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Positron annihilation studies of the multilayer Cu–Cu_3Sn system

J Dryzek†§, A Czapla‡ and E Kusior‡

† Insitute of Nuclear Physics, 31-342 Kraków, ul. Radzikowskiego 152, Poland
‡ Academy of Mining and Metallurgy, 30-059 Kraków, al. Mickiewicza 30, Poland

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Abstract. We present a diffusion–transition model of the trapping and annihilation of positrons in the grain boundaries in the form of a plane, cylinder and sphere. This model provides the closed-form expressions for the positron lifetime spectrum, the mean positron lifetime and the value of the *S*-parameter evaluated from the annihilation line. The comparison of this model with the standard trapping model has been performed. In our theoretical consideration we have extended this model for the case when trapping centres for positrons are distributed inside the grain. The validity of the model has been tested with positive results for study of the positron annihilation in the multilayer system which was produced by a sequential magnetron dc sputtering of copper and tin layers.

1. Introduction

For several years we have observed the growing interest in the properties of various types of nanoscale material. Positron annihilation spectroscopy seems to be a convenient tool for studies of such materials, for example, of open volume defects. However, the problem of positron annihilation in fine grained samples is complex because it requires establishing how the diffusion process of thermalized positrons affects the positron annihilation characteristics. By the positron characteristics we mean the positron lifetime spectrum, the mean positron lifetime and the value of the *S*-parameter obtained from the Doppler broadening of the annihilation line. It is known that the positrons emitted from the radioactive source into the matter first thermalize, and then diffuse by sampling the region of the order of the diffusion length: $L_+ = \sqrt{D_+\tau_f}$, where D_+ is the positron diffusion coefficient and τ_f is the positron mean lifetime in the bulk material. The diffusion length for various materials is of the order of 0.1 μm, and if the grain or particle size is comparable with this value the diffusion of positrons should be taken into account in the analysis of the positron characteristics.

The first systematic studies of the positron lifetime for a mean size grain in polycrystalline Cu were performed by Lynn *et al* [1]. Afterwards, the studies were extended to fine grained alloys, e.g., ZnAl [2]. The simplest approach to the analysis of the obtained data is to assume that during thermalization the positrons are located in two distinct regions of a sample, e.g., a grain and its boundary, in which they next annihilate [3]. Therefore, only the volume ratio of the two regions is important and the positron diffusion process could be neglected. Another approach takes into account the rate equations in the standard two-state trapping model (STM) [4], which predicts a positron lifetime spectrum in the

§ E-mail address: jdryzek@alf.ifj.edu.pl.

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form of the sum of two exponential decay components. These two components represent the annihilation in two regions, or states, where positrons could be localized and then annihilated. It is assumed that the first region is a region where positrons are free and can walk randomly; the second one is a region associated with positron traps where they are bound. The transition from the free to the bound state is described by the trapping rate parameter. This model is especially justified for the positrons trapped at small atomic defects, such as monovacancies, with spatially uniform concentrations, where the trapping rate parameter is small enough. This indicates that the trapping is controlled by the transition process: it is the transition-limited regime. The model in a more extended form was used for the study of inhomogeneous samples, e.g., a fatigued aluminum single crystal [5].

However, for larger defects, such as voids, where the trapping is high enough, this model does not work [6]. In this case, the diffusion rather than transition controls the trapping process; this is the diffusion-limited regime. This problem was first studied by Brandt and Paulin [7]. They applied the so-called Smoluchowski boundary condition which means they assumed that the surfaces act as ideal sinks for positrons, and they extended the formal validity of the standard trapping model with an effective trapping rate related to the geometrical factors and to the positron diffusion constant. Nevertheless, this approach was not proved satisfactory (see e.g., [8] and [9]), and several authors attacked this problem within the framework of the more general diffusion–transition regime. For point defects it was worked out in [10] and for voids in [6]. The present paper follows the exact treatment of the diffusion–transition regime presented in [11], which yielded the closed-form expression for the positron characteristics associated with positron annihilation in the spherical grain boundary. We extend this treatment to the grain boundary in the form of layers and fibres. and to the case when the defects are present also in the grain volume. Moreover, the aim of the paper is the application of the obtained theoretical results to the description of the positron annihilation in a multilayer system. The systems of bimetallic samples consisting of many thin layers were first studied by Świątkowski *et al* [12, 13]. The measurement of angular distributions of the annihilation quanta allows us to detect the different positron affinity metals and also to deduce the positron diffusion length. This study focused on the application of the diffusion trapping model (DTM) in the diffusion–transition regime.

