Review of the PhD dissertation of Tomàš Strapko on the topic of “Ion spectroscopy for analysis of surface structures”

The dissertation focuses on Low Energy Ion Scattering (LEIS), an interesting technique with growing commercial importance for the surface analysis for a wide range of applications, of which catalysis, energy storage and semiconductors are only a few.

LEIS is a quantitative technique: the intensity of the signal for an element is proportional to its concentration at the surface of the sample. The accuracy of the determination depends for a large part on the scientist’s ability to separate the relevant signal, the “surface peak”, from other components in the spectrum, the various backgrounds. Therefore, a thorough understanding of these peaks and backgrounds and a proper mathematical description are crucial for the success of LEIS as an analytical tool. Some of these contributions to the signal were not understood well or lacked a mathematical description. The candidate has made significant contributions in this area. **This makes the dissertation topic up-to-date** and **the stated objective has been met.**

The candidate has solved the mystery of a part of the background on the low energy side of the peak. He solved this convincingly: It is caused by straggling above the surface and the candidate has properly derived why a slight modification of the Gaussian peak to a L’Hoir peak is an improvement of the mathematical description of the peak.

The candidate applied the proper procedures to solve this problem.

For the background on the low energy side of the surface peak, that is caused by signal from deeper layers in the sample, he has studied the effect of the chosen background parameters on the resulting intensity of the surface peak.

The candidate applied the proper procedures to find the optimal method to choose correct background parameters. If anything, he could have stated that conclusion (that he found the optimal method to choose correct background parameters) more clearly.

Up to now, the background on the high energy side of the surface peak, caused by scattering from not one but multiple atoms, lacked any mathematical description. The candidate proposed to describe it by a combination of a Gaussian and an inverse L’Hoir function.

The candidate did not solve the problem, but made an important suggestion towards solving it, for a part of the spectrum where no solution existed before.

The candidate has improved the process of quantification of LEIS data, from the spectra that are measured to the data that application scientists need: surface concentrations. His contributions have improved the accuracy of LEIS analysis. His contributions will find their way into the LEIS analysis of “real world” samples. **This makes this work important** for the field of LEIS analysis.

Regarding the **formal arrangement of the dissertation and its linguistic level**, I have the following remarks.

When judging the level of English, it is helpful to take the author’s native language into account. Pronounced differences between Czech and English, as I understand them, are:

- In Czech, the function of the various parts of a sentence is governed by cases indicated by conjugation of the nouns and adjectives. In English, the function of the parts of a sentence follows from the word order (subject-verb-object).

- Usually, English nouns are preceded by articles (“the”, “a”, or “an”) and in some cases they aren’t. These modify the contextual meaning of the noun. Czech doesn’t use articles.
- Of course, Czech (a Slavic language) and English (Germanic) have vastly different vocabulary.

When reading the dissertation, I never noticed anything unusual in the word order. The structure of the sentences is always correct. Mistakes are made with the use of articles: at various places, an article is missing. The vocabulary is very good.

Overall, I would say that the level of English in the dissertation is very good.

The arrangement of the chapters is good.

The dissertation and message in it are understandable.

I have the following **questions regarding the work in this dissertation**:

1

In section 2.2.1 (p. 18), you explain that the background on the low energy side of the surface peak can be described as an error function, if the peak itself is a Gaussian. This is caused by the fact that the background can be seen as consisting of Gauss peaks from each layer below the surface, where each successive Gaussian has a successively lower energy, due to stopping when the particle is traveling through the sample. If these Gauss peaks are summed up, or integrated, the error function is obtained.

In section 2.2.4 (p. 22), you argue that the peak shape of the surface peak should actually be a L’Hoir function, due to the accompanied loss of energy due to electronic stopping (straggling). It would seem logical to extend the reasoning from section 2.2.1:

When the background to the left of a Gaussian is an integrated Gaussian (an error function), then the background to the left of a L’Hoir peak should be an integrated L’Hoir peak.

Nevertheless, you did not fit the background in section 2.2.4 with an integrated L’Hoir peak, but instead with an error function.

