RPE **Radiation Physics & Engineering**
An International Peer-Reviewed Journal
Published by K.N. Toosi University of Technology
http://rpe.kntu.ac.ir
Research Article

Radiation Physics and Engineering 2022; 3(3):23–27
https://doi.org/10.22034/RPE.2022.336062.1065

Investigation of the coincidence Doppler broadening ratio curve of well-annealed copper

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HIGHLIGHTS

- The detailed shape of the CDB-ratio curve is a specific signature of each element.
- The CDBS ratio curve of well-annealed copper is measured and compared with simulation.
- The annealing quality of the copper is evaluated using the PALS technique.
- The element-specific CDBS signature of the Copper shows two peaks at the ratio curve.
- The ratio curve depends on the spectrometer energy resolution and the peak to Compton ratio.

ABSTRACT

A two-dimensional coincidence technique is carried out to suppress the background for exploring the contribution of positron annihilation with core electrons. The spectrometer is composed of two face-to-face HPGe detectors. To test the performance of the system, the Coincidence Doppler Broadening (CDB) ratio curve of pure well-annealed Copper is investigated. The quality of the annealing process is measured using Positron Annihilation Lifetime Spectroscopy (PALS). For comparison of the ratio curve of different laboratories, an Aluminum sample is considered as a reference due to its simple electronic structure. The element-specific CDBS signature of Copper shows the two peaks around 12.8×10^{-3} m_0c and 19×10^{-3} m_0c at the ratio curve which is dependent on the momentum of Fermi electrons. The presented ratio curve is compared with the reference measurement and simulation. Differences and the similarities in the reported ratio curves are discussed. The comparison shows that our result is more compatible with the theoretical calculations and can be considered as a new reference for future studies on the chemical environment of defects in alloys that include copper in their contents.

KEYWORDS
Coincidence Doppler broadening
Copper
Ratio curve
Positron annihilation

HISTORY
Received: 4 April 2022
Revised: 18 May 2022
Accepted: 2 June 2022
Published: Summer 2022

1 Introduction

Coincidence Doppler Broadening Spectroscopy (CDBS) of positron annihilation radiation is a well-established method for the non-destructive assessment of defect concentration and its chemical environments in alloys, semiconductors, and polymers. In the CDBS technique, the 511 keV gamma-rays are Doppler broadened by the value of $\Delta E = \pm\frac{p_l c}{2}$ due to the initial momentums of electron-positron pairs, where p_l describes the longitudinal momentum of the electrons and c is the light velocity. There exist two main regions in the positron annihilation profiles:

1. The S-region near the 511 keV energy with the $0 < p_l < 3 \times 10^{-3}$ m_0c that is an indication of the size and concentration of defects in the samples ($m_0 = 511$ keV.c^{-2} is the electron rest mass).
2. The W-region towards the high momentum part of the spectrum with $10 < p_l < 25 \times 10^{-3}$ m_0C shows the contribution of the positron annihilation with core electrons. This region contains valuable information about the chemical environments and impurity atoms bound to vacancies.

Ratio curves have been already applied to show the differences between the doppler profiles of investigated samples (Alatalo et al., 1998). The reference in ratio curve calculation is a simple electronic structure sample such as Si or Al. The detailed shape of the CDB-ratio curve depends on the contribution of core electrons in the positron annihilation mechanism and is a specific signature of each element. Although the ratio curve of some elements has been measured, there exists a significant scatter of the data of different authors (Reiner et al., 2014; Stepanov

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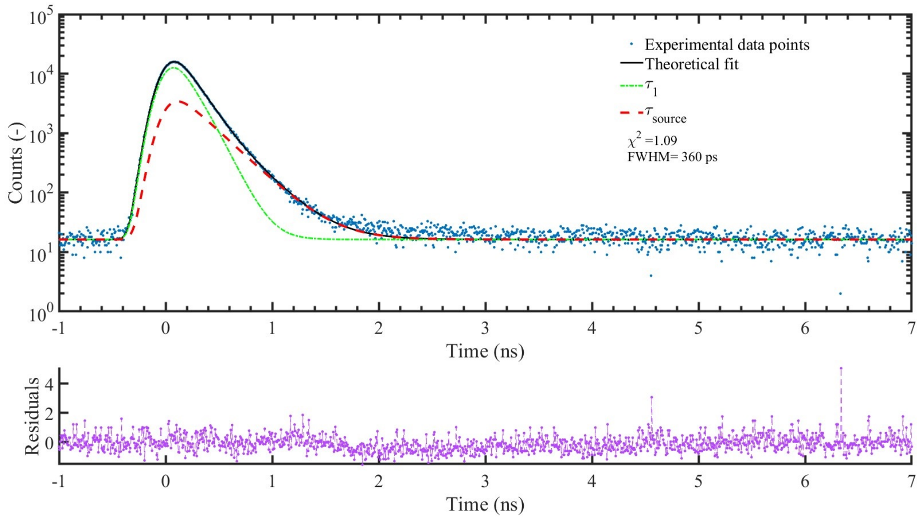

