taking into account the solution of $\tilde{N}_v$ [Eq. (9)] and the solution of differential Eq. (11) which yields

$$\tilde{n}(p) = \frac{1}{\frac{4}{3}\pi r_0^3\rho_g(0)}\left\{\left(1 + \frac{\sigma_v C_v}{\tau_v^{-1} + p}\right)\left[4\pi A\int_0^{r_0} i_0(\gamma r)r^2dr + \frac{4\pi}{3}r_0^3\frac{\rho_g(0)}{\tau_f^{-1} + \sigma_v C_v + p}\right] + 4\pi r_0^2\tilde{\rho}_b(p)\right\}. \tag{15}$$

Solving the integral after substituting $\tilde{\rho}_b(p)$ by Eq. (8), insertion of A [Eq. (12)], and introducing the Langevin function

$$L(z) := \frac{i_1(z)}{i_0(z)} = \coth z - \frac{1}{z} \tag{16}$$

yields after some algebra

$$\tilde{n}(p) = \left\{\frac{3\alpha}{r_0}\gamma DL(\gamma r_0)[\tau_v^{-1}(\tau_f^{-1} + \sigma_v C_v + p\tau_v\tau_f^{-1}) - \tau_b^{-1}(\tau_v^{-1} + \sigma_v C_v + p)] + [\alpha + \gamma DL(\gamma r_0)](\tau_b^{-1} + p)(\tau_v^{-1} + \sigma_v C_v + p)(\tau_f^{-1} + \sigma_v C_v + p)\right\}\{[\alpha + \gamma DL(\gamma r_0)](\tau_b^{-1} + p)(\tau_f^{-1} + \sigma_v C_v + p)^2(\tau_v^{-1} + p)\}^{-1}. \tag{17}$$

The Laplace transform $\tilde{n}(p)$ [Eq. (17)] represents the solution of the present diffusion and trapping model from which both the mean positron lifetime and the positron lifetime spectrum can be deduced. The mean positron lifetime $\bar{\tau}$ is obtained by taking the Laplace transform at $p=0$,

$$\bar{\tau} = \tilde{n}(p=0) = \int_0^\infty n(t)dt. \tag{18}$$

The positron lifetime spectrum follows from $\tilde{n}(p)$ by means of Laplace inversion. The single poles $p=-\lambda_i$ of $\tilde{n}(p)$ in the complex p plane define the decay rates $\lambda_i (i=0,1,2,\ldots)$ of the positron lifetime spectrum

$$n(t) = \sum_{i=0}^{\infty} I_i \exp(-\lambda_i t), \tag{19}$$

where I_i denote the relative intensities.[25] The appearance of a second-order pole at $\tau_f^{-1}+\sigma_v C_v + p = D\gamma^2 = 0$ is spurious. Closer inspection shows that the intensity associated with this pole cancels, taken into account that $\gamma DL(\gamma r_0)=0$ and $d[\gamma DL(\gamma r_0)]/dr = r_0/3$ holds for $\gamma=0$.

III. ANALYSIS

A. General case

The positron annihilation characteristics of diffusion-reaction-controlled trapping at grain boundaries and concomitant transition-limited trapping at point defects in the grains are given by Eq. (17) in combination with Eqs. (18) and (19). The mean positron lifetime Eq. (18), obtained from Eq. (17) for $p=0$, reads in the general case

$$\bar{\tau} = \frac{\frac{3\alpha}{r_0}\gamma_0 DL(\gamma_0 r_0)[\tau_b(\tau_f^{-1}+\sigma_v C_v) - (1+\sigma_v C_v \tau_v)] + [\alpha + \gamma_0 DL(\gamma_0 r_0)](\tau_f^{-1}+\sigma_v C_v)(1+\sigma_v C_v \tau_v)}{[\alpha+\gamma_0 DL(\gamma_0 r_0)](\tau_f^{-1}+\sigma_v C_v)^2}, \tag{20}$$