2. The diffusion trapping model

2.1. The defect free grain

The model characterizes the behaviour of the positrons by the following parameters: the diffusion coefficient D_+, the positron lifetime τ_f in the free state within the grain and its lifetime τ_b ($>\tau_f$) in the grain boundaries. Let us assume that at $t = 0$ the positrons are uniformly distributed in a sample and within the grain. The change of the positron concentration inside a grain in time and space is described by the diffusion equation:

$$\frac{\partial}{\partial t}C(\boldsymbol{r},t) = D_+\nabla^2 C(\boldsymbol{r},t) - \frac{1}{\tau_f}C(\boldsymbol{r},t). \tag{1}$$

The change of the number of positrons trapped at the boundary, $n_b(t)$, is governed by the following rate equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}n_b(t) = \alpha \iint_{\Sigma} \mathrm{d}S C(\boldsymbol{r},t) - \frac{1}{\tau_b}n_b(t) \tag{2}$$

where α represents the trapping rate of positrons from the grain to its boundary and Σ is the surface of the grain. The equations (1) and (2) must be completed by the continuity

equation for the positron flux at the interface between the grain and the grain boundary:

$$D_+ \iint_\Sigma \mathrm{d}\boldsymbol{S} \cdot \boldsymbol{\nabla} C(\boldsymbol{r}, t) + \alpha \iint_\Sigma \mathrm{d}S C(\boldsymbol{r}, t) = 0. \tag{3}$$

The set of equations (1)–(3) represents the DTM, which takes into account the diffusion and transition processes. No detrapping process from surface to the grain is taken into consideration. By introducing the Laplace transform and taking into account grains symmetrical in shape we may simplify the solution of these equations [11].

The final results are presented below without following the solution in detail. The positron lifetime spectrum, i.e. the probability of annihilation at time t, resulting from equations (1), (2) and (3) for the grain in the form of a $2d$ thickness layer is as follows:

$$\begin{aligned}
-\frac{1}{n_0}\frac{\mathrm{d}n(t)}{\mathrm{d}t} = {} & \frac{L_+}{d}\frac{1}{\sqrt{\tau_b^2 - \tau_b\tau_f}}\frac{\tanh(\sqrt{1-\tau_f/\tau_b}\,d/L_+)}{1+\sqrt{1-\tau_f/\tau_b}[L_+ \cdot \tanh(\sqrt{1-\tau_f/\tau_b}\,d/L_+)]/\alpha\tau} \\
& \times \exp\left(-\frac{t}{\tau_b}\right) + 2\left(\frac{\tau_b}{\tau_f} - 1\right) \\
& \times \sum_{i=1}^{\infty} \frac{[1 + (L_+^2/d^2)\xi_i]}{[\tau_b - \tau_f + (L_+^2\tau_b/d^2)\xi_i^2][1 + (L_+^2/\alpha\tau_f d)^2\xi_i^2 + L_+^2/\alpha\tau_f d]\xi_i^2} \\
& \times \exp\left[-\frac{t}{\tau_f}\left(1 + \frac{L_+^2}{d^2}\xi_i^2\right)\right]
\end{aligned} \tag{4}$$

where ξ_i ($i = 1, 2, \ldots$) denote the solution of the transcendental equation: $\xi_i \tan\xi_i = \alpha\tau_f d/L_+^2$. The annihilation probability of positrons in the free state, i.e., inside a grain, is equal to:

$$\eta_f = 1 - \frac{L_+}{d}\frac{\tanh(d/L_+)}{1 + (L_+/\alpha\tau_f)\tanh(d/L_+)}. \tag{5}$$

The annihilation probability in the bound state at the boundary can be expressed: $\eta_b = 1 - \eta_f$. Having established these both probabilities, it is easy to express the next important characteristics:

- the mean positron lifetime:

$$\bar{\tau} = \eta_f\tau_f + \eta_b\tau_b \tag{6}$$

- and the value of the S-parameter defined as a central part of the annihilation line:

$$S = \eta_f S_f + \eta_b S_b \tag{7}$$

where S_f and S_b represent the value of the S-parameter associated with the positron annihilation in the free and bound state, respectively.

The solution of the DTM for the fibre of radius r leads to the following expression for the positron annihilation spectrum:

$$\begin{aligned}
-\frac{1}{n_0}\frac{\mathrm{d}n(t)}{\mathrm{d}t} = {} & 2\frac{L_+}{r}\frac{1}{\sqrt{\tau_b^2 - \tau_b\tau_f}}\frac{F^{(2)}(\sqrt{1-\tau_f/\tau_b}\,r/L_+)}{1+\sqrt{1-\tau_f/\tau_b}(L_+/\alpha\tau_f)F^{(2)}(\sqrt{1-\tau_j/\tau_b}\,r/L_+)} \\
& \times \exp\left(-\frac{t}{\tau_b}\right) + 4\left(\frac{\tau_b}{\tau_f} - 1\right) \\
& \times \sum_{i=1}^{\infty} \frac{[1 + (L_+^2/r^2)\zeta_i^2]}{(\tau_b - \tau_f + (L_+^2\tau_b/r^2)\zeta_i^2)[(L_+^2/\alpha\tau_f r)^2\zeta_i^2 + 1]\zeta_i^2}
\end{aligned}$$

$$\times \exp\left[-\frac{t}{\tau_f}\left(1+\frac{L_+^2}{r^2}\zeta_i^2\right)\right] \tag{8}$$

where $F^{(2)}(z) = \mathrm{j}J_1(\mathrm{j}z)/J_0(\mathrm{j}z) = I_1(z)/I_0(z)$, $\mathrm{j} = \sqrt{-1}$, $J_{0,1}$ are the Bessel functions of the first kind, $I_{0,1}$ are the modified Bessel function of the first kind and ζ_i is the solution of the transcendental equation: $\zeta_i J_1(\zeta_i) - \alpha\tau_f r/L_+^2 = 0$. The annihilation probability of positrons in the free state inside a fibre is equal to:

$$\eta_f = 1 - 2\frac{L_+}{r}\frac{F^{(2)}(r/L_+)}{1+(L_+/\alpha\tau_f)F^{(2)}(r/L_+)}. \tag{9}$$

