

Ab-initio calculation of CDB spectra - a case study on transition metals

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Abstract. Experimental results of Coincident Doppler Broadening Spectroscopy (CDBS) in Si, Cr, Ni, Cu, Pt and Au references were compared with ab-initio calculations. These calculations were performed by use of the MIKA Doppler software package, which is provided for the community by Aalto University. This software calculates electron wavefunctions by an atomic superposition method. It is shown that despite this simple approach, the element specific information obtained by CDBS can be calculated with high reliability for the examined elements.

1. Introduction

Coincident Doppler broadening spectroscopy (CDBS) enables the measurement of the longitudinal electron momentum p_L even for high Doppler shifts, which stem from core electrons [1]. Due to this it can be used for an element specific analysis of trapping sites in multicomponent systems or depth profiling in layered structures. For such an analysis, experimental data can be compared with measured or calculated reference spectra.

A theoretical description of the complete electron momentum spectra requires band structure calculations for the valence electrons. Calculations based on an atomic superposition method for electron wave functions [2] can be expected to well describe the annihilation with core electrons. Software packages based on such calculations are offered for the community, e.g. the MIKA-Doppler program [3] that superposes orbital wave functions from free atoms. Within this study, it was systematically examined how calculations performed by use of MIKA-Doppler describe the element specific part of measured CDB spectra taken in various transition metals and Si.

2. Methods

2.1. Calculation of CDB spectra

The Doppler broadening of the annihilation line is given by the momentum distribution $\rho(\mathbf{p})$ of the annihilating electron-positron pair. This is given as a sum over all orbital momentum distributions $\rho_j(\mathbf{p})$ by equation (1), in which r_0 denotes the classical electron radius and c is the speed of light:

$$\rho(\mathbf{p}) = \sum_j \rho_j(\mathbf{p}) = \pi r_0^2 c \sum_j u_j(0)^2 \left| \int d\mathbf{r} \exp(-i\mathbf{p} \cdot \mathbf{r}) \psi_+(\mathbf{r}) \psi_j(\mathbf{r}) \right|^2 \quad (1)$$



The state-dependent enhancement factor $u_j(0)$ is used in order to model the electron-positron correlation for each electronic state. In this study, for the enhancement a generalized gradient approximation [4] with a parametrization based on data by Arponen and Pajanne was used [5].

In MIKA Doppler, the calculation of $\rho(\mathbf{p})$ is based on the two-component density functional theory [6] in the limit of a vanishing positron density. The orbital electron wave functions $\psi_j(\mathbf{r})$ are calculated by the code employed considering the Dirac equation for atoms. The Schrödinger equation for the positron wave function $\psi_+(\mathbf{r})$ is solved by a three-dimensional real-space solver. For comparison with the experimental data, the calculated results were convolved with a Gaussian function in order to mimic the experimental energy resolution.

2.2. Measurement of CDB spectra

The measurements were performed at the CDB-spectrometer located at the high-intensity positron beam NEPOMUC [7,8], which enables quasi background free coincident photopeak detection without any source component. In a collinear setup of High Purity Ge (HPGe) detectors, more than 10^7 counts per CDB spectrum were accumulated in the coincident photopeak with an effective energy resolution of 1.0 keV FWHM at 511 keV. CDB spectra were measured in Si, Cr, Ni, Cu, Pt and Au references and evaluated as described in [9]. For the Si reference, a Si(100)-wafer was taken; due to the measured positron diffusion length of 228 nm it can be assumed to be defect free. The metal specimens were annealed before performing the measurements.

3. Results and Discussion

3.1. Raw spectra

Fig. 1 shows the experimental and calculated spectra, which were multiplied by a scaling factor. This scaling factor was obtained by evaluating the error weighted mean ratio of measured and calculated CDB spectra in the momentum range between $30 \cdot 10^{-3} m_0 c$ and $50 \cdot 10^{-3} m_0 c$, where the annihilation with core electrons is dominant.¹ The same method also has been applied on CDB spectra of vapor deposited Cu films, in which saturated trapping of positrons in open volume defect occurs [10]. Due to the decreased core annihilation probability in these defects, one obtains a smaller scaling factor compared to the spectra of the annealed references used here.