Figure 1: Positron lifetime spectrum of annealed Cu sample.

et al., 2017). The data discrepancies are confusing and need a scientific explanation. In this study, the CDB spectrum of well-annealed pure Cu is measured and the result is compared with the simulation and measurement that have been already reported.

2 Experimental details

2.1 Sample preparation

In order to remove the intrinsic defects in the samples, Cu and Al specimens (as a reference sample) are well-annealed in the vacuum of about 10^{-6} mbar using a tube furnace for two cycles of 5 hours at temperatures up to $\frac{3}{4}$ of their melting points. The quality of annealing is measured using PALS technique. Measurement of the positron lifetime in each sample is executed using the 1274 keV (birth signal) and 511 keV (annihilation signal) gamma lines of the Na-22 source. The statistics of about 1 M total counts were built-up for each sample using two coaxial plastic scintillator detectors (NT-150). Each experiment lasts 3 days. The other details of our homemade PALS system are presented in our previous paper (Biganeh et al., 2020). Before starting the PALS data analysis, the FWHM of the timing resolution function of the spectrometer is determined 360 ps using coincidence gamma lines of Co-60 (1173 and 1332 keV). Figure 1 shows the lifetime spectrum of the annealed copper. The analysis of the PALS data is carried out using the LT-10 software (Kansy, 1996). Two-exponential model is used to decompose the lifetime spectrum to its components. Six local free parameters considered during the data analysis: $2\tau_i$, $2I_i$, zero channel, and background level. The shortest lifetime component (τ_1) and its related intensity (I_1) is due to positron annihilation in the sample. The τ_2 parameter and its related intensity are attributed to the positron annihilation in Kapton film of the source and partial contribution of annihilation in NaCl salt. Since the electron density of metals is very high (compared to polymers and other low-density materials), no positronium will be formed in metals. So, the long-lived component with τ greater than 1 ns has not appeared in this case. The residuals of fitting at each point (R_i), are also calculated using Eq. (1) and plotted at the bottom of Fig. 1:

$$R_i = \frac{T(i) - E(i)}{\sqrt{E_i}} \tag{1}$$

where $T(i)$ is the value of the theoretical curve at channel i and $E(i)$ is the value of experimental data at channel i. The even residual graph in our analysis best describes the precision of our results. The final results of the PALS experiment for the investigated samples are listed in Table 1.

The reported uncertainty in Table 1 is the combination of statistical and fitting error that is calculated by the LT-10 code. As listed in Table 1, the annealing procedure leads to a significant decrease in the τ_1 component for both the annealed Al and Cu samples. The obtained positron lifetime components for annealed Al (169 ps) and

Table 1: The results of the PALS experiment. The χ^2 describes the quality of the theoretical fits to data points.

Sample	τ_1 (ps)		I_1 (%)	τ_2 (ps)	I_1 (%)	χ^2
	Our experiment	Simulation (Wiktor et al., 2015)				
As received Al	185 ± 2	-	74.19 ± 1.12	394 ± 19	25.81 ± 1.27	1.07
Annealed Al	169 ± 7	162	79.28 ± 0.94	373 ± 17	20.72 ± 1.32	0.98
As received Cu	133 ± 1	-	76.14 ± 0.77	385 ± 13	23.86 ± 0.85	1.12
Annealed Cu	122 ± 4	123	78.01 ± 1.04	392 ± 22	21.99 ± 1.09	1.09

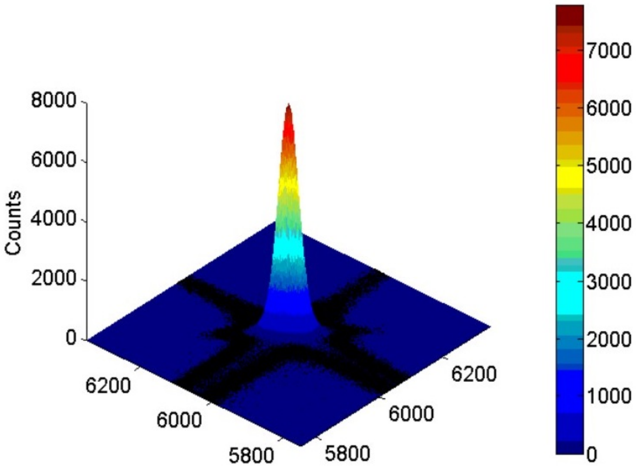

Figure 2: The 2D-coincidence doppler broadened spectrum of the annealed Cu sample. The Gaussian at the center of the graph describes the net positron annihilation events.

