Analysis of XPS and REELS spectra of beryllium

V P Afanas’ev¹, A S Gryazev¹, P S Kaplya², O Yu Ridzel¹,³ and A V Rybakova¹

¹ National Research University ”Moscow Power Engineering Institute”
Russia, 111250 Moscow, Krasnokazarmennaya str., 14
² Yandex, Russia, Moscow
³ Institut für Angewandte Physik, Vienna University of Technology, Vienna 1040, Austria

E-mail: v.af@mail.ru

Abstract. The differential inverse inelastic mean free paths (DIIMFP) of beryllium were derived from energy spectra acquired using X-ray photoelectron spectroscopy and electron energy loss spectroscopy techniques by means of the fitting of calculated spectra to experimental data. The calculation of the energy spectra is performed employing the partial intensity approach (PIA). The EELS and XPS spectra were acquired in different laboratories using different Be samples. The comparison of the obtained DIIMFPs with literature data is presented.

1. Introduction
Beryllium is of interest as from position of technological applications as from scientific research. Be is planned to utilize as material of “first wall” for controlled thermonuclear fusion, including international tokamak ITER. One of the most effective methods of process analysis, occurring with Be in extreme conditions, is electron spectroscopy. Quality and quantity sample form within several nanometers can be obtained on the basis of X-ray Photoelectron Spectroscopy (XPS) [1]. Elastic Peak Electron Spectroscopy (EPES) [2] allows to implement quantity detection of hydrogen isotopes. Analysis depth in EPES method is determined by inelastic mean free path – \( l_{\text{in}}(E) \), which value increases as the energy of probing beam grows [3]. DIIMFP is required for both the surface region \( x_{\text{surf}}(\Delta) \) and for homogeneous array in the bulk \( x_{\text{bulk}}(\Delta) \) for implementation of quality signal decipherment in considered methods of electron spectroscopy. Fig. 1 illustrates the necessity in knowledge of contribution to the spectrum of inelastically scattered electrons.
2. Methods of spectra calculation
2.1. Fitting procedure to determine DIIMFP

There is procedure of extracting $x_{\text{inf}}(\Delta)$ value from Electron Energy Loss Spectroscopy, EELS [4, 5]. It was determined theoretically and experimentally, that there are two main mechanisms of electron energy loss:

1) non-local energy loss for excitation of plasma oscillations, spectra of which has Lorentzian profile $x_{\text{pl}}(\Delta)$;
2) local energy loss for ionization, definition of which can be implemented in classic Thomson theory, spectra of ionization losses has hyperbolic form $x_{\text{ion}}(\Delta)$.

We calculate DIIMFP in each layer $x_{\text{inf}}(\Delta)$, $x_{\text{as}}(\Delta)$ according to equations:

$$x_{\text{pl}}(\Delta) = \sum_{i=1}^{N_{\text{pl}}} \lambda_{\text{pl}} x_{\text{pl}}^i(\Delta) + \sum_{j=1}^{N_{\text{ion}}} \lambda_{\text{ion}} x_{\text{ion}}^j(\Delta), \quad \sum_{i=1}^{N_{\text{pl}}} \lambda_{\text{pl}} + \sum_{j=1}^{N_{\text{ion}}} \lambda_{\text{ion}} = 1;$$  

(1)

$$x_{\text{pl}}^i(\Delta) = A_{\text{pl}}^i \int_{K_1}^{K_2} \frac{1}{k} \left[ \left( E_{\text{pl}}^i + \frac{h^2 k^2}{2m} \right)^2 - \Delta^2 \right] + \Delta^2 \frac{1}{\hbar^2} \left( \sqrt{E_0^2 + \Delta^2} - E_0 \right);$$  

(2)

$$x_{\text{ion}}^j(\Delta) = A_{\text{ion}}^j \eta \left( \frac{\Delta - J_{\text{ion}}^j}{\Delta_{2+\alpha}^j} \right).$$  

(3)

Equation (2) presents modified version of equation, obtained in the frameworks of elementary dispersion theory considering spatial dispersion phenomenon, where $e_{\text{pl}}$, $b$ are parameters, which correspond to plasmon peak position and plasmon attenuation (half width of peak), coefficients $\lambda_{\text{pl}}$ and $\lambda_{\text{ion}}$ indicates contribution of corresponding processes; $A_{\text{pl}}$ and $A_{\text{ion}}$ are normalization coefficients.
Ionization cross section are described by Thomson equation considering screenage (3), where $J_{ion}$ – ionization energy; $a$ – screenage parameter; $\eta(\Delta - J_{ion})$ – Heaviside step function.