with

$$\gamma_0^2 = \frac{\tau_f^{-1}+\sigma_v C_v}{D}. \tag{21}$$

The positron lifetime spectrum [Eq. (19)] as deduced from the poles of $\tilde{n}(p)$ [Eq. (17)] consists, on the one hand, of the e^+ annihilations rates in the point-defect-trapped state (τ_v^{-1}) and grain-boundary-trapped state (τ_b^{-1}). From the residues of $\tilde{n}(p)$ [Eq. (17)] the relative intensity,

$$I_v = \sigma_v C_v \frac{[\alpha+\gamma_v DL(\gamma_v r_0)](\tau_f^{-1}+\sigma_v C_v - \tau_v^{-1}) - \frac{3\alpha}{r_0}\gamma_v DL(\gamma_v r_0)}{[\alpha+\gamma_v DL(\gamma_v r_0)](\tau_f^{-1}+\sigma_v C_v - \tau_v^{-1})^2}, \tag{22}$$

of the lifetime component τ_v with

$$\gamma_v^2 = \frac{\tau_f^{-1}+\sigma_v C_v - \tau_v^{-1}}{D} \tag{23}$$

and the relative intensity

$$I_b = \frac{\frac{3\alpha}{r_0}\gamma_b DL(\gamma_b r_0)}{[\alpha+\gamma_b DL(\gamma_b r_0)](\tau_f^{-1}+\sigma_v C_v - \tau_b^{-1})} \tag{24}$$

of the lifetime component τ_b with

$$\gamma_b^2 = \frac{\tau_f^{-1}+\sigma_v C_v - \tau_b^{-1}}{D} \tag{25}$$

is obtained.

The remaining poles $p=-\lambda_{0,j}$, on the other hand, are the roots of the transcendental equation $\alpha+\gamma_j DL(\gamma_j r_0)=0$ with $\gamma_j^2=(\tau_f^{-1}+\sigma_v C_v - \lambda_{0,j})D^{-1}$. For $\lambda_{0,j} > \tau_f^{-1}+\sigma_v C_v$ the transcendental equation reads as

$$\gamma_j' r_0 \cot \gamma_j' r_0 = 1 - \frac{\alpha D}{r_0}, \tag{26}$$

with

$$\gamma_j'^2 = \frac{\lambda_{0,j} - \tau_f^{-1} - \sigma_v C_v}{D}. \tag{27}$$

Calculation of the residues of $\tilde{n}(p)$ [Eq. (17)] for $\lambda_{0,j}$ yields the relative intensities as follows:

$$I_{0,j} = \frac{\frac{6\alpha}{r_0}[\tau_b^{-1}(\tau_v^{-1} + \sigma_v C_v - \lambda_{0,j}) - \tau_v^{-1}(\tau_f^{-1} + \sigma_v C_v - \tau_v \tau_f^{-1}\lambda_{0,j})]}{(\tau_b^{-1} - \lambda_{0,j})(\tau_f^{-1} + \sigma_v C_v - \lambda_{0,j})(\tau_v^{-1} - \lambda_{0,j})\left[1 - \frac{\alpha r_0}{D} + \frac{r_0}{\alpha}(\tau_f^{-1} + \sigma_v C_v - \lambda_{0,j})\right]}. \quad (28)$$

In summary, the e^+ lifetime spectrum reads as

$$n(t) = I_v \exp\left(-\frac{t}{\tau_v}\right) + I_b \exp\left(-\frac{t}{\tau_b}\right) + \sum_{j=1}^{\infty} I_{0,j} \exp(-\lambda_{0,j} t). \quad (29)$$

