Spin selectivity by Auger-photoelectron coincidence spectroscopy

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Abstract. The $M_3M_{4,5}M_{4,5}$ Auger transition from a Cu(111) surface is studied using Angular Resolved Auger-PhotoElectron Coincidence Spectroscopy (AR-APECS). In the experiment two different geometrical configurations of the electron analyzers allow us to sample different emission angles of the ejected electrons leading to different weights of the singlet and triplet contributions in the studied transition. The experimental spectra are modeled within a two-step approach using the Cini theory for the closed band case so as to properly consider the spin-orbit interaction and the hole-hole correlation energy. Ingredients for the theory, like density of states, are obtained fully ab-initio in the framework of density functional theory by performing all-electron calculations. The obtained results confirm the recently discovered selectivity of AR-APECS in the final spin-state.

1. Introduction

In this paper a theoretical and experimental study of the $M_3M_{4,5}M_{4,5}$ Auger coincidence spectrum from a sample of Cu(111) is presented. The purpose is to achieve a better understanding of the role of correlation effects on the analyzed line shapes and to deepen investigations of multiplet term selectivity of the AR-APECS (Angular Resolved Auger PhotoElectron Coincidence Spectroscopy) technique.

2. The Experiment

The experiment was performed at the beamline ALOISA of the synchrotron ELETTRA (Trieste). The apparatus is discussed in details elsewhere [1].

We used a single crystal of Cu(111) cleaned using the usual procedure of cycles of sputtering and annealing. The sample chemical cleanness and the absence of lattice defects were verified by photoemission, reflection of high energy electron diffraction (RHEED) and photoelectron diffraction (PED) measurements.

Monochromatic p-polarized radiation of energy $h\nu = 241$ eV impinged on the sample at a grazing incident angle of about 6°, where the surface normal lied in the plane determined by the photon beam direction and its polarization vector ε. Among the seven hemispherical analysers contained in the experimental chamber, two of them are mounted 18° apart on an array termed bimodal frame, rotating around the photon beam axis and around an axis normal to it. The other five analysers (18° apart) are positioned on a plane (axial frame) containing the photon beam axis and rotating around it.
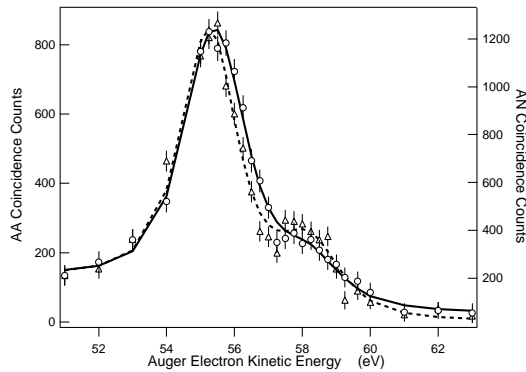

Figure 1. Comparison between the M_3VV coincidence Auger spectra of Cu(111) measured in configuration AA (open circles and solid line) and AN (open trianglesand dashed line). The solid and dashed lines are only guides to the eye.
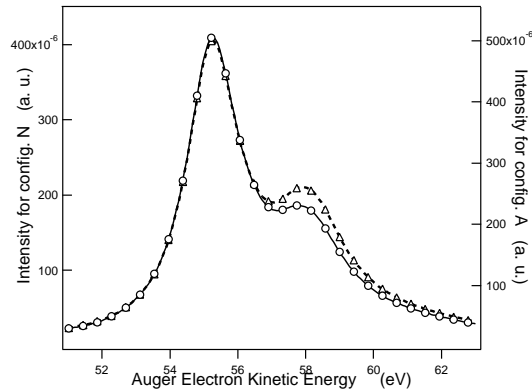
Figure 2. Comparison between the calculated M_3VV Auger line shape of Cu(111) obtained using angle-resolved Auger matrix elements for the Auger electron detected at 0° (open circles and solid line) and 40° (open triangles and dashed line) from the sample surface normal. Arbitrary units are employed.

To perform the coincidence measurements the bimodal analysers (with an energy resolution of 2.16 eV) were tuned to a fixed kinetic energy of $E_k = 157.8$ eV, which corresponds to the high kinetic energy side of the $3p$ photoemission peak. This energy was chosen in order to avoid the detection of photoelectrons coming from the ionization of the $3p_{1/2}$ shell. The axial analysers (with an energy resolution of 0.9 eV) sampled instead the energy range of the Auger spectrum.

For the experiment two configurations were used and in the following they will be referred to as condition AN and AA. In the former geometry one electron of the pair was aligned (A) with the polarization vector, ε, while the other one (the Auger electron) was collected at more than 40° from the surface normal, so it was not aligned (N) with ε. In the latter condition instead both axial and bimodal frames were mostly close to the surface normal (at angles mainly $\leq 20^o$) and thus most of them can be assumed to be aligned (A) with ε. In Fig.(1) the comparison between the M_3VV experimental coincidence Auger spectra measured for the configuration AN (open triangles) and AA (open circles) is shown: from this graph it is clear that the patterns relative to the two different geometries differ one from the other for the relative intensity ratio of the two main peaks of the spectra which are due to the final two-hole terms ^1G (the principal peak) and ^3F (the peak on the high kinetic energy side of the main one).