The same solution for the grain in the form of a sphere of radius R gives us the following expression for the positron lifetime:

$$\begin{aligned}-\frac{1}{n_0}\frac{\mathrm{d}n(t)}{\mathrm{d}t} = {} & 3\frac{L_+}{R}\frac{1}{\sqrt{\tau_b^2-\tau_b\tau_f}}\frac{F^{(3)}(\sqrt{1-\tau_f/\tau_b}R/L_+)}{1+\sqrt{1-\tau_f/\tau_b}(L_+/\alpha\tau_f)F^{(3)}(\sqrt{1-\tau_f/\tau_b}R/L_+)} \\ & \times \exp\left(-\frac{t}{\tau_b}\right) + 6\left(\frac{\tau_b}{\tau_f}-1\right) \\ & \times \sum_{i=1}^{\infty}\frac{[1+(L_+^2/R^2)\varsigma_i^2]}{[\tau_b-\tau_f+(L_+^2\tau_b/R^2)\varsigma_i^2][1-L_+^2/\alpha\tau_f R+(L_+^2/\alpha\tau_f R)^2\varsigma_i^2]\varsigma_i^2} \\ & \times \exp\left[-\frac{t}{\tau_f}\left(1+\frac{L_+^2}{R^2}\varsigma_i^2\right)\right]\end{aligned} \tag{10}$$

where $F^{(3)}(z) = \coth(z) - 1/z$, and ς_i is the solution of the transcendental equation: $\varsigma_i F^{(3)}(\varsigma_i) + \alpha\tau_f R/L_+^2 = 0$. The annihilation probability of positrons in the free state inside a sphere is equal to:

$$\eta_f = 1 - 3\frac{L_+}{R}\frac{F^{(3)}(R/L_+)}{1+(L_+/\alpha\tau_f)F^{(3)}(R/L_+)}. \tag{11}$$

If we look carefully at the above relations, we can see that they depend on the parameters which always contain the diffusion length: $L_+/\alpha\tau_f$, and for a layer the ratio d/L_+, for a cylinder r/L_+ and for a sphere R/L_+. In comparison to the STM we have only one parameter more in this model. In figure 1 we present the effect of these parameters on the mean positron lifetime $\bar{\tau}/\tau_f$, (figure 1(a)), the ratio τ_1/τ_f (figure 1(b)) and the intensity of the lifetime components associated with the annihilation at the grain boundary, (figure 1(c)).

In the diffusion and/or transition-limited regime the presented solutions approximate to the well known solutions of the STM. For instance in the case of a layer in the diffusion regime when α is big and L_+ is small then $\alpha\tau_f d/L_+^2 \to \infty$, the solution of the transcendental equation for $i = 1$ is equal to $\xi_1 = \pi/2$. If we neglect the terms for $i > 1$ the equation (4) is reduced to the well known relation on the positron lifetime spectrum within the STM with the trapping rate parameter equal to $\kappa = \xi_1^2 L_+^2/(\tau_f d^2)$. Such results can also be found in the work of Brandt and Paulin [7]. We can obtain the similar reduction of the relation presented above in the transition-limited regime, when $\alpha\tau_f d/L_+^2 \to 0$ but now the trapping rate is equal to $\kappa = \alpha/d$. Table 1 presents the trapping rate parameters evaluated for a fibre and a sphere. We should notice that the trapping rate parameter within the STM depends only on the trap concentration which localizes positrons, and on the trapping efficiency which is characterized by the cross section additionally. The trapping rate deduced from the DTM depends on the distance between the traps.

The positron lifetime spectra equations (4), (8), (10) deduced from the DTM consist of an infinite number of lifetime components, the longest of which equals τ_b and the other

