Quantitative elastic peak electron spectroscopy

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Abstract. New quantitative method of hydrogen isotopes detection in engineering materials used for fusion is introduced. The study proposes a theory of small-angle atomic particle elastic reflection from multicomponent materials. A method for interpreting Elastic Peak Electron Spectroscopy signals considering the multiple scattering effect was developed. It is shown that ignoring the multiple scattering effect results in significant errors with quantitative evaluation of Elastic Peak Electron Spectroscopy signals.

1. Introduction

Instruments with high-resolution energy measurements correctly identify peaks associated with electrons quasi-elasitically reflected from various atoms in a multi-component sample provided that the Rayleigh criterion is met [1]. A new Electron Spectroscopy capability was found: target atom identification by their atomic weights. Maarten Vos [1,2] demonstrated the capabilities of a new Electron Spectroscopy (ES) type, The Elastic Peak Electron Spectroscopy (EPES), also known as 'Electron Rutherford Back Scattering' (ERBS.) ERBS enabled to detect hydrogen and helium [4] isotopes in the samples which were not possible with conventional ES [3]. New opportunities of EPES analysis of engineering materials used in fusion are described in [5] along with traditional Nuclear Reaction Analysis and Elastic Recoil Detection Analysis. The emergence of EPES calls for a new method for processing the experimental spectra to get layer by layer quantitative estimates of the target composition. It results in a number of problems to be solved:

1. Estimation of the area under a peak associated with elastically reflected electrons. The background generated by the non-elastically scattered electrons should be subtracted. A similar problem exists in X-Ray photoelectron spectroscopy (XPS) as well [3], some solutions are proposed in papers [6,7].
2. Considering the effect of multiple elastic scattering on the broadening and shifting the peak associated with elastically reflected electrons. For a single elastic electron scattering from nuclei at the angle the energy loss is $\Delta E$ as described by the energy and impulse conservation laws,

$$\Delta E = \frac{2m}{M} E_0 (1 - \cos \Psi) = \frac{4m}{M} E_0 \sin^2 \frac{\Psi}{2}$$

(1)

where $m$ and $M$ are the masses of the electron and the nucleus correspondingly, $E_0$ is the impinging electron energy. Equation (1) shows that, for instance, for a double scattering at the $\Psi / 2$ angles an electron enters the energy analyzer with a lower energy loss than for a single scattering at $\Psi$. So, multiple elastic scattering leads to both broadening and shifting of the peak towards the area with lower energy loss. Please refer to [7] for a detailed analysis of this effect.

3. Stepwise tracking of the multiple elastic scattering effect on the EPES signal intensity. The first two problems are addressed in papers [6-8]. This paper deals with the third problem.

2. Methods

We considered a two-component target. As we showed, the generalization to more components is easy. Solving the boundary problem using the equation for electrons transfer in a two-component environment was based on the invariant approximation method [9,10]. The equations can be simplified since the elastic scattering cross-section is greatly extended $\omega_{el}(\Psi)$:

$$\omega_{el}(0) \gg \omega_{el}(\pi).$$

(2)

The equation for the flux density of the electrons that change their direction inside the target from downward to upward by reflecting from the first component, or $R_{01}(\mu_0, \mu)$ expressed as a small-angle approximation is (refer to [9,10])

$$R_{01}(\mu_0, \mu) = \frac{\mu_0 \mu}{\mu_0 + \mu} \lambda x_{1}(\mu_0, \mu) + \lambda \int_{0}^{1} R_{y0}(\mu_0, \mu') x(\mu', \mu) d\mu'.$$

(3)

The equation for the total reflection function $R_0 = R_{01} + R_{02}$ is:

$$R_0(\mu_0, \mu) = \frac{\mu_0 \mu}{\mu_0 + \mu} \lambda x(\mu_0, \mu) + \lambda \int_{0}^{1} R_{y0}(\mu_0, \mu') x(\mu', \mu) d\mu'$$

