

Loss Functions of Iron and Palladium

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(Received: 21 April 1995)

Loss functions of metal iron and palladium have been deduced using XPS background optimization method. The optimized loss function reproduces the observed background. It shows characteristic peaks reported so far and their shapes are very similar to those determined by Reflection Electron Energy Loss Spectroscopy whose analysis procedure is based on the same physical origin. This strongly demonstrates that the dielectric information of the medium carried by the inelastic photoelectrons is not smeared out, but possible to be restored.

1. Introduction

The Landau's formula¹⁾ which describes the energy loss of a particle traveling through the medium was simplified by Tougaard and co-workers to a numerically tractable form²⁾. 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.

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

Where j and j_0 denotes spectra after and before background subtraction. E and E' the electron kinetic energies. λ the inelastic mean-free path of the electron of kinetic energy E . $K(E', E)$ describes the probability of an electron of E' being inelastically scattered to E ($< E'$) per unit time and unit traveling path in the solid. Hereafter it is denoted as "loss function". Very recently³⁾, I showed that the numerical solution of (1) can be directly obtained by analyzing Al and Au metal spectra. In this report, as the second example, iron and palladium have been analyzed

2. Formalism

Detailed description of the formalism are given elsewhere³⁾. Only brief overview will be made in this section.

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 two functions defined below (strictly, functionals of unknown loss function) as small as possible, by searching for the correct form of the loss function.

$$P[K] \equiv \text{const} \cdot \sum_i \left| \frac{A_i}{S_i \cdot a_i} - \frac{A_j}{S_j \cdot a_j} \right| \quad (2)$$

$$Q[K] \equiv \int_{Tail} |j(E)| dE \quad (3)$$

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 the core level excitation cross section, a the correction term for asymmetry factor difference, deduced from an integration of each asymmetry factor in the actual measurement geometry. This is not included in the present study since the compared peaks, 2p1/2 and 2p3/2 for Fe, and 3p1/2 and 3p3/2 for Pd, have the same asymmetry factors. $P[K]$ 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. Once $K(E',E)$ is given, the background is calculated using eq.(1). Next P and Q are calculated using eqs. (2) and (3).

By Tougaard's assumption⁴⁾, $K(E',E)$ is expressed as follows,

$$K(E',E) = \frac{1}{\lambda(E')} K''(E' - E) \quad (4)$$

This means the dependency on initial kinetic energy comes only from the inelastic mean-free path part

In order to find correct loss function K , initial form K'' is, for convenience, set to the same as that of Tougaard's universal function with appropriate B and C. Then one modifies the shape of K'' slightly and observes the changes of $P[K]$ and $Q[K]$. This is done by Successive Quadratic Programming method written by Fukushima⁵⁾, which is capable of finding minimal solution of an arbitrary twice continuously differentiable function of many variables.

3. Data and Conditions

Analyzed Fe and Pd spectra was measured by Crist using SSI M-Probe

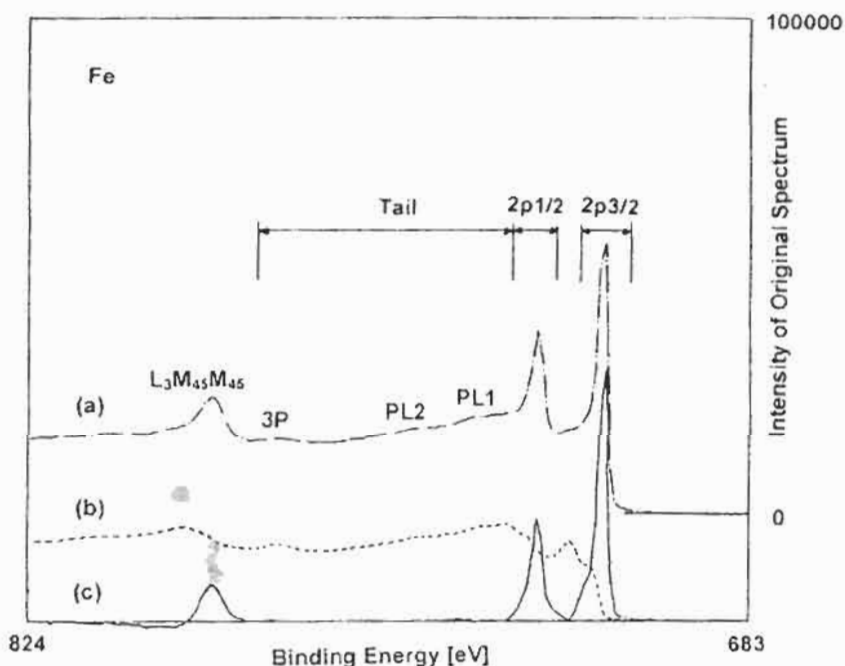


Fig.1 Fe 2p spectrum. (a) Original data. (b) Background. (c) Spectrum after background subtraction.

spectrometer, and have been registered in the spectrum data bank compiled by the Surface Analysis Society of Japan⁶⁾. The sample was Ar⁺-bombarded before the measurement. The X-ray source is monochromated Al K α . For inelastic mean free path, values calculated by Tanuma et al.⁷⁾ were used. Constant background is removed prior to the analysis because the lower binding energy side of the analyzed spectral region is almost flat. The energy interval of defining the trial loss function is 2 eV.