Generally, for all elements good quantitative agreement can be seen for electron momenta $p_L > 30 \cdot 10^{-3} m_0 c$, where the annihilation with core electrons dominates [11–14]. The agree-

¹ The spectra of each element (except Si) were multiplied by an additional factor for a better visibility in fig. 1.

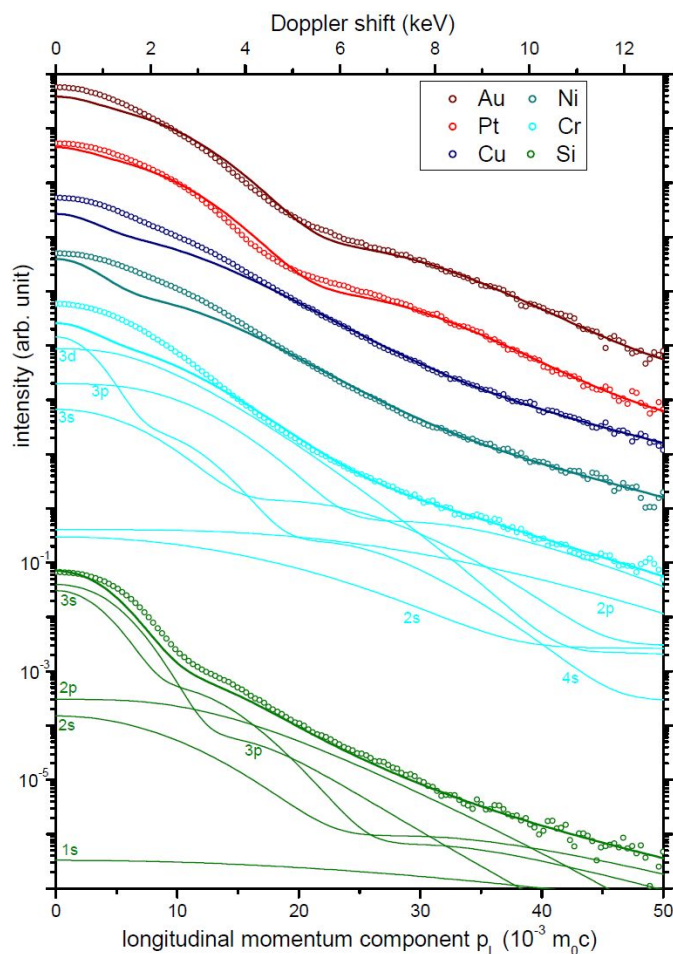


Figure 1: Measured (o) and calculated (—) CDB spectra.

ment is not that good for smaller momenta, where the annihilation with valence electrons gets dominant and hence, the applied atomic superposition method cannot be expected to give full agreement.

In the case of Si, the calculations exactly fit the data for $p_L > 30 \cdot 10^{-3} m_0 c$. The small discrepancy for smaller momenta is attributed to the rough calculational treatment of the annihilation with valence electrons (from the 3s- and 3p-shell), which also cannot describe the well known anisotropy of the valence electron momentum distribution in Si [15].

For the 3d transition metals, i.e. Cr, Ni and Cu, calculations and measurements compare in the same way. The applied calculation method clearly underestimates the contribution of low momentum valence electrons to the annihilation, which leads to a discrepancy in the small momentum area. Here, the calculated curves also exhibit a shape different from that of the measured ones. But already above $20 \cdot 10^{-3} m_0 c$, and in the case of Cr even above $15 \cdot 10^{-3} m_0 c$, the ab-initio calculations well agree with the experimental data. For Ni and Cu, the contribution of the various electronic states are very similar as in Cr. Details will be discussed in the following (sec. 3.2).

In the case of the 5d transition elements Au and Pt, in addition to the quantitative agreement in the high momentum area, theoretical and experimental curves show the same qualitative behavior for small momenta. The dip seen in the experimental data at $20 \cdot 10^{-3} m_0 c$ is also exhibited by the calculated curves, but slightly shifted to higher momenta. Furthermore, it seems that the annihilation with low momentum valence electrons ($p_L < 20 \cdot 10^{-3} m_0 c$) is slightly underestimated. The characteristic features of the spectra cannot be attributed to a single electronic state, because for a wide range of momenta three or four different electronic states contribute in a similar extent to the annihilation.

