Extracting Energy Loss Mechanism from XPS Data

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The Landau's formula[1] which describes the energy loss of a particle traveling through the medium was simplified by Tougaard and co-workers to a numerically tractable form[2]. They widely applied the formula to XPS background subtraction using the 'universal function', which approximates the loss function of noble metals. Its simplest version treats the situation that the photoelectron source distribute exponentially from the topmost layer, which includes uniform distribution as a special case.

$$j(E) \propto \frac{j_0(E)}{\lambda(E)} - \int_E^\infty j_0(E')K(E',E)dE' \qquad (1)$$

Very recently[3], I found that the numerical solution of (1) can be directly obtained as a pair of a realistic loss function and a realistic background by only making quite natural assumptions explained below. In this comment, a brief overview of this method, together with some results and its potential usages, will be given..

The assumptions for solving the problem comprises two independent requirements for an ideal primary excitation spectrum (spectrum after background subtraction). First, if the spectrometer's transmission function is already calibrated, different core level peaks of the same atomic species are expected to have a fixed intensity ratio, which is predicted by their photoelectron excitation cross-sections. Second, far from the core level peak, observed intensity should be ascribed entirely to the result of inelastic scattering, in other words the primary excitation spectrum should show no signal outside the core level peak. These conditions are formulated to an optimization problem of making the following two functions (strictly, functionals of unknown loss function) as small as possible, by searching for the correct form of the loss function.

$$P[K] = const \cdot \sum_{i,j} \left| \frac{A_i}{S_i \cdot a_i} - \frac{A_j}{S_j \cdot a_j} \right| \qquad (2) \qquad Q[K] = \int_{Tail} |j(E)| dE \qquad (3)$$

K denotes the loss function. In eq.(2), i and j are the different core levels of the same atom, A the observed peak intensity (peak area), $S \cdot a$ the effective cross-section. $P[K]$ becomes zero (minimum) only if different core level peaks give the same atomic density. In eq.(3), $j(E)$ is the spectrum after subtracting inelastic background. E is the kinetic energy of detected electron. Integration is performed outside the peak. $Q[K]$ becomes zero (minimum) only if no intensity is observed outside the peak.

In order to find correct loss function, its initial form is, for convenience, set to the same as that of Tougaard's universal function with appropriate B and C. Then one modifies the function's shape slightly and observes the changes of $P[K]$ and $Q[K]$. This is done by Successive Quadratic Programming method written by Fukushima[4], which is capable of finding minimal solution of an

arbitrary twice continuously differentiable function of many variables.

Fig.1 shows the Au spectrum[5] thus analyzed. Optimization was performed so that the ratio of 4d and 4f peak should show a given value, and area of the region indicated as TAIL in the figure should be zero. Fig.2 is optimized loss function. It is very similar to that by Monte Carlo simulation[6]. It is remarkable that the optimized solution indeed give a very good result not only in the neighborhood of the peaks used, but also almost through the analyzed range. Furthermore, all peak intensities, except valence band which is slightly smaller, are proportional to the excitation cross-sections by Scofield. Taking into account that peaks other than 4d or 4f are not considered at all during the calculation, it is very likely that above assumptions are indeed correct assumptions.

The meaning of the present method is at least eight-fold. (1) One can determine the loss function of the unknown material without knowing the detail if one have an appropriate peak pair. This is essentially a new spectroscopy. (2) One can obtain correct peak shape after background subtraction. This is important in solid state physics. (3) Further, the present method extracts all the part that is produced by inelastic scattering, which is described by eq.(1), the rest, which cannot be explained by eq.(1), is therefore ascribed to the primary excitation spectrum. including main peak and satellites.(4) One can check calculated excitation cross-section by examining the consistency of the result. (5) One can measure the correct intensity ratio of peaks that is necessary for quantitative analysis, if λ is known or estimated. (6) One can check if the element is uniformly distributed or not, because eq.(1) strictly holds only if the distribution is uniform. (7) One can check if the compared elements are in the same electronic environment or not, because the different environment would give different loss function. (8) One can estimate the ratio of λ if one measures the unknown sample by calibrated spectrometer, because the peak intensities of the same element can be predicted as discussed above.

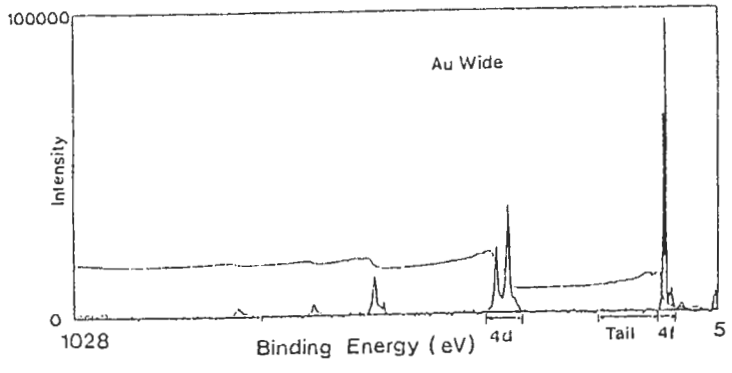

Fig.1 Background and primary excitation spectrum of Au.

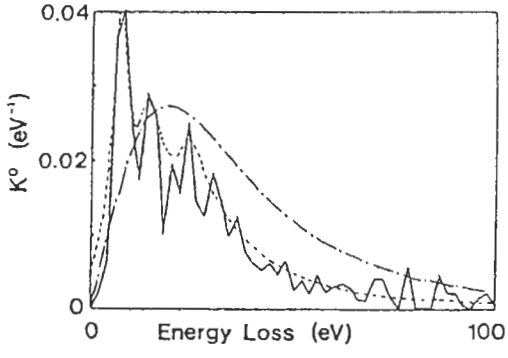

Fig.2 Loss function of Au (solid line), universal function (dashed-dotted line), Monte Carlo result by Yoshikawa et al.

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