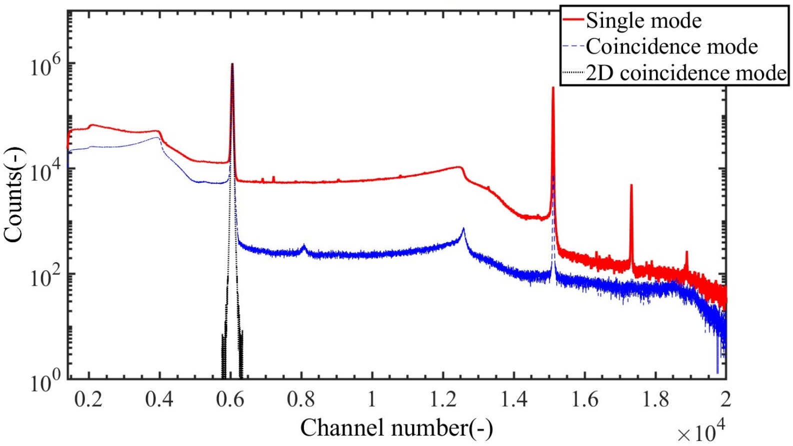

Figure 3: The gamma spectrum of Na-22 source measured in single mode (solid line), Coincidence mode (dashed line), and 2D coincidence mode (dotted line).

Cu (122 ps) are in excellent agreement with the theoretical simulation. The results of simulation that have been carried out for a perfect lattice of Cu and Al by the two-component Density Functional Theory (DFT) within the Projector Augmented Wave (PAW) method (Blöchl et al., 2003) in open source code ABINIT is also listed in Table 1 (Wiktor et al., 2015). Therefore, we can confirm the effective elimination of the intrinsic defects after annealing. The prepared samples are used for the investigation of the characteristics of the CDBS ratio curve of Cu in the next section of this paper.

2.2 *CDBS experiment*

Measurement of the CDBS spectrum is carried out at the PAS laboratory of NSTRI using our modern 2D digital spectrometer. The details of the spectrometer implementation and its calibration procedure can be found in our previous paper (Biganeh et al., 2019). The CDBS experiment is performed for Cu and Al samples. The measurements of gamma-rays are kept on using two face-to-face HPGe detectors (ORTEC GEM-20200, Canberra 3001c) until 10^6 counts were built-up at the 511 keV annihilation line. Each experiment lasts 6 days. The detected events are recorded in a list mode file (a file that contains the timestamp and energy of each event). Since the contribution of the core electron in positron annihilation is less than 0.01%, the level of background and Compton events on the spectrum should be suppressed (Alatalo et al., 1996). So, the list-mode data is analyzed offline by a homemade Matlab code to extract the correlated positron annihilation evens. For data analysis, a coincidence time window of 50 ns is selected and the coincidence correlated events are realized and stored in an $E_1 \times E_2$ square matrix, where E_1 and E_2 are the correlated energy recorded by detectors 1 and 2, respectively. Figure 2 shows the 2D coincidence doppler broadened spectrum of the Cu sample. The ellipse at the center of the spectrum shows the doppler broadening of the positron annihilation line. This region is free from unwanted events such as noise, background, Compton scattering, and pile-up and contains valuable information about the CDBS experiment. To extract the 1D positron annihilation spectrum, a diagonal cut of the 2D spectrum with $E_1 + E_2 = 1022$ keV and a bandwidth of 25 keV is selected. Finally, the 2D spectrum of annihilation