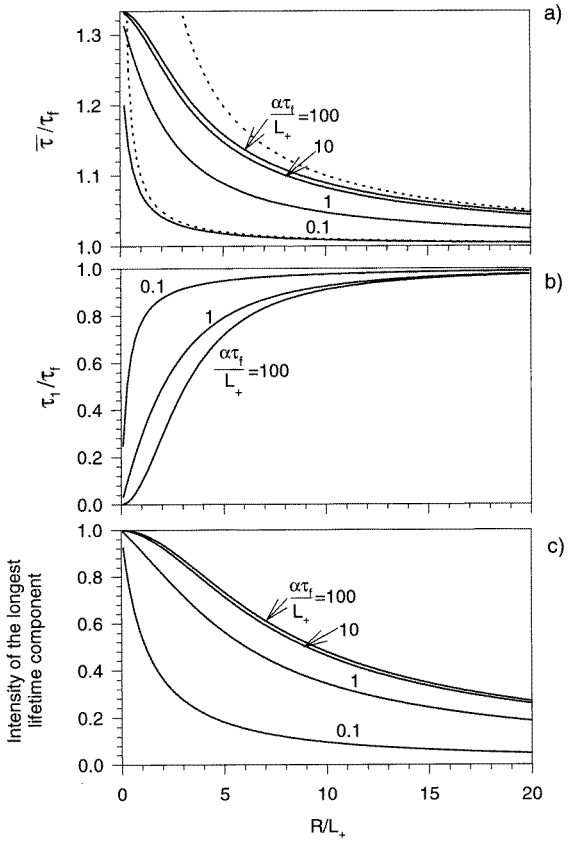

Figure 1. (a) The mean positron lifetime, (b) the first lifetime component of the sum (10) normalized to the τ_f value and (c) the intensity of the lifetime component associated with the positron annihilation at the grain boundary. The calculations were performed for the sphere of different $\alpha\tau_f/L_+$ values, as a function of the grain radius divided by the diffusion length L_+. The dotted upper and lower lines present the asymptotic relations. In the calculations it was assumed that $\tau_b/\tau_f = 4/3$.

Table 1. The solution of the transcendental equation in the diffusion-limited and transition-limited regime and the values of the trapping rate parameter used in the STM. The evaluations were performed for the grains in the form of layer, fibre and sphere.

	Layer	Fibre	Sphere
diffusion-limited	$\xi_1 = \pi/2$	$\zeta_1 = 2.4048$	$\varsigma_1 = \pi$
regime	$\kappa = \frac{\pi^2}{4}\frac{L_+^2}{d^2\tau_f}$	$\kappa = 5.7831\frac{L_+^2}{r^2\tau_f}$	$\kappa = \pi^2\frac{L_+^2}{R^2\tau_f}$
transition-limited	$\xi_1 = \sqrt{\alpha\tau_f d/L_+^2}$	$\zeta_1 = \sqrt{2\alpha\tau_f r/L_+^2}$	$\varsigma_1 = \sqrt{3\alpha\tau_f R/L_+^2}$
regime	$\kappa = \alpha/d$	$\kappa = 2\alpha/r$	$\kappa = 3\alpha/R$

components $\tau_i < \tau_b$ $(i = 1, 2, \ldots)$ and $\tau_{i+1} < \tau_i$. The authors believe that experimental detection of such a series of components would be an excellent proof of the validity of the DTM. But we are aware that this is not an easy task. The values of the components

τ_i for $i > 1$ are smaller than the value of τ_f because the solutions of the transcendental equation are bigger than unity, and increase with increasing i [14]. At present on the basis of the experimental positron lifetime spectrum it is not possible to evaluate the lifetime components whose values are smaller than 30 ps, thus we believe that one can detect at most two components of the lifetime series. We should notice the fact that their intensities decrease very fast with increasing i. We think that experimental studies of the DTM should focus on the measurement of the S-parameter as a function of the grain size. This quantity decreases with increasing grain size in the same way as the mean positron lifetime (figure 1(a)).

2.2. The grain with defects

In the subsection above we assumed that no defects able to localize positrons are present inside the grain. This cannot be true in some applications. Let us assume that vacancies of one type are uniformly distributed inside the grain and they create a new state for positrons. The positron lifetime inside the vacancy is denoted as τ_v and the trapping rate of positron from the free to vacancy state as κ. In this case we must complete the DTM equations because we have to include the new positron state. The equation (1) will have the following form:

$$\frac{\partial}{\partial t}C(\boldsymbol{r},t) = D_+\nabla^2 C(\boldsymbol{r},t) - \left(\frac{1}{\tau_f}+\kappa\right)C(\boldsymbol{r},t) \tag{12}$$

and we can express the rate equation for the number of positrons trapped at a vacancy as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}n_v(t) = -\frac{1}{\tau_v}n_v(t) + \kappa\iiint_{\Omega}\mathrm{d}\boldsymbol{r}C(\boldsymbol{r},t) \tag{13}$$

where Ω is the volume of the grain. The equations (2) and (3) have the same form as before. No detrapping of positrons from the vacancy is taken into account. The solution of the equations (12), (13), (2) and (3) using the method as above leads to the following form for the mean positron lifetime:

$$\bar{\tau} = \tau_b + \frac{\tau_f}{1+\kappa\tau_f}\left[\kappa(\tau_v-\tau_b) + \left(1-\frac{\tau_b}{\tau_f}\right)\right]\eta_f. \tag{14}$$

For the grain in the form of a layer, fibre and sphere the probability η_f is expressed by the equations (5), (9) and (11), respectively. Please note that now in these equations as well as in the equation for $L_+\ \tau_f$ must be replaced by $\tau_f/(1+\tau_f\kappa)$. The value of the S-parameter now is given as follows:

$$S = \frac{1}{1+\kappa\tau_f}\eta_f S_f + (1-\eta_f)S_b + \frac{\kappa\tau_f}{1+\kappa\tau_f}\eta_f S_v \tag{15}$$

where S_v is the S-parameter associated with the positron annihilation at the vacancy state. Note that if $\tau_v = \tau_b$ or $S_v = S_b$ and $\eta_f = 1$, equations (14) and (15) reduce to the well known relations obtained within the two-state STM.

