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Computer simulations of positron-lifetime spectroscopy on thermally generated vacancies in copper and comparison with experimental results

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Computer simulations of positron-lifetime spectra on thermally generated vacancies in copper have been carried out in order to separate possible artifacts of the analysis procedure from physical effects. We use experimental results of absolute vacancy concentration measurements and the conventional two-state trapping model to generate input parameters for the simulation. The computed spectra are analyzed by means of the programs POSITRONFIT and PATFIT-88. The comparison of the input parameters with the fitted parameters demonstrates the validity of the fitting procedure for lifetimes greater than 40 ps. We have applied the simulation to the analysis of recent positron-lifetime measurements, which have shown a nonlinear temperature dependence of the calculated bulk lifetime in the vacancy region. It has been suggested that this nonlinearity could be an artifact of the fitting procedure. However, this study shows clearly that application of these fitting procedures to our simulated spectra produces no artifacts here; the output agrees with the input.

In the last two decades, positron-lifetime spectroscopy has turned out to be one of the most powerful tools for the investigation of vacancy formation in metals (see Ref. 1 for a review). The two-state trapping model, which was introduced by Goldanskii and Prokopev[2] as well as by Brandt[3] and generalized by Bergerson and Stott[4] and Connors and West,[5] establishes the connection between the measured spectra (e.g., the lifetimes τ_1, τ_2 and corresponding intensities I_1, I_2) and the concentration of thermal vacancies under four basic assumptions: (i) two positron states of annihilation, (ii) no detrapping, (iii) trapping of thermalized positrons only, and (iv) a constant specific trapping rate. While no contradictions are found to (i) and (ii) in noble metals,[6–11] several authors[10–18] interpreted observed deviations of their measurement from the two-state trapping model as the result of prethermal trapping of positrons (for a review, see Ref. 18). Nielsen, Lynn, and Chen[19] determined the influence of nonthermal trapping on the specific trapping rate by performing slow positron beam experiments.

Kluin and Hehenkamp[18] compared the results of positron-lifetime spectroscopy with absolute measurements of equilibrium vacancies in copper. The authors pointed out a significant deviation between the formation enthalpies extracted from positron annihilation and those from the absolute technique as shown in Table I. In a temperature range in which two lifetimes (τ_1 and τ_2) are detectable, one can calculate the lifetime τ_f' using a solution of the conventional two-state trapping model[1–5]

$$\frac{1}{\tau_f'}=\lambda_f'=I_1\lambda_1+I_2\lambda_2 \ . \tag{1}$$

Furthermore, the authors found a nonlinear increase of τ_f' compared to the extrapolation of τ_f from the prevacancy region where $\tau_1=\tau_f$, as depicted in Fig. 1. The same deviations have been observed in earlier investigations of copper,[14] aluminum,[15] and lead.[16] An extended

TABLE I. Vacancy formation enthalpies for copper obtained by different investigators in positron annihilation experiments and differential dilatometric measurements.

Method	H_v^f (eV)	Ref.	Remarks
Positron	1.20±0.02	20	
Annihilation	1.28±0.07	21	
	1.28±0.10	22	
	1.28±0.04	10	
	1.28±0.04	11	
	1.13±0.04	23	
	1.28±0.04	18	Conventional model
	1.19±0.04	18	Model with prethermal trapping
Dilatometric	1.19±0.03	18	Absolute technique
	1.18	24	Absolute technique
	1.17±0.11	25	Absolute technique

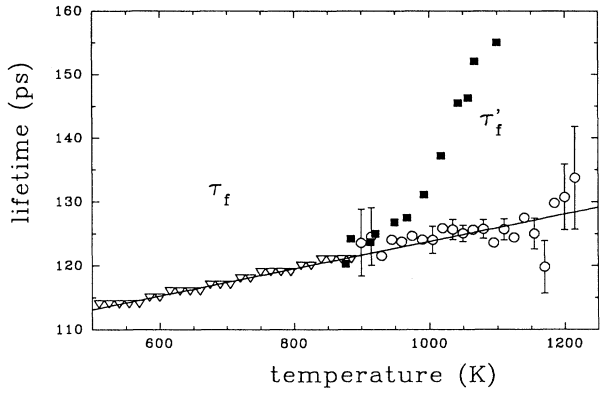

FIG. 1. Temperature dependence of τ'_f in copper as calculated using Eq. (1) and experimental data by Kluin and Hehenkamp (Ref. 18) (filled squares). A nonlinear increase of τ'_f is observable in the two-component region. The calculated τ'_f in the simulation is depicted as open circles. The interpolation of τ_f (open triangles) of the prevacancy region is plotted as a solid line. No deviation from this interpolation of τ'_f except scattering is observed here.

model, from Warburton and Shulman,[12] establishes a relationship between the fraction of prethermally trapped positrons with the difference between the calculated τ'_f and the extrapolated τ_f. The application of this extended model by the authors to the experimental data eliminated the differences between enthalpies found by positron annihilation and those found by the absolute technique.