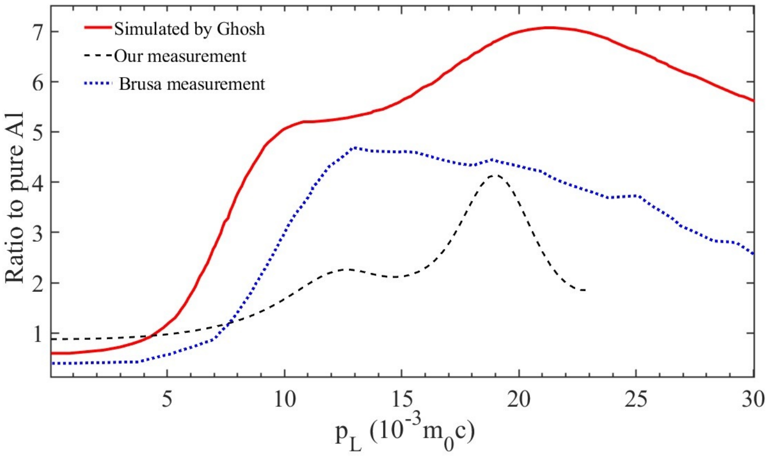

Figure 4: CDBS ratio curve of copper, simulated by Ghosh et al. (solid line) (Ghosh et al., 1999), measured by Brusa et al. (dotted line) (Brusa et al., 2002), and measurement carried out in this work (dashed line).

events is projected to 1D to obtain the doppler-broadened positron annihilation profile. Figure 3 shows the gamma spectrum of the Na-22 source measured in single, Coincidence, and 2D coincidence mode. As shown in Fig. 3, the peak to Compton ratio up to 10^6 is achieved in 2D coincidence mode (dotted line) and it is possible to measure the contribution of core electrons into the annihilation mechanism.

3 Results and discussion

To obtain the probability of positron annihilation versus the longitudinal momentum of the annihilated electrons compared to the Al reference sample, the Cu spectrum should be divided by the Al spectrum. Since the calculation of the ratio curve is influenced by the slight shift of the annihilation line during a long time of data acquisition, a penalized spline function provided by CDB Tools software is applied to the Cu spectrum and the shift in the 511 keV gamma line is compensated (Petriska et al., 2016). Finally, the Doppler broadening spectrum of Cu is divided by Al and presented in Fig. 4. As shown in this figure, the element-specific CDB signature of Cu shows two peaks around 12.8×10^{-3} m_0c and 19×10^{-3} m_0c at the ratio curve. The first peak position depends on the momentum of Fermi electrons while the second peak partially represents the primary annihilation of core electrons (Lynn and Goland, 1976). This ratio curve has been already measured by Brusa et al. using coincidence measurement by HPGe-NaI(Tl) (Brusa et al., 2002). Due to the use of HPGe-NaI(Tl) for the coincidence measurement of the annihilation radiation reported by Lynn et al. and Brusa et al., the peak to Compton ratio for the both mentioned spectrometers are not better than 10^3 (Lynn and Goland, 1976; Brusa et al., 2002).

We limit the comparison of the ratio curves to $0 < p_l < 23 \times 10^{-3}$ m_0c because the statistics lower than 10^7 counts at the annihilation line leads to a significant error in the calculation of the ratio curve for $p_l > 23 \times 10^{-3}$ m_0c (Szpala et al., 1996). The Doppler measurement reported by Brusa et al. also shows a peak at 12.8×10^{-3} m_0c and a small bump at 19×10^{-3} m_0c. These peaks are attributed to the dominant positron annihilation with $4s^1 3d^{10}$ and some contribution from $3p^6$ orbitals (Brusa et al., 2002). As shown in Fig. 4, the second peak is not well recognized in the work have been done by Brusa et al. We believe that this is due to the poor peak to Compton ratio of their CDB spectrometer. Moreover, a numerical investigation that has been done by Ghosh et al. on the effect of the spectrometer energy resolution on the ratio curve of Cu confirms that the two peaks are more distinguishable by an improvement in the resolution of the spectrometer (Ghosh et al., 1999). This conclusion has been extracted by the results of calculations of the positron annihilation spectra that are convoluted with different resolution functions. Therefore, due to our better spectrometer energy resolution and the possibility to provide the peak to Compton ratio around 10^5, our measurement is more consistent with the simulation results. The measured data can be considered a reliable reference for studies on the chemical environment of defect sites in Cu content alloys.

4 Conclusions

We used the PALS technique to evaluate the intrinsic defects in the Cu and Al samples. The results of PALS confirmed the effective elimination of the defect after annealing. We measured the positron annihilation profile for the prepared samples using our modern digital 2D spectrometer. The values of the ratio curve for the Cu sample that have been measured in different laboratories revealed certain differences. The origin of the discrepancies between the reported data was discussed. The results show that identifying the measured value of the ratio curve as a specific signature of elements depends strongly on the spectrometer energy resolution and the peak to Compton ratio. Hence, when the results from the different laboratories are compared to each other, these parameters should be reported and considered. Further to this work, we are going to initiate systematic measurements of the pure metals to create a comprehensive database of ratio curves.

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