It is noted that optimization of Pd was not performed completely automatically. Due to the numerical difficulty in continuing calculation, modification of the initial loss function was necessary

4. Results and Discussion

Fig. 1a shows the original Fe spectrum. Optimization was performed so that the ratio of 2p_{3/2} and 2p_{1/2} peaks (limits of integration are also indicated in the figure) should show a given value, i.e., Scofield's values⁸⁾, and area of the region indicated as Tail in the figure should be zero after background subtraction. In the Tail region, there are three very weak but noticeable structures, denoted as PL1, PL2 and 3P, respectively. Fig. 2 shows the optimized loss function as a reduced form, $\lambda \cdot K / K''$. In the present optimization condition, all these peaks are reproduced by this function. The peak at ~ 25 eV which was ascribed plasmon excitation⁹⁾ explains the structures both PL1 and PL2 as the

Fig.2. Loss functions of Fe.
Solid line: Present Result
Dashed line: Result REELS¹⁰⁾ with $E_p=300$ eV.

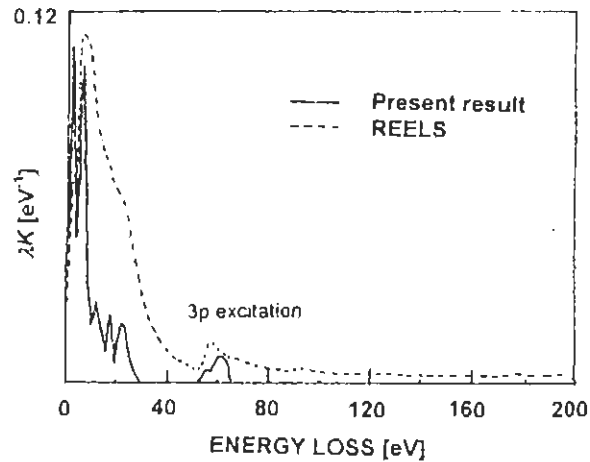


Fig.3 Pd spectrum around 3p core level.
(a) Original spectrum.
(b) Calculated background.
(c) Spectrum after background subtraction.

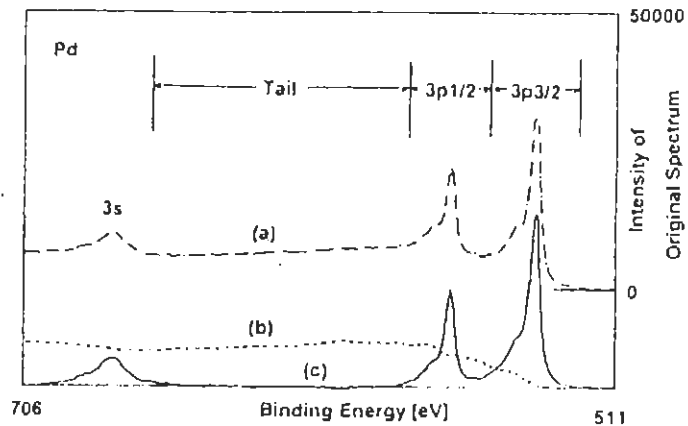
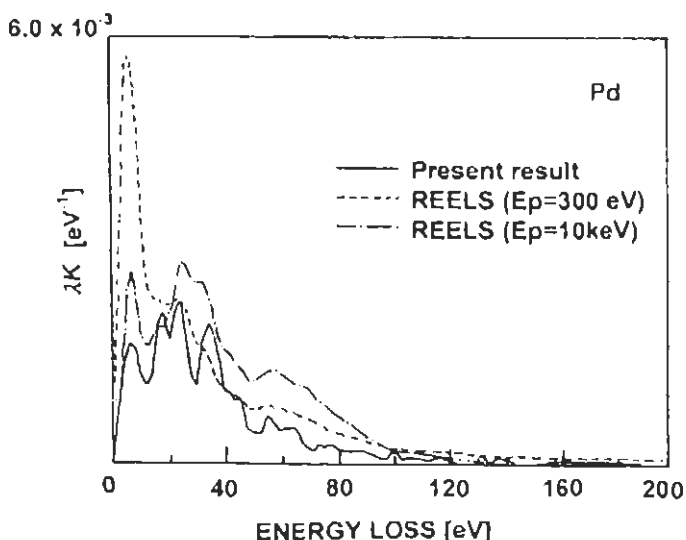


Fig.4 Loss functions of Pd.