We present the expression for the positron lifetime spectrum only when the grain has a spherical form:

$$-\frac{1}{n_0}\frac{\mathrm{d}n(t)}{\mathrm{d}t} = 3\frac{L_+}{r}(\tau_b^2 - \tau_b\tau_f/(1+\kappa\varsigma_f))^{-1/2}F^{(3)}(\sqrt{1-[\tau_f/\tau_b(1+\kappa\tau_f)]}R/L_+)$$
$$\times\exp(-t/\tau_b)[1+\sqrt{1-\tau_f/\tau_b(1+/\kappa\tau_f)}/[L_+(1+\kappa\tau_f)/\alpha\tau_f]$$

$$\times F^{(3)}(\sqrt{1-\tau_f/\tau_b(1+\kappa\tau_f)}R/L_+)]^{-1} + 6\left(\frac{\tau_b(1+\kappa\tau_f)}{\tau_f}+1\right)$$
$$\times\sum_{i=1}^{\infty}\{[1+(L_+^2/R^2)\varsigma_i^2]\exp\{-[t(1+\kappa\tau_f)/\tau_f][1+(L_+^2/R^2)\varsigma_i^2]\}$$
$$\times[(\tau_b-\tau_f/(1+\kappa\tau_f)+(L_+^2\tau_b/R^2)\varsigma_i^2)[1-L_+^2(1+\kappa\tau_f)/\alpha\tau_f R$$
$$+(L_+^2(1+\kappa\tau_f)/\alpha\tau_f R)^2\varsigma_i^2]\varsigma_i^2]^{-1}\} + \frac{\kappa\tau_f\exp(-t/\tau_v)}{\tau_v(1+\kappa\tau_f)-\tau_f}$$
$$\times\left\{1-3\frac{L_+}{R}[1-\tau_f/\tau_v(1+\kappa\tau_f)]^{-1/2}\right.$$
$$\times[F^{(3)}(\sqrt{1-[\tau_f/\tau_v(1+\kappa\tau_f)]}R/L_+)][1+\sqrt{1-\tau_f/\tau_v(1+\kappa\tau_f)}$$
$$\left.\times[L_+(1+\kappa\tau_f)/\alpha\tau_f]F^{(3)}(\sqrt{1-\tau_f/\tau_v(1+\kappa\tau_f)}R/L_+)]^{-1}\right\}. \qquad (16)$$

The ς_i parameter is the solution of the transcendental equation: $\varsigma_i F^{(3)}(\varsigma_i)+\alpha\tau_f R/L_+^2(1+\kappa\tau_f)=0$. Equation (16) can be obtained from equation (10) by replacing τ_f by $\tau_f/(1+\kappa\tau_f)$ and adding the last term associated with the lifetime component τ_v. The expression in the square brackets of this component is easy to deduce if we subtract from unity the intensity of the component associated with the lifetime component τ_b and we substitute τ_b by τ_v. Following this procedure we may write the positron lifetime expression when the grain has the form of a layer or a fibre.

The following section shows the application of the results presented above to the description of positron annihilation results in the multilayer system.

3. Experimental results and discussion

Our multilayer samples were prepared by a sequential magnetron dc sputtering of two cathodes: Sn and Cu in the argon atmosphere under the pressure of 5×10^{-3} Torr. As a substrate we used a Cu plate of 2 mm thickness and 1.5 cm × 1.5 cm in size. Before deposition the plates had been well annealed under a vacuum for several hours at 900 °C and then slowly cooled to room temperature. The substrates were moved under the sputtered targets, and the films of Cu and Sn were deposited. During deposition the temperature of the substrate was controlled. The thickness of each Sn film was the same and equal to 20 nm, but the thickness of a single Cu film changed from sample to sample from 0.25 μm to 3 μm. The thickness of films was controlled by measuring the time of the deposition under the cathodes. The number of films was also varied in order to ensure the same total thickness of the multilayer system; it was equal 15 μm for each sample. We found experimentally that in such a case almost 70% of positrons emitted from the ^{22}Na source were stopped in the multilayer system and the rest passed to the substrate.

The samples prepared were tested by x-ray diffraction, using a Philips Analytical X-Ray B.V. device. We observed the well defined picks from the Cu but instead of Sn picks we detected the well defined Cu_3Sn ε-phase. The lattice constant of the Cu layer was equal to $0.316\,14\pm0.000\,10$ nm which is in agreement with the bulk value: 0.316 150 nm.

For the set of samples with different thickness of Cu layer we measured the *S*-parameter of the annihilation line by using the HP Ge detector, with the energy resolution (the full width at half of maximum) evaluated to be equal to 1.29 keV at 511 keV, using the ^{22}Na source of about 20 μCi, sandwiched between thin Kapton foils. Additionally, the positron lifetime measurements were carried out at the *fast–fast* spectrometer type with NE111 scintillator

equipment with time resolution of 310 ps. The data were analysed using the LT computer program [15].