However, this is not a proof of the existence of prethermal trapping, because artifacts of the fitting procedure could possibly result in significant deviations between τ'_f and the extrapolation of τ_f. Therefore, computer simulations of positron-lifetime spectra on thermally generated vacancies in copper were performed to separate possible artifacts of the analysis from physical effects. Details of the simulation procedure are described elsewhere.[26] In order to choose the input parameters as a function of temperature (in a range between 500 and 1350 K, steps of 15 K), we use the following solutions of the conventional two-state trapping model:

$$\mu c_v = \mu \exp(-H_v^f/k_B T)\exp(S_v^f/k_B) , \tag{2}$$

$$I_1 = 1 + \frac{\mu c_v}{\lambda_2 - \lambda_1} , \tag{3}$$

$$I_2 = \frac{\mu c_v}{\lambda_1 - \lambda_2} , \tag{4}$$

$$\lambda_1 = \lambda_f + \mu c_v , \tag{5}$$

and formation data obtained from measurements,[18,27,28]

$H_v^f = 1.19$ eV , vacancy formation enthalpy ,

$S_v^f = 3k_B$, vacancy formation entropy ,

$\mu = 1.3 \times 10^{14}\ \mathrm{s}^{-1}$, constant specific trapping rate .

The vacancy lifetime was kept constant at the measured value $\tau_2 = 158$ ps and a source term of $\tau_s = 450$ ps and $I_s = 2\%$ was always included in the simulation to come close to the experiment. The randomly generated events were accumulated to create a decay spectrum which contains 1.4×10^6 counts. After this procedure the time resolution function of the experiment of 190 ps full width at half maximum (FWHM) was introduced by convoluting the decay spectrum with the appropriate Gaussian function. Finally an average background was added randomly until a signal-to-noise ratio of 2000:1 was achieved.

For the analysis of the spectra the fitting program POSITRONFIT (Ref. 29) was employed. As in real measurements, first the source term was evaluated in the one-component temperature ranges (e.g., see Fig. 2: $T < 800$ K and $T > 1100$ K) where only the bulk lifetime τ_f or the vacancy lifetime τ_v is observable by a two-component fit. The source lifetime τ_s was determined to be almost 30 ps less than originally simulated and the corresponding intensity I_s was found to be 10% higher (in average) compared to the input value. These source values were subtracted uniformly at temperatures where two lifetimes τ_1 and τ_2 were detectable simultaneously. All spectra were analyzed from the time zero channel of the peak into the background on the right side. The χ^2 ranged between 0.77 and 0.95. The time resolution function was found invariable in every spectrum as simulated with 190 ps FWHM. There were no constraints for τ_1, τ_2 and I_2, except $I_1 = 1 - I_2$, and the background as well as the time zero channel have been fitted freely.

The results of the lifetime evaluation are depicted in Fig. 2. In both simulations the fitted bulk lifetime τ_1 was found to describe the input data very well with a small deviation where the vacancy lifetime τ_2 was not yet separable. In these perfect spectra, lifetimes τ_1 shorter than 40 ps could not be properly resolved by the fitting program. The values of τ_1 start to scatter at an intensity I_1 less than 10% and become unphysical. The vacancy lifetime

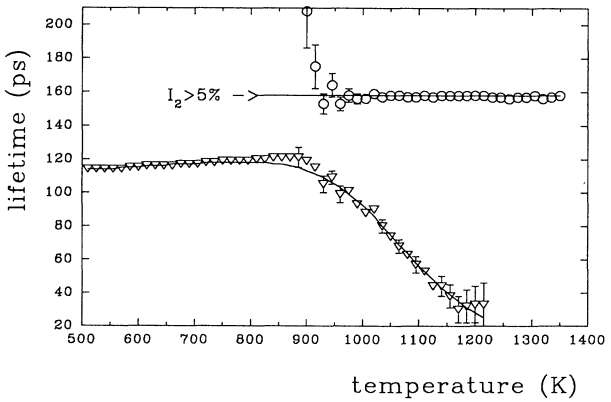

FIG. 2. Lifetimes τ_1 and τ_2 analyzed by the fitting program POSITRONFIT. The lifetime input values generated for the simulation program are depicted as solid lines as long as the corresponding intensity is higher than 5%. Deviations between input parameters and fitted values are found where the vacancy lifetime becomes detectable.