3.2. Ratio curves

In order to reveal to what extent the calculations can be used for the element specific analysis of CDB spectra, the ratio curves to the calculated Si spectrum were investigated (fig. 2) and are shown in the high momentum area ($20 \cdot 10^{-3} m_0 c < p_L < 50 \cdot 10^{-3} m_0 c$). The measured Si spectrum

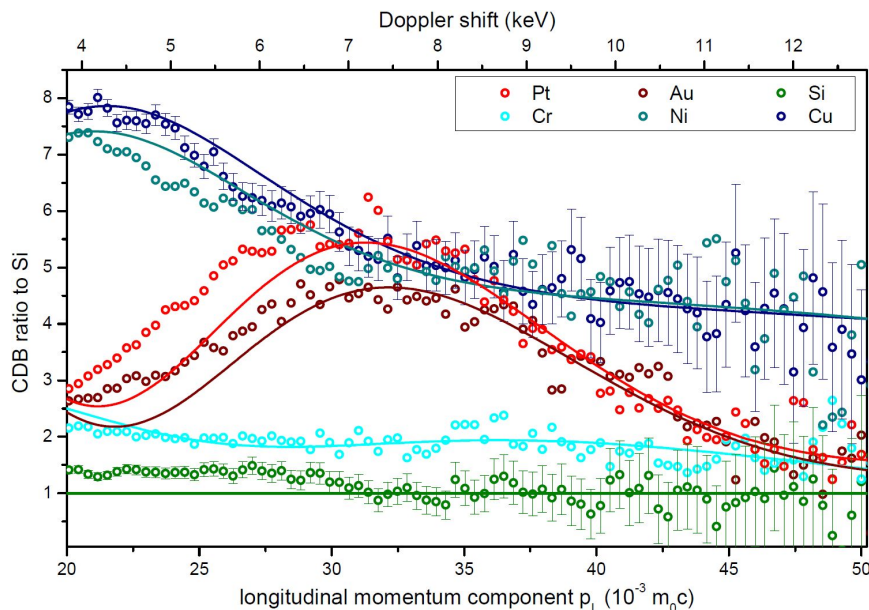


Figure 2: Measured (o) and calculated (–) CDB ratio curves to Si (calculated) in the high momentum area.

could serve as reference for the other measured spectra, which leads to the same results for momenta smaller than $30 \cdot 10^{-3} m_0 c$. For higher momenta the increasing statistical error of the measured Si spectrum complicates a comparison between theory and experiment and hence, the calculated Si spectrum is used as reference for all measured spectra.

It is noteworthy that both the theoretical and measured Cu ratio curve show a nearly identical decrease between $20 \cdot 10^{-3} m_0 c$ and $50 \cdot 10^{-3} m_0 c$. In former studies based on band structure calculations, where the 3d band of Cu was treated as semicore orbital and attributed to the valence electrons, it was found that for Cu the annihilation with core electrons is dominant for momenta higher than $30 \cdot 10^{-3} m_0 c$ [16]. The astonishingly good agreement already above $20 \cdot 10^{-3} m_0 c$, despite the rough treatment of the 3d electrons within the atomic superposition method, was also reported in previous studies [12, 17] and is very similar for Ni and Cr (fig. 1).

Furthermore, the element specific CDB signatures of Au and Pt with their maximum at $31 \cdot 10^{-3} m_0 c$ are well described by the calculations. Although the agreement is not that good for $p_L < 30 \cdot 10^{-3} m_0 c$, calculations and measurements show the same tendency. Hence, a distinction of both elements is possible due to a qualitative comparison.

4. Conclusion

The MIKA Doppler software package with its simple atomic superposition method has been applied for various transition metals and Si. It was shown that the element specific high momentum part of the CDB spectra can be calculated with high reliability. For 3d transition metals, a very good quantitative agreement was found for even smaller momenta, where the annihilation with valence electrons plays a significant role. In the case of 5d transition metals, for these momenta at least a qualitative agreement was found.

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