(4)

where $x_{1}(\cos \Psi) = \omega_{el,1}(\cos \Psi) / \sigma_{el,1}$ is the normalized scattering cross-section from the first component of the target substance; $x_2$ is the normalized scattering cross-section from the second component of the target substance; $\sigma_{el}$ is the integral elastic scattering cross-section,

$$x = \frac{\alpha_1 \sigma_{1} x_1 + \alpha_2 \sigma_{2} x_2}{\alpha_1 \sigma_{1} + \alpha_2 \sigma_{2}} = \frac{x_1 + \xi x_2}{1 + \xi}, \quad \lambda_1 = \frac{\alpha_1 \sigma_{1}}{\alpha_1 \sigma_{1} + \alpha_2 \sigma_{2} + \sigma_{in}}$$

is the probability of elastic scattering from
the first component of the target substance, and $\lambda_2 = \frac{\alpha_2 \sigma_2}{\alpha_1 \sigma_1 + \alpha_2 \sigma_2 + \sigma_m}$ is the probability of elastic scattering from the second component of the target substance; $\lambda = \frac{\alpha_1 \sigma_1 + \alpha_2 \sigma_2}{\alpha_1 \sigma_1 + \alpha_2 \sigma_2 + \sigma_m} = \lambda_1 + \lambda_2$ is the probability or a single elastic scattering albedo, $\alpha_i$ is the share of the $i$th component in the substance.

$$\sum \alpha_k = 1, \quad \lambda_2 \lambda_1 = \frac{\alpha_2 \sigma_2}{\alpha_1 \sigma_1} \xi$$

respectively $\lambda_2 = \lambda_1 \xi, \lambda_1 = \lambda / (1 + \xi), \lambda_2 = \lambda \xi / (1 + \xi)$

We solved equation (2) with the iterative method:

$$R_{0i}^{(j)} (\mu_0, \mu) = \frac{\mu_0 H}{\mu_0 + \mu} \lambda_1 x_i (\mu_0, \mu).$$

Equation (6) that ignores multiple scattering is conventionally applied to estimating the relative concentrations of the target substance components as a first approximation [11].

By solving equations (3) and (4) with the iterative method and using an analytic integral continuation to the (0, 1) range as proposed in paper [4] we obtained the total and the $j$th reflection functions:

$$R_0 (\mu_0, \mu) = \frac{\mu_0 H}{\mu_0 + \mu} \left[ \lambda x(\mu_0, \mu) + \frac{\lambda^2}{2} \int x(\mu_0, \mu') x(\mu', \mu) d\mu' + \frac{\lambda^3}{3} \int d\mu'' \int x_i (\mu_0, \mu') x(\mu', \mu'') d\mu' x(\mu'', \mu) + \frac{\lambda^4}{k} \int x_i^{k-1} (\mu_0, \mu') x(\mu', \mu) d\mu' + \ldots \right]$$

$$R_{0j} (\mu_0, \mu) = \frac{\mu_0 H}{\mu_0 + \mu} \lambda_j \left[ x_j (\mu_0, \mu) + \frac{\lambda^2}{2} \int x_j (\mu_0, \mu') x(\mu', \mu) d\mu' + \frac{\lambda^3}{3} \int d\mu'' \int x_j (\mu_0, \mu') x(\mu', \mu'') d\mu' x(\mu'', \mu) + \frac{\lambda^4}{k} \int x_j^{k-1} (\mu_0, \mu') x(\mu', \mu) d\mu' + \ldots \right]$$

The spherical harmonic method [9,10] was used to estimate equation (7), (8):
\[
R'_0 = \frac{\mu_0 \mu}{\mu_0 + \mu} \left[ \lambda \chi' + \frac{(\lambda \chi')^2}{2} + \frac{(\lambda \chi')^3}{3} + \ldots + \frac{(\lambda \chi')^k}{k} + \ldots \right]
\]  
(9)

\[
R^j_0 = \frac{\mu_0 \mu}{\mu_0 + \mu} \frac{\lambda_j \chi_j}{\lambda \chi'} \left[ \lambda \chi' + \frac{(\lambda \chi')^2}{2} + \frac{(\lambda \chi')^3}{3} + \ldots + \frac{(\lambda \chi')^k}{k} + \ldots \right] =
\]
\[
= \frac{-\mu_0 \mu}{\mu_0 + \mu} \frac{\lambda_j \chi_j}{\lambda \chi'} \ln(1 - \lambda \chi') = -\frac{\mu_0 \mu}{\mu_0 + \mu} \frac{\chi_j}{\chi_1 + \chi_2} \ln(1 - \lambda \chi')
\]
(10)

\[
R_{0j}(\mu_0, \mu) = \frac{-\mu_0 \mu}{\mu_0 + \mu} \sum_{l=0}^{\infty} \frac{2l + 1}{2} P_l(\mu) P_l(\mu_0) \frac{\chi_j}{\chi_1 + \chi_2} \ln(1 - \lambda \chi')
\]
(11)

\[
R_0(\mu_0, \mu) = \frac{-\mu_0 \mu}{\mu_0 + \mu} \sum_{l=0}^{\infty} \frac{2l + 1}{2} P_l(\mu) P_l(\mu_0) \ln(1 - \lambda \chi')
\]
(12)

where \(\chi_j\) are the serial expansion factors of the normalized scattering cross-sections \(x_j(\mu_0, \mu)\) using the Legendre polynomials \(x' = \frac{x_1 + \chi_2}{1 + \chi}\).

