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Microarticle

HAXPES study of Sn core levels and their plasmon loss features

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ABSTRACT

Hard X-ray Photoelectron spectra have been recorded for elemental Sn. Electron loss features, prominent in all core level spectra of the metal, are analyzed at several photo energies for the 3*p* core level. For higher photoelectron kinetic energies the intensity of the plasmonic features follows a simple exponential law. The data and models presented here will aid the modeling of spectra where tin is present and especially if its spectrum overlaps with those from other sources.

The determination of binding energies (and chemical shifts) of core level photoelectron lines depends critically on how spectra can be decomposed into components. One possible process that may influence the spectral fingerprint of an electronic system is the excitation of *plasmons*.

A plasmon is a collective excitation of the electron gas in a metal upon a sudden change, *i.e.* photoionization [1,2] – in a free electron model the plasmon energy may be estimated as $\hbar\omega_p = \hbar\sqrt{ne^2/m\epsilon_0}$ which only depends on the electron density and natural constants. The bulk plasmon energy is denoted by $\hbar\omega_p$ and the surface plasmon energy is $\hbar\omega_s = \hbar\omega_p/\sqrt{2}$ [3]. In this paper we show that, in elemental tin, it suffices to model the plasmonic satellites' intensities with an exponential function.

The Hard X-ray Photoelectron Spectroscopy (HAXPES) data were obtained at the Bessy II synchrotron at Helmholtz-Zentrum Berlin at the double crystal monochromator (DCM) equipped dipole beamline KMC-1 [4] – using the HIKE end station [5,6].

For the HAXPES measurements photon energies of 2, 3 and 6 keV were used. All spectra were calibrated with an Au standard with the Au $4f_{7/2}$ binding energy taken to be 84.00 eV [7].

The pure Sn which was delivered as a thin (0.05 mm) foil from Alfa Aesar had a stated purity of 99.9985%. The foil was sputtered with a current of 10 mA Ar^+ ions at 1 kV energy, for 20 min to remove the oxide overlayer.

The binding energies have been obtained from a least squares fit to the data using a Doniach–Sunjic linshape [8]. Apart from a constant background, a Shirley-type background has been used in all fits to the data [9]. The least squares fits were carried out using the SPANCF (by E. Kukk).

The Sn $3p_{3/2}$ (binding energy 714.66 eV) and Sn $3p_{1/2}$ (756.64 eV) were recorded at 2, 3 and 6 keV photon energies. The Sn 2*p* core level was recorded with 6 keV photon energy only using the third order diffraction of the 2 keV settings of the Si(1 1 1) DCM. The inset in Fig. 1 shows the latter spectrum with plasmonic features highlighted.

The bulk plasmon energy $\hbar\omega_p$ is 14.3 eV, as deduced from the shift of the satellite feature relative to the main core photoelectron line; our measured value coincides with the theoretical value of Ref. [10]. Reflected electron energy loss spectroscopy of Sn finds 14.07 eV and 10.02 eV for bulk and surface plasmon loss features [11].

In Fig. 1 the relative intensities of the plasmons to the indicated photoelectron line feature are plotted. The error bars – obtained from standard error propagation of Monte Carlo estimates of the areas' errors – are of the same size as the markers. The intensities are similar to those obtained by Pollak and co-workers [12].

A fit to the data, using Matlab, in Fig. 1, a power law $I_n/I_0 = b^n$ where n is the nth plasmon and I_0 the area of the parent photoelectron line gives b between 0.34 and 0.52 – hence the exponential was added to the figure as a guide to the eye ($e^{-1} \approx 0.37$).

The intrinsic plasmon intensity can be modeled as a power law $b_n = b^n$, or as Poisson $b^n/n!$ [13]. The extrinsic plasmon contribution can also be modeled as a power law [14], *i.e.* $a_n = a^n$, with:

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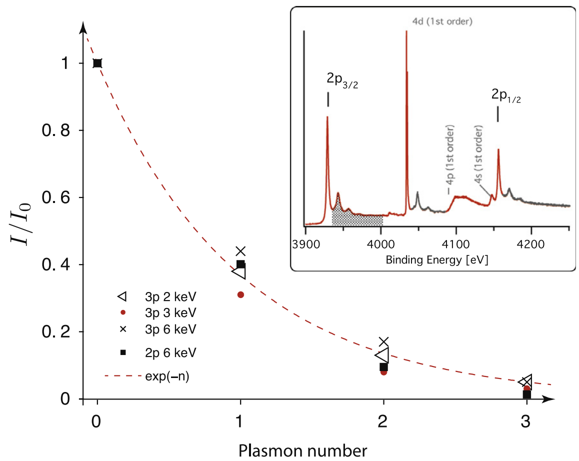

Fig. 1. Bulk plasmon intensities relative to the main line. The exponential model has been included as an aid for the eye. The inset shows the Sn $2p$ core levels measured with 6 keV photon energy, interleaved with the valence and $4d$, $4p$ and $4s$ from X-rays of first order diffraction. The features of plasmonic character are shown with the dotted area for the $2p_{3/2}$ core level and drawn as gray above other levels.

$$a = \frac{\lambda}{\lambda_p} = \lambda\left[4 \cdot a_0 \cdot \frac{E_{kin}}{\hbar\omega_p} \Big/ \ln\left(\frac{E_{kin}}{E_F}\right)\right]^{-1} \tag{1}$$

where the Fermi energy (E_F) of Sn is 10.2 eV [15]; a_0, the Bohr radius, 0.529 Å; E_{kin} is the electron's kinetic energy, here: 1.3, 2.3 and 5.3 keV for the $3p$ data and 2 keV for the $2p_{1/2}$. The electron mean free path, λ in Sn has been measured to be 43 Å for 2.3 keV [16]. This gives a value for a approximately equal to 0.67 for the energies concerned; if we would be using the 31 Å calculated by Penn [17] we would get $a \approx 0.46$ concurrent to our experimentally obtained value as estimated by the power law fit above. The value of a is thus strongly dependent on the inelastic mean free path.

Last but not least, we also model the intensities in Fig. 1 as a mixture between intrinsic and extrinsic contributions; we use models given in Refs. [13,14], *i.e.* modeled as power laws, using $a = 0.67$, $b = 0.25$ and giving $c = 33\%$ of the intensity to extrinsic processes ($I_0 = 0.75$) we get a reasonable fit to the data with the equation $I_n = b^n + c \cdot a \cdot I_{n-1}$.

In Fig. 1 these intensities fall exactly on the open triangles. This last exercise is *ad hoc* but serves to show that the intensities in the plasmon spectrum can indeed be modeled with more or less advanced formulae, however, in the case of Sn it suffices to consider their intensities as decaying exponentially at the energies considered here.

Every core level spectral main line in Sn has an accompanying plasmon progression with intensities distributed (at the energies considered here) as exponentially decaying. A careful investigation of plasmonic features gives the possibility for determination of the mean free path of electrons in a solid with the more elaborate expression given by Eq. (1).

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