Ability of presenting DIIMFP in the form (1)-(3) allows to realize the process of deriving values $x_{\text{diff}}(\Delta)$, $x_{\text{abs}}(\Delta)$ on the basis of fitting technique, which is more reliable technique for solving inverse problem [6]. Applying such procedure allow us to use as EELS spectra (Reflected geometry – R and Transmitted geometry – T), as energy XPS spectra (Photoelectron Spectroscopy – PES) – $Q$.

The representation of spectra $R$, $T$, $Q$ as inelastic scattering series, is the basis of analytical approaches, used for realization fitting procedure; it is called partial intensities method [7, 8].

\begin{align}
R(\Delta, \mu_0, \mu, \varphi) &= R_0(\mu_0, \mu, \varphi)\delta(\Delta) + \sum_{k=1}^{\infty} R_k(\mu_0, \mu, \varphi)x_k^R(\Delta), \\
Q(\Delta, \mu_0, \mu, \varphi) &= Q_0(\mu_0, \mu, \varphi)\delta(\Delta) + \sum_{k=1}^{\infty} Q_k(\mu_0, \mu, \varphi)x_k^Q(\Delta).
\end{align}

(4)

Partial intensities method is used for determination of $x_{\text{diff}}(\Delta)$ and $x_{\text{abs}}(\Delta)$ in the form (1)–(3), for EELS spectra – function $R(\Delta, \mu_0, \mu, \varphi)$ and XPS spectra – $Q(\Delta, \mu_0, \mu, \varphi)$. Experimental data of EELS spectra are obtained in three different scientific laboratories, XPS data are obtained in two laboratories including Handbook [9].

Representing sample in two-layer model, we calculate spectrum according to [10, 11]:

\begin{align}
R_{\text{BS}} &= R_S(d_S) + T_S(d_S) \otimes R_B \otimes T_S(d_S), \\
Q_{\text{BS}} &= Q_S(d_S) + Q_B \otimes T_S(d_S).
\end{align}

(5)

\textbf{Figure 2.} EELS spectrum of Be. The energy of the probing electron beam $E_0 \approx 1.5$ keV, probing angle $\theta_0 = 0^\circ$, viewing angle $\theta = 60^\circ$.

Calculation by Eqs. (4) – (5), in accordance with [10, 11], leads to spectrum, represented in Fig. 2, corresponding DIIMFP $x_{\text{diff}}(\Delta)$ and $x_{\text{abs}}(\Delta)$ are represented in Fig. 3 where the DIIMFP reconstructed from optical data is also shown and will be described further in the text.
Figure 3. Differential inverse inelastic mean free paths of Beryllium.
* – the DIIMFP, derived from optical data.

DIIMFP \(x_{\text{inB}}(\Delta)\), \(x_{\text{inS}}(\Delta)\), are received, and thickness of surface layers, where energy losses occur according to \(x_{\text{inS}}(\Delta)\), adequately describing a wide range of energies.

2.2. Calculation of the DIIMFP using optical data

Along with technique of extracting DIIMFP \(x_{\text{inB}}(\Delta)\) and \(x_{\text{inS}}(\Delta)\), represented above, there is an approach allowing to use experimentally measured dielectric response from the solid. The main problem of the fitting procedure, represented above, is in its laboriousness and high requirements to qualification of its performer. The DIIMFP \(x_{\text{inB}}(\Delta)\) in terms of the energy loss function (ELF) can be obtained experimentally \([12, 13]\). The ELF represents the probability to lose a certain amount of energy \(\Delta\), accompanied by a momentum transfer \(q\) and is described in the following way:

\[
\text{Im} \left[ \frac{-1}{\varepsilon(\Delta, q)} \right] = \frac{2nk}{(n^2 - k^2)^2 + 4n^2k^2} = \frac{\varepsilon_2(\Delta, q)}{\varepsilon_2(\Delta, q) + \varepsilon_2(\Delta, q)},
\]

where \(n\) is the refractive index, \(k\) is the extinction coefficient, \(\varepsilon_1\) and \(\varepsilon_2\) are the real and imaginary parts of the dielectric function, respectively. The values which are measured experimentally are the optical constants \(n\) and \(k\) \([12, 13]\) which are related to \(\varepsilon_1\) and \(\varepsilon_2\) values as follows:

\[
\varepsilon_1 = n^2 - k^2, \\
\varepsilon_2 = 2nk.
\]

By means of the experimental optical constants we can calculate the ELF at the optical limit \((q=0)\) and fit it with a set of model parameters. For that there are several models available which can be elsewhere, e.g. in \([14]\). In the present work a sum of Mermin type loss functions was used to fit optical data for Be from Palik’s Handbook at \(q=0\) \([12, 15]\). The results of the fitting is depicted in Fig. 4.
Figure 4. The results of the fitting of the model ELF for Be to optical data [12] using the Mermin model.