τ_2 is almost constant but it also scatters at intensities I_2 less than 30%. Here a tendency towards higher values is found at lowest detectable intensities I_2 as has been also observed experimentally.[23] Apparently the small difference between the lifetimes τ_1 and τ_2 for small intensities I_2 leads to artifacts in the fitting procedure.

The intensity I_2 shows the usual S shape in the wide range of 15–95 %. In measurements[10,11,18] intensities $I_2 > 80\%$ are not observable. Strong scattering limits the detectability of short-lifetime components $\tau_1 < 60$ ps there. These problems do not occur in simulations because lifetimes are only limited by the accuracy of calculation. Here the highest intensities I_2 are detectable more precisely than the lower, where scattering starts rapidly at $I_2 < 50\%$. It is, therefore, clear that the scattering effects mentioned above are apparently caused by fitting uncertainties.

In order to test the accuracy of the fitting procedure in another way, we determine the vacancy formation enthalpy by means of the usual Arrhenius evaluation:

$$\mu c_v = I_2(\lambda_1 - \lambda_2) \ . \tag{6}$$

This leads to $H_v^f = 1.20 \pm 0.04$ eV which is in very good agreement with the input data. The given error describes the statistical uncertainty only.

The solution of the conventional trapping model Eq. (1) allows us to calculate the bulk lifetime τ_f' in the two-component region from the measured lifetimes and intensities. In Fig. 1, τ_f' is plotted versus temperature where the solid line is the extrapolation of τ_f from the prevacancy region into the two-component section. No deviation is observed from this interpolation except the scatter of the data at the beginning and at the end of the two-component region, where the corresponding intensities are low and fitting uncertainties appear. The fitting program does not generate a nonlinear increase of τ_f' for the simulated spectra. Thus, the experimentally observed nonlinear increase cannot be attributed to an artifact of the fitting program.

In a previous work Fluss *et al.*[15] investigated the effect of the variation of the time resolution function on the τ_f' behavior. They modified the FWHM (while using the POSITRONFIT EXTENDED program) in the analysis of measured data between possible limits. In any case a nonlinear increase of τ_f' was observed, but this cannot serve as a general proof because other fitting problems can cause this deviation, too.

Therefore, we analyzed our simulations again with the PATFIT–88 data processing system (Ref. 30) which contains the RESOLUTION program. This program allows one to fit the time resolution function as a free parameter to data and we determined FWHM (190±1) ps as invariable in all simulated spectra. Furthermore, we got the same results (deviation smaller than the error bars) in lifetimes and corresponding intensities as well as in τ_f' and the Arrhenius evaluation as while using the older version of POSITRONFIT.

However, we reanalyzed our data again using different time resolution functions. Disagreements in FWHM of +2 ps or −2 ps (uncertainty ±1% as estimated from Eldrup, Huang, and McKee[31]) to the evaluated value do not affect the τ_f' behavior. But the experimenter would not accept all of those relatively "bad" fits because of the larger variance and his fitting experience. Larger deviations in FWHM (190±5 ps) led to nonphysical spectra which would not be accepted by any experimenter. Eldrup, Huang, and McKee[31] determined the fitting to be dependent on the start channel. In this perfect spectra analysis the variance of the fitting increases significantly when starting more than two channels to the right side of the maximum channel. Up to this an effect on the τ_f' behavior is not found.

Small deviations in source lifetime or intensity (about 5%) from the analyzed source term lead to significantly different lifetimes τ_1 and τ_2, especially in the two-component region. This behavior is also mentioned by Eldrup, Huang, and McKee.[31] The smaller the used source lifetime and the higher the source intensity, the bigger is the artifact of an increasing τ_2 at lowest intensities I_2. Here the τ_f' slope is not influenced until the fitting results become nonphysical.

In conclusion, we are able to determine artifacts of the analysis and prove the validity of the fitting procedure. We found that lifetimes $\tau_1 < 40$ ps could not be properly resolved. A tendency to higher values of τ_2 at lowest intensities I_2 was observed which has turned out to be an artifact of the analysis. The experimentally observed nonlinear increase of τ_f' does not appear in the simulation and is obviously not caused by the fitting process.

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