Solid line: Present result.

Dashed line: REELS⁹⁾ result with $E_p = 300$ eV.

Dashed-dotted line: REELS⁹⁾ result with $E_p = 10$ keV.



losses of $2p_{3/2}$ and $2p_{1/2}$ photoelectrons, respectively. Peak around 56 eV is the $3p$ core excitation edge. The structure $3P$ is ascribed to a $3p$ core excitation loss of $2p_{3/2}$ electron.

The results of background subtraction are shown in Fig.1b and 1c. Especially, $2p_{3/2}$ peak seems to be considerably asymmetric, however it would require more precise spectrum to make a conclusion. Only asymmetry due to Doniach-Šunjić type has been reported so far. for $2p$ peaks.⁹⁾ In addition, the $L_3M_{45}M_{45}$ Auger transition is indicated in the figure.

Also shown in Fig.2 is the loss function deduced from reflection electron energy-loss spectroscopic (REELS) analysis by Tougaard and Kraer ($E_p = 300$ eV)¹⁰⁾. Both are very similar, especially in the peak positions. However, this is not surprising because the present method is based on the Tougaard's formula. It is noted that, both in Figs. 2 and 4, the vertical scale of REELS result is different and is adjusted to that of the present result for comparison. This is considered to be due to the difference in inelastic mean free path used.^{3,7,10)}

Fig.3 shows the Pd spectra. Intensities of $3p_{1/2}$ and $3p_{3/2}$ peaks are adjusted. The shoulders shown on both peaks are included in the peak areas, because they are considered as

the intrinsic satellites produced by core-hole screening.¹¹⁾

Within the author's experience, the result seems still not perfect. This is partly because the original spectrum is a portion of a wide scan spectrum and therefore the resolution is poor (the data point interval is 1 eV). These become the restrictions against defining peak region precisely.

Fig. 4 shows the loss function λK together with the results from REELS. Again, the peak positions are in good agreement. Especially, the structure around 60 eV is considered to be $4p$ excitation edge.

As shown above, the present method extracts the realistic information of the system even from a rather smooth and coarse spectrum which seems "not informative". If one has a spectrum whose every fine structure is indeed a meaningful structure, then the obtained knowledge will be a maximum.

Acknowledgment

I am grateful to Dr. B. V. Crist (Fisons Instruments) for supplying spectral data. I thank Drs. H. Okushi and K. Arai for continuous encouragement.

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Comments & Replies

(translated from Japanese)

Referees

- A: Tetsu SEKINE (JEOL Ltd.)
B: Michiko YOSHITAKE (NRIM)

A-1: I am interested in your method as a tool for knowing the loss function, rather than as a tool for background subtraction. I hope you will try on various materials.

Author-A1: The method has several meanings. Knowing the loss function is the most important aspect. I think this can be regarded as a new spectroscopy. In addition, it will be used to know the correct shape of primary excitation spectrum which carries the information how the photoelectron excitation occurs. Unfortunately, I am working only on the spectrum data bank of Surface Analysis Society because I do not have my own instrument now. I am anticipating your collaboration. Also as I talked at the symposium, 7th March, the analysis program will soon be released. Please try

A-2: If the separation between the peaks for ratio adjustment, eq.(2), is very large, in other

words the kinetic energies are very different, is it still possible to make the optimization?

Author-A2: For a complete analysis, the spectrum must satisfy the following two conditions. (1) The spectrometer's transmission is already calibrated. (2) At least the ratio of IMFP's at the peak points is known. In the last work³⁾ Au spectrum satisfied these requirements and therefore 4d and 4f peaks were able to be used. The present spectra, Fe and Pd, are not calibrated because I found a difficulty in calculating transmission of SSI spectrometer. There were steps at the peak points when SSI's Au spectrum is divided by Yoshitake's standard spectrum. However, even if one does not know the transmission, analysis will be possible by the following procedure. Do calculations while changing the ratio S_i/S_j . The result as a whole will be satisfactory only if the ratio is near a given value. Then this is the effective ratio taking transmission (and IMFP variation) into account. If transmission is known, then the effective ratio includes IMFP variation, and vice versa. The present program mentioned above does not support this automatic search, but has an easy interface to change them.

A-3: Have you examined your method's sensitivity to the noise? Does the noise change the loss function's shape considerably?