B. Limiting case of negligible trapping inside the grains

For negligible trapping inside the grains, i.e., $\sigma_v C_v \ll \tau_f^{-1}$, our model contains as limiting case the solutions of the diffusion-reaction model for positron trapping in grain boundaries with grain boundaries as the single type of trap.[21] In this case the model yields for the mean positron lifetime [Eq. (20)]

$$\bar{\tau} = \tau_f \frac{\frac{3\alpha}{r_0}\gamma_0 DL(\gamma_0 r_0)(\tau_b - \tau_f) + \alpha + \gamma_0 DL(\gamma_0 r_0)}{\alpha + \gamma_0 DL(\gamma_0 r_0)}, \quad (30)$$

for the intensity of the grain-boundary-trapped state [Eq. (24)]

$$I_b = \frac{\frac{3\alpha}{r_0}\gamma_b DL(\gamma_b r_0)}{[\alpha + \gamma_b DL(\gamma_b r_0)](\tau_f^{-1} - \tau_b^{-1})} \quad (31)$$

and for the sequence of intensities [Eq. (28)]

$$I_{0,j} = \frac{\frac{6\alpha}{r_0}(\tau_b^{-1} - \tau_f^{-1})}{(\tau_b^{-1} - \lambda_{0,j})(\tau_f^{-1} - \lambda_{0,j})\left[1 - \frac{\alpha r_0}{D} + \frac{r_0}{\alpha}(\tau_f^{-1} - \lambda_{0,j})\right]} \quad (32)$$

of the decay rates $\lambda_{0,j}$ [Eqs. (26) and (27) with $\sigma_v C_v = 0$] in agreement with Ref. 21.[30]

C. Limiting case of high e^+ diffusivity and/or small grain size

If the e^+ diffusivity is high or the grain size is small ($\gamma r_0 \ll 1$), the Langevin function [Eq. (16)] can be expanded. Restricting the expansion of Eq. (16) up to the first order [$L(z) = z/3$] yields

$$\gamma DL(\gamma r_0) = \frac{r_0}{3}(\tau_f^{-1} + \sigma_v C_v + p) \quad (33)$$

for which the Laplace transform [Eq. (17)] becomes independent of the diffusivity D as follows:

$$\tilde{n} = \frac{\frac{3\alpha}{r_0}(\tau_v^{-1} + p) + (\tau_b^{-1} + p)(\tau_v^{-1} + \sigma_v C_v + p)}{\left(\tau_f^{-1} + \frac{3\alpha}{r_0} + \sigma_v C_v + p\right)(\tau_b^{-1} + p)(\tau_v^{-1} + p)}. \quad (34)$$

By means of Laplace inversion of Eq. (34) the well-known solution of the simple trapping model for two types of e^+ traps[15,26] is recovered. From the poles of Eq. (34), the e^+ annihilation rates in the point-defect-trapped state (τ_v^{-1}) and grain-boundary-trapped state (τ_b^{-1}), and, in addition, the rate constant

$$\frac{1}{\tau_0} = \frac{1}{\tau_f} + \frac{3\alpha}{r_0} + \sigma_v C_v \quad (35)$$

follows. τ_0^{-1} characterizes e^+ annihilation and trapping from the free state with the trapping rate $3\alpha r_0^{-1}$ and $\sigma_v C_v$ of grain boundaries and intragranular point defects, respectively. Calculation of the residues yields the corresponding relative intensities

$$I_b = \frac{\frac{3\alpha}{r_0}}{\tau_0^{-1} - \tau_b^{-1}}, \quad I_v = \frac{\sigma_v C_v}{\tau_0^{-1} - \tau_v^{-1}}, \quad I_0 = 1 - I_b - I_v. \quad (36)$$

With $\tilde{n}(p)$ [Eq. (34)] for $p = 0$ the mean positron lifetime [Eq. (18)] reads as

$$\bar{\tau} = \tau_f \frac{1 + \frac{3\alpha}{r_0}\tau_b + \sigma_v C_v \tau_v}{1 + \frac{3\alpha}{r_0}\tau_f + \sigma_v C_v \tau_f}. \quad (37)$$