Equation (9) produces the contribution of single (the first term on the right-hand side), double (the second term), etc. elastic scatterings to the reflection function:

\[
R^k_0 = \frac{\mu_0 \mu}{\mu_0 + \mu} \sum_{l=0}^{\infty} \frac{2l + 1}{2} P_l(\mu_0) P_l(\mu) \frac{(\lambda \chi')^k}{k}, \quad R^j_0 = \frac{\mu_0 \mu}{\mu_0 + \mu} \frac{\lambda_j \chi_j}{\chi_1 + \chi_2} \frac{2l + 1}{2} P_l(\mu_0) P_l(\mu) \frac{(\lambda \chi')^k}{k}
\]
(13)

\[
R_0^l = \frac{\mu_0 \mu}{\mu_0 + \mu} \left[ \alpha_1 \alpha_2(\mu_0, \mu) + \alpha_2 \alpha_3(\mu_0, \mu) \right] \alpha_1 \sigma_1 + \alpha_2 \sigma_2 + \sigma_m
\]
(14)

3. Results and discussion

Monte Carlo simulations of EPES signals was presented in [12]. Figure 1 shows the analysis \(R^0_0\) for TiO\(_2\) and HfO\(_2\) with equation (13) as compared to the results presented in paper [11].
Figure 1. Contributions of various multiple reflections to the peak intensity associated with elastic reflection from HfO$_2$ and TiO$_2$. Dash curve: TiO$_2$ solid curve: HfO$_2$; curves: estimated with equation (13), circles: TiO$_2$; stars: HfO$_2$ Monte Carlo simulation [12].

Figure 1 represents a good agreement between the analysis based on the small-angle reflection model covered in this paper and the Monte Carlo simulation results [12]. Paper [12] also shows a good agreement between the Monte Carlo simulation and the experimental results. Figure 1 and the analysis presented in papers [9,10,13] indicates sufficient accuracy of the atomic particle elastic scattering description with equations (11) – (13).

EPES signals can be used to estimate relative concentrations of the elements in a substance provided that the following ration is available:

$$\frac{R_{01}}{R_{02}}.$$  \hspace{1cm} (15)

Figure 2. Under peak areas ratios (15) approximately estimated for a single scattering for HfO$_2$ sample: solid line, and considering the multiple elastic scatterings: $R_{01} / R_{02}$: dash line.
Figure 2 shows the ratio (15) for HfO$_2$. The ratio (15) is obtained experimentally as the ratio of areas under the peaks associated with the ions reflected by the target components. Then we estimated the sought ratio of element concentrations in the target: $\alpha_1 / \alpha_2$.

Figure 2 implies that the multiple elastic scattering effects should be taken into account. Ignoring them may lead to large and systematic fractional analysis errors.

Following the some EPES analysis processes, we assumed that CH$_2$ is analyzed. We found the density ratios of the electron fluxes reflected from various target components approximately estimated for a single scattering: $R_{01}^1 / R_{02}^1$ and accounting for multiple elastic scatterings: $R_{01} / R_{02}$ with equations (6) and (11).

![Figure 3](image1.png)

**Figure 3.** Ratios estimated as functions of the scattering angle: single reflection approximations $R_{01}^1 / R_{02}^1$ (bottom curve) and taking into account multiple elastic scatterings: $R_{01} / R_{02}$ (top curve.)

CH$_2$ target, normal incidence angle, probe beam energy: 2 keV.

Figure 3 represents that the composition stoichiometry estimation error is 20% if the multiple scattering effects are ignored.

The effects on the scattering geometry on the analysis results further. Figures 4, 5, and 6 show that the multiple elastic scattering contribution varies greatly with the scattering geometry.
Figure 4. Ratios estimated as functions of the scattering angle: single reflection approximations $R_{01}^1 / R_{02}^1$ (bottom curve) and taking into account multiple elastic scatterings: $R_{01} / R_{02}$ (top curve.) CH$_2$ target, 10° incidence angle, probe beam energy: 2 keV.