Author-A3: I have not examined because it is not easy to make a correct estimation. If you want to do this, you must superpose artificial noise on the ideal spectrum and watch the difference. However, within my experience, random noise will not generate serious effects unless it is too intense. The quality registered in the data bank seems sufficient. Please see the noise level of Au result in Ref.3. The reason is considered to be as follows. $P[K]$ and $Q[K]$ covers considerably wide energy range. If the program tries to reproduce a noise structure at a narrow region, overall coincidence will be worse because it will fail to adjust in the rest of the energy range. This mechanism will cancel the local noise. It is noted that the energy interval to model the loss function is 2 eV, whereas that of the spectrum data is 1 eV. This setting also

makes the loss function insensitive to the noise. On the other hand, relatively broad structures, e.g. ghosts, will appear in the result because you cannot distinguish them from the true peaks. This sensitivity is demonstrated by the fact that the very small structures in Fig. 1 are indeed shown in the loss function (Fig. 2).

A-4: The loss function depends on the initial electron kinetic energy. Did you compare the results deduced from an optimization in a narrow energy range and that done in regions separated apart?

A-5: The loss function of Fe was calculated using ~700 eV kinetic energy electron, for Pd using 900 eV. The REELS results are 300 eV and 10 keV. I would like to compare the results by much closer energies.

A-6: Is it possible to use other peak pairs, such as Pd4d5/2 and Pd3d3/2, Pd4s and Pd4p, Pd3s and Pd2s, ...?

Author-A4,5,6: There are few spectra in the data bank that allows several different region settings. Wide scan spectrum's resolution is too poor to separate doublets such as Pd3d3/2 and Pd3d5/2. High resolution spectrum is too narrow to set Tail region in it. Practically, loss function deduced from a certain region setting well describes the rest of the energy range that is not included in the calculation as noticed in Ref.3. This may suggest that the Tougaard's assumption, eq.(4), holds in a wide range than generally accepted. I think the strong variation on kinetic energy of REELS experiment would be due to the variation of electron penetration depth. For Pd, tentative S_i 's for other peaks are estimated by the peak areas calculated by the present loss function. Then one can restart calculation using these values.

A-7: Is it possible to use Pd MNN Auger peak?

Author-A7: This is the very problem I am attacking now. I talked at the Applied Physics Society Meeting this spring. Because Auger electron comes from a decayed hole which had been created by photoelectron emission, and because its path during escaping the solid has no difference from that of photoelectron except the

kinetic energy, there must be one-to-one correspondence between photoelectron and Auger electron peak intensities. For Cu L_{2,3}MM case, the relative peak intensities are proportional to those predicted by Auger transition rates, however the absolute intensities are stronger than those expected from photoelectron (2p) peaks. One obvious reason is Coster-Kronig transition of L₁ shell. Other possibilities will be discussed elsewhere including ICSS-9 at Yokohama next September. Once the relation is settled, the user have more choices for surface analysis. Further, materials such that have only 1s core peak available, e.g., graphite, will be able to be analyzed by using KLL peak as a counterpart, though the energy is very much different.

B-1: Electrons of different kinetic energies come from different depth. Is the factor S_i , a_i for calibrating this effect?

Author-B1: No. The factor a_i is a value close to 1 coming from an integration of photoelectron emission asymmetry factor in the actual measurement geometry. In the present study 2p and 3p peaks are compared, therefore this factor is equal to 1. The difference of escape depth is already included in eq. (1) ($1/\lambda$ is the factor).

B-2: I understand that, once K is given, the spectrum is calculated by eq.(1), then P and Q are evaluated by eqs.(2) and (3). The present method searches for the correct spectrum that makes P and Q minimum by changing K . If so, "=" in eqs. (2) and (3) should be replaced by "≡" because they are the definitions of P and Q . Please add explanations above to make the sentence clear.

Author-B2: I have followed the referee's suggestion.

B-3: Could you explain what is the physical meaning of subtracting constant background?

Author-B3: Suppose that you have a flat (constant) spectrum everywhere. Then, from eq (1), the inelastic background of this spectrum is also constant. Because Q is minimum after optimization, this constant value equals to the spectrum intensity itself, strictly the 1st term of

eq. (1). This means that, if the low binding energy side of the peak is flat, the generated background has the same height where the peak is observed. Therefore, constant background subtraction is the subtraction of this contribution, which makes no effect on the result spectrum. In addition the region of flat intensity should be sufficiently large. The analyzed Fe 2p and Pd 3p satisfy this condition.

B-4: In Fig. 1c, the 2p_{3/2} peak after background subtraction looks considerably asymmetric. Is this also because of intrinsic satellite, as shown in Pd case?

Author-B4: In the literature, only Doniach-Sunjic type asymmetry has been reported so far⁹⁾. On the other hand, Fe 3s peak has a satellite [J.Phys. F: Metal Phys., 10, 169 (1980)]. I feel high resolution spectrum is necessary for the further discussion.