IV. DISCUSSION

The presented model with the exact solution of diffusion-reaction-controlled trapping at grain boundaries and competitive transition-limited trapping at intragranular point defects yields closed-form expressions for the mean positron lifetime $\bar{\tau}$ [Eq. (20)] and for the relative intensities I_b [Eq. (24)] and I_v [Eq. (22)] of the e^+ lifetime components τ_b and τ_v of the grain-boundary and point-defect-trapped states, respectively. As a main consequence of the diffusion-limited e^+ trapping a sequence of decay rates $\lambda_{0,j} > \tau_f^{-1}$ [Eq. (26)] with relative intensities $I_{0,j}$ [Eqs. (28) and (27)] occurs instead of a single component τ_0^{-1} as in the standard rate theory [Eq. (35)]. The model contains as limiting cases the solution of the simple trapping model for two types of e^+ traps in the case of high e^+ diffusivity and/or small grain size (Sec. III C)

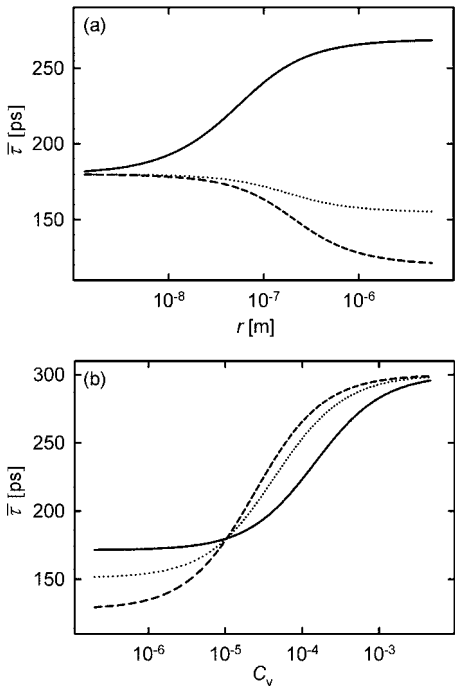

FIG. 1. Mean positron lifetime $\bar{\tau}$ [Eq. (20)] (a) in dependence of grain radius r_0 for intragranular point-defect concentration $C_v = 10^{-4}$ (—), 5×10^{-6}(···), and 0(– – –) and (b) in dependence of intragranular point-defect concentration C_v for grain radius $r_0 = 50$ nm (—), 200 nm (···), and 1 μm (– – –). Parameters: $\tau_f = 120$ ps, $\tau_b = 180$ ps, $\tau_v = 300$ ps, $D = 0.5\times10^{-4}$ m^2 s^{-1}, $\alpha = 10^3$ ms^{-1}, and $\sigma_v = 4\times10^{14}$ s^{-1}.

as well as the solution of the diffusion-reaction model for positron trapping in grain boundaries with grain boundaries as the single type of trap (Sec. III B).

To complete the picture, we note that also the diffusion-reaction model approach of Dupasquier *et al.*[20] and of Cizek *et al.*[10] is included in the present theory. Transcendental Eq. (26) which determines the annihilation rates $\lambda_{0,j}$ is identical to those given in Refs. 10 and 20. With some algebra it can further be shown that the corresponding intensities $I_{0,j}$ for the general case [Eq. (28)] and for the case with grain boundaries as single trap [Eq. (32)] agree with Refs. 10 and 20, respectively. However, it is worthwhile to point out that the present theory goes beyond the previous ones in so far as closed-form expressions for the major parameters [$\bar{\tau}$, Eqs. (20) and (30); I_b, Eqs. (24) and (31); and I_v, Eq. (22)] are derived which allow direct physical insight in the details of the e^+ annihilation characteristics.