In the multilayer system produced by the procedure described above the layer of the ε-phase plays the role of an interface or a boundary where positrons could be localized. Note that this phase has the orthorhombic structure with lattice constants: $a = 0.434$ nm, $b = 0.556$ nm and $c = 3.82$ nm which indicates the large misfit between the crystalline structure of the Cu layer. This boundary may be the place where point defects like vacancy clusters appear, which enhances the positron localization process. Positron characteristics associated with positron annihilation in such a place should be different from those when a positron annihilates between the Cu_3Sn layers, i.e., inside the Cu layers. In consequence, these characteristics measured for the system should exhibit a dependency on the thickness of the Cu layer, as was suggested by the DTM discussed previously. Indeed, figure 2 presents the measured value of the S-parameter as a function of the thickness of the Cu layer (d_{Cu}). The value of the S-parameter decreases with the increase of this thickness, which can be described using the formula:

$$S(d_{Cu}) = \varepsilon S_{sub} + (1 - \varepsilon) S_{sys}(d_{cu}) \tag{17}$$

where ε is the fraction of positrons implanted into the substrate after passing through the multilayer system, S_{sub} is the value of the S-parameter measured only for the substrate and it was equal to 0.5085 ± 0.0006, and $S_{sys}(d_{Cu})$ is the value of the S-parameter associated with the positron annihilation in the multilayer system, which should depend on the thickness of Cu layer. The value ε can be treated as a fitting parameter or calculated by using the formula [16]: $\varepsilon = -\alpha_+ \int_D^\infty \mathrm{Ei}(-\alpha_+ t)\,\mathrm{d}t$, where α_+ is the linear absorption coefficient of a positron in matter, D is the thickness of the multilayer system and $\mathrm{Ei}(z)$ is the exponential integral function. If we assume that $\alpha_+ = 0.027\ \mu\mathrm{m}^{-1}$ as for Cu [17] and $D = 15\ \mu$m we can evaluate that $\varepsilon = 0.297$. The same value, within the accuracy, was also obtained from the fits, which suggests the validity of the above formula.

We start analysing the obtained dependency by using the formula for the S-parameter for the diffusion regime. According to Brandt and Paulin [7] we can use the formula evaluated from the STM where the trapping rate depends on the diffusion length L_+ and the size of the grain (see table 1). In this case the S-parameter can be expressed as follows:

$$S_{sys}(d_{Cu}) = \frac{S_f + 2\pi S_b L_+^2/d_{cu}^2}{1 + 2\pi L_+^2/d_{cu}^2}. \tag{18}$$

In this relation it is assumed that the multilayer system consists of the same layers. The dotted line marked by (a) in figure 2 presents the best fit of equation (17) with (18) to the experimental points. The values of the parameters obtained from this fit are equal to: $S_f = 0.5288 \pm 0.0002$, $S_b = 0.5349 \pm 0.0007$ and $L_+ = 0.44 \pm 0.22\ \mu$m. Equation (18) describes the obtained data well but the value of the diffusion length is too high. The measurement of this quantity with the use of the slow positron beam indicates the value $0.130 \pm 0.005\ \mu$m for Cu at room temperature [18]. In the case discussed we should observe a rather lower value because the value of the S-parameter for positrons which annihilate in the Cu layer is higher than S_{sub}.

We can conclude that we have not made a proper assumption. The description can be improved using the relation from the DTM which takes into account the transition regime. Nevertheless, we assume that positrons diffuse in the layer, hence we apply equation (7) to the description of our data. The dashed line (b) in figure 1(a) presents the best fit with the following values of the parameters: $S_f = 0.5370 \pm 0.0001$, $S_b = 0.5458 \pm 0.0002$, $\alpha\tau_f = (9.8 \pm 6.0) \times 10^2\ \mu$m and $L_+ = 0.35 \pm 0.04\ \mu$m. In this case the description of the

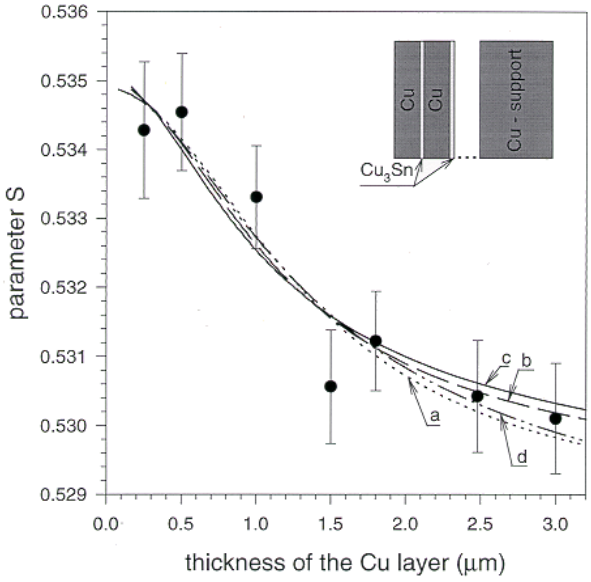

Figure 2. The value of the S-parameter versus the thickness of the Cu layer in the multilayer Cu–Cu_3Sn system. The dotted line presents the best fit from the STM, equations (18) and (17). The other lines are presenting the best fits from the DTM (see text).