3. The Model

To explain the trend shown by the experimental data the closed band Cini theory [2] was used but with a slight modification represented by the introduction of the off-site interaction and the spin-orbit coupling also for the two holes in the final state. It has been possible to introduce solid state effects thanks to the use of off-diagonal one-particle local density of states matrix elements, which were calculated within Density Functional Theory (DFT). Futhermore, to take into proper account spin-orbit interaction, the intermediate coupling scheme was used and the spin-orbit coupling parameter,

$\zeta_{3d} = \frac{\hbar^2}{2m_e c^2 a_0^3} \langle \varphi_{3d}(r) | \frac{1}{r} \frac{\partial U}{\partial r} | \varphi_{3d}(r) \rangle$, was taken from a DFT calculation on atomic Copper [3]. In the hole picture the Hamiltonian of the system can be decomposed as $\widehat{H} = \widehat{H}_0 + \widehat{H}_{int}$, where $\widehat{H}_0$ is the non-interacting Hamiltonian given by the sum of one-particle operators, while instead $\widehat{H}_{int}$ is the interaction Hamiltonian, made up of the Coulomb interaction and the spin-orbit coupling term. In the basic Cini model the correlated two-hole density of states is obtained within a two-step approach from the imaginary part of the interacting two-hole Green's function $\widehat{\Phi}$ resulting from a Dyson-like equation of the type:

$$\widehat{\Phi}(\omega) = \widehat{\Phi}^{(0)}(\omega) + \widehat{\Phi}^{(0)}(\omega)\widehat{H}_{int}\widehat{\Phi}(\omega) \tag{1}$$

where $\widehat{\Phi}^{(0)}$ is the non-interacting two-hole Green's function which can be built from the non interacting two-hole local density of states matrix and their Hilbert transforms. The total spectrum is proportional to:

$$S(\omega) = \Sigma_{XY\sigma} A_X^* A_Y D_{XY\sigma}(\omega) \tag{2}$$

where X and Y contain the quantum numbers identifying a particular two hole multiplet term and $D_{XY\sigma}$ represents the correlated two-hole local density of states matrix elements calculated on the states X and Y. A_Y and A_Y^* are respectively the Auger matrix elements and their hermitian conjugates for an Auger transition from the deep initial core hole state to the final two hole multiplet term Y. The amplitudes A_Y were obtained by using the PHAGEN code (PHAses GENerator) to calculate both bound state and excited radial wave functions. This code is based on a self consistent procedure within the single configuration Dirac-Fock scheme, where Breit interaction is included only as a first-order perturbative correction. Excited state radial wave functions are calculated using the muffin tin approximation for the potential, adding an exchange correlation part calculated within the LDA scheme. Multiple scattering effects have been neglected, i.e. only the direct waves (those which directly reach the detector) have been considered. At the low kinetic energies of the outgoing electron considered here, such effects could influence the diffraction patterns, but we neglect them in the calculation of the energy spectrum. The two-hole correlation energies for each multiplet term were given by atomic Hartree-Fock estimates taken from [4]. The effective Coulomb interaction felt by the two final holes is diminished by a screening energy, Δ, due to initial and final state effects because the photoelectron and the Auger electron come from different electrostatic potentials and by the screening operated by all the valence electrons. Finding a rigorous way to evaluate this screening energy is still an open problem at the state of the art today. Some attempts have been done in this direction [5,6] but, at the standard level of DFT, the accuracy is far from the chemical one required to disentangle small effects. For these reasons the procedure described in [7,8] was adopted to obtain a better theoretical line shape: the Auger profile was calculated by fitting the screening energy Δ to get the line shape which best reproduces the experimental one, without caring about its absolute position. The remaining energy shift was attributed to the off-site interaction Ξ or else the energy that has to be subtracted from the Coulomb interaction U together with the screening energy Δ to reach the effective hole-hole interaction. Ξ is due to the fact that also when they are some distance apart, the two final holes can still interact because of an incomplete screening. The best values found in this way are $\Delta = 20$ eV and $\Xi = 2.5$ eV. The latter result is very similar to the value obtained for Ag [8]. The total FWHM of the calculated line shape has been fixed to 1.8 eV, a value which takes into account several broadening mechanisms such as the core-hole lifetime [9], dispersive and phonon broadening [10]. In Fig.(2) we report the comparison between the calculated M_3VV Auger line shape using Auger matrix elements obtained for the Auger electron at 0° (open circles and solid line) and 40° (open triangles and dashed line) from the sample surface normal. These two configurations correspond to the geometries in which the Auger electron is aligned (A) or not-aligned (N) with ε respectively. This comparison clearly shows that, similarly to the trend of the AR-APECS measured data, the relative intensity ratio of the two main peaks depends on the emission angles, although the calculation was done in a two-step model and only the alignment of the Auger electron was considered.

4. Discussion and Conclusions

In this paper the angular-resolved coincidence M_3VV spectrum of Cu(111) was measured for two different geometrical configurations. There are clear differences between the corresponding experimental patterns and this shows the capability of the AR-APECS technique of selecting final spin-state terms thanks to the particular choice of the experimental geometry. Besides the selection rules of the involved transitions and the filtering role of the electron diffraction from the solids, the directions of detection of the photo and the Auger electron relative to the system quantization axis (fixed by the polarization vector) act on the partial wave of the emitted electrons in such a way to enhance or suppress some of the two hole final spin state terms with respect to others.

The theoretical spectra were calculated in the framework of the Cini theory using only two free parameters which are the screening energy and the off-site hole-hole Coulomb interaction. The obtained value for the off-site hole-hole Coulomb interaction is similar that for Ag [8]. The on-site hole-hole Coulomb interaction agrees well with other values found in literature [4,11]. Further calculations in the framework of one-step theory with multiple scattering effects are needed in the attempt to predict not only the trend but more accurate values of the measured intensity ratio $^1G/^3F$ for the two geometrical configurations studied in the present work.

Acknowledgements

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