In order to visualize the predictions of the model, Fig. 1 shows the mean positron lifetime $\bar{\tau}$ according to the exact solution [Eq. (20)] in dependence of the (a) grain radius r_0 and (b) the intragranular point-defect concentration C_v. Characteristic values of the e^+ annihilation parameters are used for the example, i.e., a specific e^+ trapping rate $\alpha = 10^3$ ms^{-1} at grain boundaries[20] and $\sigma_v = 4\times10^{14}$ s^{-1} at lattice vacancies,[27] a e^+ diffusion coefficient $D = 0.5\times10^{-4}$ m^2 s^{-1} (Ref. 28), and a free positron lifetime $\tau_f = 120$ ps as typical for metals. For the grain-boundary and point-defect-trapped states, a positron lifetime $\tau_b = 180$ ps characteristic of a structural free volume of the size of one

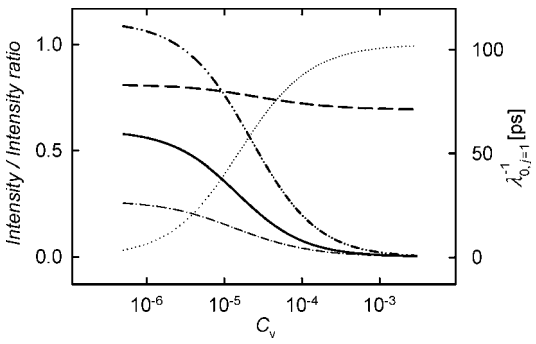

FIG. 2. Relative intensity $I_{0,j=1}$ (—) [Eq. (28)] and respective lifetime $\lambda_{0,j=1}^{-1}$ (–·–·–) of the first component of the series [Eqs. (26) and (27)], intensity ratio $I_{0,j=1}\times(\Sigma_{j=1}^{\infty}I_{0,j})^{-1} = I_{0,j=1}\times(1-I_b-I_v)^{-1}$ (– – –), and intensities I_b (–·–·–) [Eq. (24)], I_v(···) [Eq. (22)] in dependence of intragranular point defect concentration C_v. Parameters: $\tau_f = 120$ ps, $\tau_b = 180$ ps, $\tau_v = 300$ ps, $D = 0.5\times10^{-4}$ m^2 s^{-1}, $\alpha = 10^3$ ms^{-1}, $\sigma_v = 4\times10^{14}$ s^{-1}, and $r_0 = 1$ μm.

missing atom in the grain boundaries[5,7] and $\tau_v = 300$ ps as characteristic of vacancy agglomerates[29] is assumed, respectively. For $C_v = 0$, the mean positron lifetime increases with decreasing crystallite size due to the increase in the fraction of e^+ that reach the grain boundaries in their lifetime [Fig. 1(a)]. For $C_v > 0$, competitive e^+ trapping at grain boundaries and at intragranular point defects occurs. For high values of C_v [10^{-4} in the example of Fig. 1(a)] saturation trapping of e^+ prevails, for large grain sizes exclusively at intragranular point defects, for small grain sizes exclusively at grain boundaries, and for the intermediate regime of grain sizes both in point defects and grain boundaries. For low values of C_v [5×10^{-6} in the example of Fig. 1(a)] partial annihilation in the free state sets in with increasing grain sizes as shown by the value $\bar{\tau} < \tau_b$.

The same trend is reflected in the C_v dependency of $\bar{\tau}$ [Fig. 1(b)]. For grain sizes in the nm regime [$r_0 = 50$ nm in the example of Fig. 1(b)], saturation trapping at grain boundaries for small concentrations C_v turns into saturation trapping at point defects with increasing C_v. For larger grain sizes, partial annihilation in the free state and the grain-boundary-trapped state occurs for small values $C_v(\bar{\tau} < \tau_b)$. With increasing C_v competitive trapping at intragranular point defects sets in and dominates for large value of C_v when $\bar{\tau}$ reaches τ_v.