Figure 5. Ratios estimated as functions of the scattering angle: single reflection approximations $R_{01}^1 / R_{02}^1$ (bottom curve) and taking into account multiple elastic scatterings: $R_{01} / R_{02}$ (top curve.) CH$_2$ target, 20° incidence angle, probe beam energy: 2 keV.

Figure 6. Ratios estimated as functions of the scattering angle: single reflection approximations $R_{01}^1 / R_{02}^1$ (bottom curve) and taking into account multiple elastic scatterings: $R_{01} / R_{02}$ (top curve.) CH$_2$ target, 30° incidence angle, probe beam energy: 2 keV.

To identify the root cause of such a great multiple scattering contribution we used equation (13) to estimate the angular distributions of scattering electrons vs. the number of reflections.
Figure 7. Relative contribution of various more-than-once elastic scatterings from the PE target components to the reflected flux. Contribution of elastic scatterings from carbon: dash line; from hydrogen: solid line. Probe beam energy: 2 keV, normal incidence angle, 135° scattering.

Figure 7 shows a substantial contribution of multiple elastic scattering. The reason is that the electron elastic scattering cross-section from carbon is 36 times higher than that from oxygen. At the same time, the contribution of more-than-once reflections does not exceed the contribution of a single reflection because the single elastic scattering albedo is 0.4.

4. Conclusion

Multiple elastic scattering greatly affects the intensity and angular distribution of atomic particles reflected from the target without any non-elastic energy losses. For high-resolution energy measurements $\delta E_{\text{ratio}} : \delta E_{\text{ratio}} < \Delta E$, the spectrum range would be peak-shaped. In paper [11], the Monte Carlo simulations point to the substantial contribution of multiple elastic scattering to the peak intensity of the elastically reflected particles.

In this study, we proposed a small-angle approximation for the direct problem of estimating flux densities of atomic particles quasi-elastically reflected into the specified solid angle from the target substance components. The small-angle estimation results were in good agreement with the Monte Carlo simulations.

In ISS spectroscopy similar to EPES the multiple scattering effects on the peaks associated with the ions reflected by the target components can be ignored since the single scattering albedo is low. For the same reason, the BeH$_x$ target stoichiometry can be assessed with the single reflection model (6).

The study identified the processes when ignoring the multiple elastic reflection leads to substantial errors. The reverse problem is finding the target components ratio. A self-consistency procedure is required to solve the reverse problem: 1. Finding the approximate concentration ratio for a single reflection (6). 2. Finding the albedo for the approximated concentration ratio. 3. Estimating the concentration ratio with equation (11) 4. Items 2 and 3 are repeated to the new concentration ratio, and so on.

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6. References

[1] Went M R and Vos M 2007 *Surf. Interface Anal.* **39** 871 – 876
[2] Went M R and Vos M 2007 *Appl. Phys. Lett.* **90** 072104
[3] Hofmann S 2013 *Auger- and X-Ray Photoelectron Spectroscopy in Materials Science* (Berlin, Heidelberg: Springer Berlin Heidelberg)
[4] Vos M 2002 *Ultramicroscopy* **92** 143 – 149
[5] Kostanovskiy I.A., Afanas’ev V P, Naujoks D., Mayer M. 2015 *J. Electron. Spectrosc. Relat. Phenom.* **202** 22-25.
[6] Afanas’ev V P, Gryazev A S, Efremenko D S, Kaplya P S and Ridzel O Yu 2016 *J. Phys.: Conf. Ser.* **748** 012005
[7] Afanas’ev V P, Gryazev A S, Kaplya P S, Köppen M, Ridzel O Yu, Subbotin N Yu and Hansen P 2017 *J. Phys.: Conf. Ser.* **891** 012303
[8] Afanas'ev V P, Afanas'ev M V, Lubenchenco A V, Batrakov A A, Efremenko D S and Vos M 2010 *J. Electron. Spectrosc. Relat. Phenom.* **177** 35
[9] Afanas’ev V P, Kaplya P S and Lisitsyna E D 2016 *J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech.* **10** 326 – 331
[10] Afanas’ev V P, Efremenko D S and Kaplya P S 2016 *J. Electron. Spectrosc. Relat. Phenom.* **210** 16 – 29
[11] Vos M and Went M R 2007 *Surf. Sci.* **601** 1536 – 43
[12] Vos M, Marmitt G G and Grande P L 2016 *Surf. Interface Anal.* **48** 415 – 421
[13] Salvat-Pujol F and Werner W 2011 *Phys. Rev.* **83** 195416