data is also satisfactory but the value of the diffusion length is still too high. In the next step we have decided to change the assumption that the layer is ideal for positrons. From other experiments, e.g., the measurement of electrical conductivity of optical properties we know that the layers obtained by sputtering exhibit the grain structure which correlates with its thickness. Thus, let us assume that in our case spherical grains are present in Cu layer, whose diameter is equal to the thickness of the layer. This assumption is supported by the fact that the growing process of the grains is stopped by covering the Sn layer, and finally the grain size is limited by the two thin Cu_3Sn layers. For the description of our data we use equations (17) and (7) together with (11). The solid line (c) in figure 2 presents the best fit and the values of the fitted parameter are following: $S_f = 0.5370 \pm 0.0001$, $S_b = 0.5459 \pm 0.0002$, $\alpha\tau_f = (2.45 \pm 1.0) \times 10^3$ μm and $L_+ = 0.138 \pm 0.05$ μm. In this approach the value of the diffusion length corresponds much better to the values obtained by other methods.

So far we have assumed that the Cu grain is free of defects, which may be supported the x-ray measurements above but it contradicts positron experiments reported in the literature [19]. Let us take into consideration equations (15) and (11) which describe the S-parameter when positrons diffuse inside the spherical grain where vacancies are present. In order to reduce the number of fitted parameters we assumed that $S_f = 0.5085$, which was measured above. The line (d) in figure 2 presents the best fit and the obtained parameters are as follows: $S_b = 0.5457 \pm 0.0007$, $S_v = 0.5378 \pm 0.0005$, $\alpha\tau_f = (2.97 \pm 2.0) \times 10^3$ μm, $L_+ = 0.177 \pm 0.04$ μm and $\kappa\tau_f = 11.8 \pm 2.0$. From the lifetime measurements we know that for the Cu $\tau_f = 122 \pm 1.0$ ps and if we take the value for the trapping efficiency parameter as equal to $\mu = 11 \times 10^{14}$ s^{-1} [20] we can evaluate the concentration of vacancies in the grain: $C_v = \kappa/\mu = (8.8 \pm 2.0) \times 10^{-5}$. This value is quite reasonable.

The measurement of positron lifetime supports this approach. Nevertheless, as has been mentioned in section 2.1 this type of measurement for the study of the DTM is not

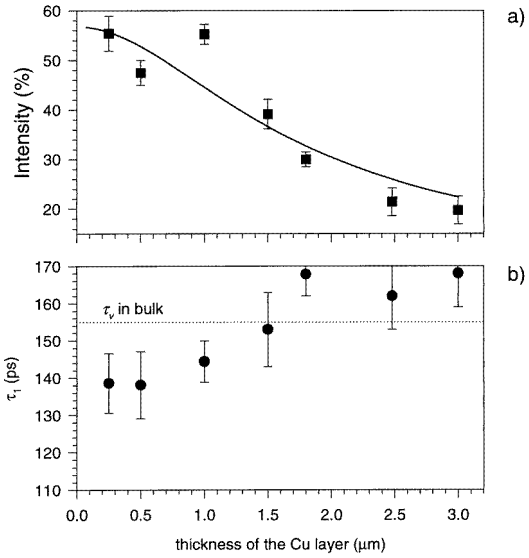

Figure 3. The intensity of the longest lifetime component (a) and the value of the shortest lifetime component (b) versus the thickness of the Cu layer in the multilayer Cu-Cu_3Sn system. For the lines see text.

convenient because of the complex relation describing the spectrum. In our analysis we evaluated only two lifetime components from the spectrum with the χ^2 value close to unity (the contribution from the positron source and the support in which it was fixed). We detected that the value of the longest lifetime component, which was equal to 308 ± 20 ps, did not change significantly with the thickness of the Cu layer. This value originates from positron annihilation at the grain boundary defects, which is supported by the fact that its intensity decreases with the increase of the thickness (figure 3(a)). Such a dependency is predicted by the DTM (figure 1(c)). The high value of this component indicates the presence of large vacancy clusters at the boundary. The value of the shortest lifetime component slightly increases with the increase of the thickness of the Cu layer, (figure 3(b)). Because the average value of this component is equal to 150 ± 11 ps which is close to the positron annihilation trapped at vacancies in bulk (155 ps [20]), we believe that this component is associated with the positron annihilation at such defects distributed inside the grain. The observed small changes can be understood as the influence of the size of a grain on the environment of a vacancy. In our deconvolution procedure we did not observe the other components τ_i mentioned in subsection 2.1. In figure 3(a) the solid line presents the intensity of the longest lifetime component calculated from equation (16) where vacancies inside the grain were taken into account. The layer parameters were taken from the measured *S*-parameter as above. We did not fit the curve. However, in both cases we multiplied the theoretical values by the factor 0.568 in order to obtain a good agreement with the experiment.