The intensities $I_{0,j}$ [Eq. (28)] of the components $\lambda_{0,j} > \tau_f^{-1}$ [Eqs. (26) and (27)] usually fall off rapidly with increasing order j so that in most practical cases only the first component of the sequence will be of relevance. For instance, Fig. 2 shows for the typical parameter set given above that the intensity $I_{0,j=1}$ of the first component comes to approximately 80% and more of the entire intensity of the sequence $\Sigma_{j=1}^{\infty}I_{0,j} = 1-I_b-I_v$ in the range where trapping from the free state can be detected experimentally. Therefore, a three-component analysis of experimental positron lifetime spectra will yield the two relevant e^+ annihilation rates τ_b^{-1}, τ_v^{-1} and their relative intensities I_b [Eq. (24)] and I_v [Eq. (22)] with reasonable accuracy along with a third component λ_0 (intensity $I_0 = 1-I_b-I_v$) which represents an average value of the sequence $\lambda_{0,j}$ close to the dominant component $\lambda_{0,j=1}$.

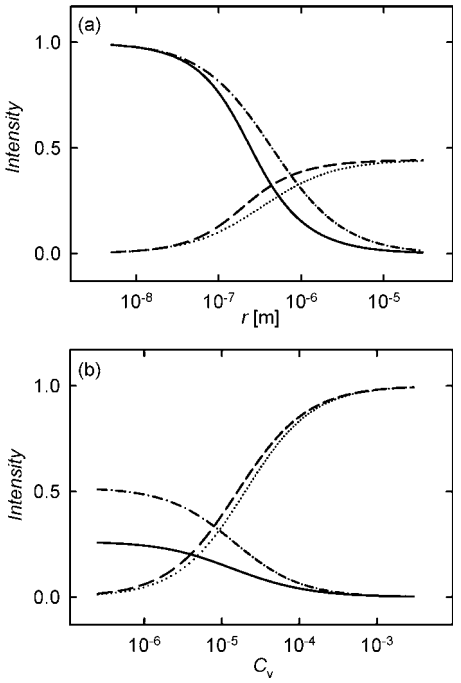

FIG. 3. Relative intensities I_b (—) [Eq. (24)] and I_v (– – –) [Eq. (22)] in dependence of (a) grain radius r_0 and (b) intragranular point defect concentration C_v. The solutions according to standard rate theory [Eq. (36)] are shown for comparison: I_b (–·– ·–), I_v(···). Parameters: τ_f=120 ps, τ_b=180 ps, τ_v=300 ps, D=0.5 $\times 10^{-4}$ m^2 s^{-1}, α=10^3 ms^{-1}, σ_v=4$\times 10^{14}$ s^{-1}, (a) C_v=10^{-5}, and (b) r_0=1 μm.

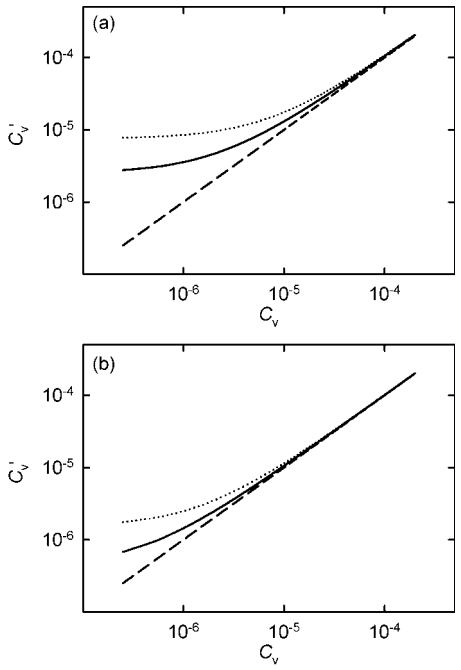

FIG. 4. Relation between true vacancy concentration C_v and the apparent vacancy concentration C_v' (—) obtained under the simplifying assumption that the sum intensity I_b+I_v [Eqs. (24) and (22)] of the lattice vacancy and the grain-boundary component with identical e^+ lifetime (τ_b=τ_v=180 ps) is exclusively due to vacancies [Eq. (38), see text]. Grain radius r_0=1 μm (a) and 5 μm (b). The relation according to standard rate theory [Eq. (36)] is shown for comparison (···). (– – –): reference line, C_v'=C_v. Parameters: τ_f =120 ps, D=0.5$\times 10^{-4}$ m^2 s^{-1}, α=10^3 ms^{-1}, and σ_v=4 $\times 10^{14}$ s^{-1}.