The DIIMFP $x_{inB}(\Delta)$ then can be obtained by calculating the Mermin ELF at all momentum transfers as follows:

$$x_{inB}(\Delta, E_0) = \frac{1}{\pi E_0} \int q' \left( \frac{-1}{\varepsilon(\Delta, q)} \right) dq \ .$$

(8)

$$q^+ = \sqrt{2E_0} \pm \sqrt{2(E_0 - \Delta)} .$$

In order to take into account surface effects a theory proposed by Li [16] was employed. According to [16] $x_{inS}(\Delta)$ depends on the direction along which an electron crosses the surface area and at which depth inside the solid the electron is. The signal from the surface can be calculated as follows:

$$R_s = \sum_{k=0}^{\infty} P_k (\eta_s) L_k (\Delta)$$

(9)

where the function $P_k$ is the Poisson distribution:

$$P_k (\eta_s) = \frac{\eta_s^k e^{-\eta_s}}{k!} ,$$

(10)

and $L_k(\Delta)$ represents the $k$-fold self-convolution of $x_{inS}(\Delta)$. The resulting signal from bulk and surface is then given by:

$$R_{BS} = R_s \otimes R_B \otimes R_S .$$

(11)

The DIIMFP calculated using Eq. 8 was used to calculate the spectrum by means of Eq. 11. The results are shown in Fig. 5.
Figure 5. Comparison of the energy loss spectrum for Be obtained by employing optical data for the calculation of the DIIMFP with experimental data.

As can be seen from Fig. 5 a quite a good agreement with experimental data is achieved.

Conclusion
Two techniques of extracting DIIMFP of Be are represented in this work. DIIMFP, derived on the basis of represented methods, adequately describes both PES (XPS) spectra and REELS spectra of scattered electrons in beryllium. The advantage of the first technique is possibility of determination DIIMFP $x_{inb}(\Delta)$ and $x_{ias}(\Delta)$ directly from experimental data of PES (XPS) and REELS spectra. The first technique does not need the knowledge of optical data. The disadvantage of the first technique is necessity of independent definition of $x_{inb}(\Delta)$ and $x_{ias}(\Delta)$ on the basis of fitting method, that represents labour intensive procedure. The second method is that the use of optical constants makes the entire procedure of getting inelastic properties of a material much easier and provides a reasonable result. However these data are not always available especially in a wide range of energy losses. In this case the oscillator parameters in the Mermin model should be fitted by minimizing the residue between calculated and experimentally measured spectrum.

The work was performed within the framework of State Task of the Russian Federation No. 3/1414/2017 ПЧ.

References
[1] Köppen M., Oberkofler M., Riesch J., Schmid K., Vollmer A., Linsmeier Ch. 2013 J. Nucl. Mater. 438 S766
[2] Afanas’ev V.P., Gryazev A.S., Kaplya P.S., Köppen M., Ridzel O.Yu., Subbotin N.Yu., Hansen P. 2017 J. Phys.: Conf. Ser. 891 012303
[3] Tanuma S., Powell C.J., Penn D.R. 2011 Surf. Interface Anal. 43(3) 689–713.
[4] Tougaard S., Chorkendorf I. 1987 Phys. Rev. B. 35 6570.
[5] Werner W.S.M. 2006 Phys. Rev. B. 74 075421.
[6] Tikhonov A.N., Arsenin V. Ya. Solutions of Ill-Posed Problems (Nauka, Moscow, 1979; Halsted, NewYork, 1977).
[7] Afanas’ev V.P., Fedorovich S.D., Lubchenko A.V., Ryjov A.A., Esimov M.S. 1994
   Z. Phys. B: Condens. Matter. 96 253–259.
[8] Werner W. 1995 Surf. Interface Anal. 23 737.
[9] Moulder J., Stickle W., Sobol P., Bomben K. 1995 Handbook of X-Ray Photoelectron
   Spectroscopy (Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie,
   Minnesota).
[10] Afanas’ev V.P., Efremenko D.S., Kaplya P.S. 2016 J. Electron Spectrosc. Relat. Phenom. 210
    16.
[11] Afanas’ev V.P., Gryazev A.S., Efremenko D.S., Kaplya P.S. 2017 Vacuum 136 146.
[12] Palik E.D. 1998 Handbook of Optical Constants of Solids (Academic Press).
[13] Henke B.L., Gullikson E.M., Davis J.C. 1993 Atomic Data and Nuclear Data Tables 54 (2)
    181-342.
[14] Vos M., Grande P.L. 2017 Surf. Interface Anal. 49 809–821.
[15] Mermin N.D. 1970 Phys. Rev. B 1(5) 2362–2363.
[16] Li Y.C., Tu Y.H., Kwei C.M., Tung C.J. 2005 Surf. Sci. 589(1-3) 67–76.