We should point out the large value of the $\alpha\tau_f$ parameter evaluated from the data responsible for the localization of the positron at the boundary. For instance, this parameter evaluated by Dupasquier *et al* [21] for Al-based alloys was four orders smaller, about 0.4 μm. This can be explained by the different type of trap responsible for the localization of positrons in both cases. For multilayers these can be large voids for which the trapping

efficiency value is a bigger quantity than for single vacancies present in alloys. Note that the accuracy of this parameter is poor.

Because the vacancies were present inside the grain we should expect a value for the diffusion length smaller than 0.138 ± 0.05 μm or 0.177 ± 0.04 μm obtained from the final fits. The great value may be explained by the fact that the ratio d/L^+ mainly contributes in the DTM. It means that if we overestimate the thickness of the layers or grain size, we overestimate the diffusion length as well. The studies performed by Huttunen *et al* [22] on epitaxial Cu/Ag(111) and Ag/Cu(111) structures indicate that within the layer defect concentration close to the interface exhibits a profile with characteristic attenuation length of 0.15 μm for this system. Taking this into account we can obtain the reduction of the diffusion length of about 10% and obtain a good description of our data. Higher values of the diffusion length were evaluated also by Dupasquier *et al* [21]. According to Dupasquier *et al* this discrepancy results from statistical dispersion of the grain size which should be reflected in the reduction of their effective radii. It cannot be excluded that both these reasons are responsible for the increase of the diffusion length parameter evaluated from the DTM. In [23] we concluded that the shapes of the grains also play an important role.

It is worth noting the type of defect present in the layers differs from that which we can find, e.g. in highly deformed Cu. We pressed a pure polycrystalline Cu sheet and reduced its thickness by 83%. The measurement of the *S*-parameter for this pressed polycrystalline Cu sheet gives the value: 0.5337 ± 0.0008; we have found only one lifetime component equal to 187 ± 1 ps and in its lifetime spectrum. The comparison suggests that the layers of the multilayer which we have produced start to recover.

In conclusion, the solution of the differential equations (1), (2) and (3) of the DTM in the case of grains which have a symmetric shape: layer, cylinder and sphere can be presented in a closed-form expression even if vacancies inside the grain are present. The DTM is able to describe the observed dependency of the positron annihilation characteristics as a function of thickness of the Cu layer in the produced multilayer system. From the data we evaluated the diffusion length for positron in the Cu layer which was equal to: 0.138 ± 0.05 μm or 0.177 ± 0.04 μm depending on the type of datum evaluation.

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References

[1] Lynn K, Ure R and Byrne J G 1974 *Acta Metall.* **22** 1075
[2] McKee B T 1980 *Phil. Mag.* **41** 65
[3] Dong Y, Xiong L Y and Lung C W 1991 *J. Phys.: Condens. Matter* **3** 3155
[4] Bergensen B and Stott M J 1969 *Solid State Commun.* **7** 1203
[5] Hjelmorth E, Rasmussen G and Träff J 1977 *Nuovo Cimento* B **41** 284
[6] Nieminen R, Laakkonen J, Hautojärvi J and Vehanen A 1979 *Phys. Rev.* B **19** 1397
[7] Brandt W and Paulin R 1972 *Phys. Rev.* B **5** 2430
[8] Paulin R, Ripon R and Brandt W 1974 *Appl. Phys.* **4** 343
[9] Soininen E, Huomo H, Mäkinen P A, Hautojärvi P and Vehanen A 1990 *Phys. Rev.* B **41** 6227
[10] Frank W and Seeger A 1974 *Appl. Phys.* **3** 61
[11] Würschum R and Seeger A 1996 *Phil. Mag.* A **73** 1489
See also Kögel G 1996 *Appl. Phys.* A **63** 227
[12] Świątkowski W, Rozenfeld B, Kołodziej H B and Szuszkiewicz S 1975 *Acta Phys. Pol.* A **47** 79
[13] Ewertowski R and Świątkowski W 1987 *Phys. Scr.* **35** 745

[14] Crank J 1975 *The Mathematics of Diffusion* (Oxford: Clarendon)
[15] Kansy J 1996 *Nucl. Instrum. Methods* A **374** 235
[16] Dryzek J 1997 *Nukleonika* **42** 95
[17] Paulin R 1983 *Positron Solid-State Proc. Int. School of Physics 'Enrico Fermi'* ed W Brandt and A Dupasquier (Amsterdam: North-Holland) p 565
[18] Britton D T, Huttunen P A, Mäkinen J, Soininen E and Vehanen A 1989 *Phys. Rev. Lett.* **62** 2413
[19] Schut H, van Veen A, Britton D T, Hollanders M A and Thysse B J 1989 *Positron Annihilation* ed L Dorikens-Vanpraet, M Dorikens and D Segers (Singapore: World Scientific) p 428
[20] Schaefer H-E, Stuck W, Banhart F and Bauer W 1987 *Mater Sci. Forum* **15–18** 117
Schaefer H-E 1987 *Phys. Status Solidi* a **102** 47
[21] Dupasquier A, Romero R and Somoza A 1993 *Phys. Rev.* B **48** 9235
[22] Huttunen P A, Mäkinen J and Vehanen A 1990 *Phys. Rev.* B **41** 8062
[23] Dryzek J and Czapla A 1998 *J. Phys.: Condens. Matter* **10** L547