The description within the framework of the exact diffusion-reaction model is a prerequisite since the relative intensities of the exact solution I_b [Eq. (24)] and I_v [Eq. (22)] will differ in the general case from those of the standard trapping model [Eq. (36)]. As an example, Fig. 3 shows the variation in the relative intensities I_b and I_v with (a) grain radius and with (b) intragranular point-defect concentration. For a given point-defect concentration the intensity I_b of the grain-boundary component increases and the intensity I_v of the point-defect component decreases with decreasing grain radius due to the increasing fraction of e^+ that reaches the grain boundaries [Fig. 3(a)]. Likewise, for a given grain radius, I_v increases and I_b decreases with increasing point-defect concentration [Fig. 3(b)]. Compared to the exact solution of the present model, the standard trapping model shows qualitatively the same trend for the intensities I_b and I_v; however, the relative fraction of the grain-boundary component is systematically overestimated since diffusion limitation of the grain-boundary trapping is neglected in the standard trapping model [Fig. 3].

From a practical point of view the situation is of particular relevance where the e^+ lifetime in the intragranular point defects (τ_v) and the grain boundaries (τ_b) are similar and, therefore, the two components τ_v and τ_b cannot be discerned experimentally by e^+ lifetime spectroscopy. If in such cases diffusion-limited e^+ trapping at grain boundaries is not taken into consideration, the vacancy concentration derived from the experimentally determined intensity of the trap component may substantially differ from the true value. This is exemplary demonstrated in Fig. 4 which shows the relation between the true vacancy concentration C_v and the apparent vacancy concentration C_v' obtained under the simplifying assumption that the sum intensity I_b+I_v [Eqs. (24) and (22)] of the lattice vacancy and the grain-boundary component with identical e^+ lifetimes (τ_b=τ_v=180 ps) is exclusively due to trapping at lattice vacancies; i.e.,

$$I_b + I_v = I_v' = \frac{\sigma_v C_v'}{\tau_f^{-1} + \sigma_v C_v' - \tau_v^{-1}}. \tag{38}$$

For a grain radius of 5 μm the apparent vacancy concentration exceeds the true value in the concentration range C_v $<10^{-5}$ [Fig. 4(b)] and for 1 μm in an even larger concentration range [Fig. 4(a)]. Assuming transition-limited trapping at grain boundaries, the discrepancies between the true and apparent vacancy concentration would be even higher [Fig. 4] since a larger fraction of e^+ are trapped at grain boundaries when diffusion limitation is neglected. We conclude that for a precise determination of trapping rates in lattice vacancies concomitant trapping in vacancy-type free volumes in grain boundaries has to be taken into account even in such common cases that the grain size is in the regime of 1–10 μm.

V. CONCLUSIONS

The present model with the exact solution of the diffusion-reaction theory for the trapping of e^+ at grain boundaries and competitive transition-limited trapping at intragranular point defects yields a basis for the quantitative description of the e^+ behavior in polycrystals. It could be shown that the model includes as special case the simple trapping model, but generally this is not applicable to e^+ trapping in grain boundaries. For the full model, closed-form expressions were obtained for the mean positron lifetime $\bar{\tau}$ and for the intensities of the e^+ lifetime components associated with trapping at grain boundaries and at intragranular point defects. Compared to solutions in form of infinite series, these closed-form expressions allow deeper insight in the physical details of e^+ annihilation characteristics and can be conveniently applied for the analysis of experimental data. It turned out that the model is not only essential for e^+ annihilation studies which aim at issues of grain-boundary physics or nanoscaled material but is also of relevance when trapping rates of intragranular point defects are to be determined with high precision in polycrystalline materials with grain sizes in the micrometer range.

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