Could you please explain to the committee why it is also correct in this case to describe the background with the error function, the integral of the Gaussian, and not an integral of a L’Hoir peak?

2.

In figure 2.10 (p. 27), you depict a top view of the (111) plane of an Al crystal. Since you have been studying Al foils and the (111) plane is the most closely packed, and hence, most stable plane, this is the surface that is most abundant in your samples.

Since the primary ions are directed perpendicularly towards the sample, the top view is the view that the ion source irradiates. As the figure shows, the ion source is able to irradiate the top 3 layers of Al.

However, there is another consideration or, if you will, another view that is just as important: The view from the analyzer towards the sample. The analyzer does not look perpendicularly towards the sample, but under an angle of 180° – 145° = 35°.

a) How does this affect your view on the atomic layers that will be seen by LEIS?

In addition, aluminum is a metal. Figure 2.10 depicts the positions of the nuclei of the Al atoms. To put it graphically, these nuclei are the meatballs in a soup of electrons in the conductance band of Al.

b) Could you comment on the probability that a He^{+}-ion will remain ionized while traveling through this “soup” and how this affects the number of layers that LEIS can see?

3.

You have shown in figures 3.6 and 3.7 (p. 56) that fitting data to a combination of an error function and a Gaussian can be complicated. This is due to the fact that the error function itself is a sum of Gaussians. Shifting the error function is equivalent to adding or subtracting a Gaussian to/from it.

The figures show the effect that the position (figure 3.6) and the width (figure 3.7) of the error function have on the resulting integral of the surface peak: Even for a clear signal such as the Al peak in the spectra of your work, these can vary by a few percent. This means that in quantitative surface analysis with LEIS, it is imperative to define good parameters for the error function in relation to the Gaussian surface peak.

You have argued in section 2.2 that a difference in the positions for the error function and Gaussian of 30 eV is a good choice. This is also the value that is used in practice, e.g. in the manufacturer’s software.

This leaves the width of the error function still up for debate.

a) When you consider figure 3.7, what would be your recommendation for the optimal value for the multiplicator x to obtain the best reproducible fit results, that are least sensitive to the chosen value of x?

b) Given that the width of the error function corresponds to the width of the Gaussian representing scattering from the second layer in the sample, what would be the best guess for a value for the multiplicator x?

I recommend that, as a result of this work, the candidate is awarded with a PhD degree.

Sincerely yours,

Oss, The Netherlands, November 11th, 2024

Hendrik Rintcius Jacob (Rik) ter Veen, Ph.D.

Brief statement on the submitted thesis

“Ion spectroscopy for analysis of surface structures” by Tomàš Strapko focuses on Low Energy Ion Scattering (LEIS), an interesting technique that uses collisions between light ions and surface atoms for the quantitative chemical analysis of the outermost atomic layer of a sample. As with macroscopic collisions, the velocity of the ion after the collision depends on the mass of the surface atom it collided with (“scattered of”). LEIS has commercial importance in fields such as catalysis, energy storage and semiconductors. The LEIS spectroscopist evaluates the LEIS spectrum to determine surface properties such as surface concentrations of elements, whether a thin film on a substrate is closed or contains holes, or how thin the film is.

To perform this evaluation correctly, the LEIS spectroscopist needs to understand the phenomena that give rise to the signals in the LEIS spectrum. Some of these, such as the signal due to single scattering of a surface atom, were already well understood and mathematically described. Others, such as the background due to multiple scattering events, lacked any mathematical description. The purpose of this dissertation is to further understand and mathematically describe these phenomena. This enables a more accurate determination of surface properties from the LEIS spectrum.

The dissertation has clarified why the peak from the binary is asymmetric. It is caused by a loss of energy of the probe ion due to interactions with the electrons above the surface. In addition, it derives a clear mathematical model predicting this loss, and thereby, the actual shape of the peak, which fits well with experimental data. Contributions are also made in the description of the signal due to multiple collisions, as well as the signal due to collisions deeper into the material.

The result of this improved understanding and the novel models to describe the spectra is that more data can be derived from LEIS spectra than before and that it can be done with better accuracy.

Rik ter Veen, Ph.D.