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50 years anniversary of the discovery of the core level chemical shifts. The early years of photoelectron spectroscopy

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ABSTRACT

The pioneering years of photoelectron spectroscopy in Uppsala are discussed, especially the work leading to the discovery of the core level chemical shifts. At a very early stage of the project, the pioneering group observed what they described as evidence for chemical shifts in the core level binding energies. However, it can now be seen that the initial observations to a large extent was due to charging of the samples. It is interesting to note that the decisive experiment was realized, not as a result of a systematic study, but was obtained with a large element of serendipity. Only when a chemical binding energy shift was observed between two S2p electron lines in the same molecule, the results were accepted internationally, and the fascinating expansion of modern core level photoelectron spectroscopy could start.

1. Introduction

The development of electron spectroscopy as a tool for physics, chemistry, biology and industry has been remarkable since the first pioneering experiments in the 1950s. With modern database tools it is possible to follow this development and, as an example, we show in Fig. 1 the results of a search for *electron spectrosc** in Web of Science.

The diagram shows the impact of electron spectroscopy in a large number of disciplines. The solid line in the diagram is a fit to an exponential curve. Of course this curve should just be taken as an indication of a very rapid development.

One of the main reasons for this development relates to the core level binding energy shifts, which make it possible to investigate the local chemical environment around individual atoms in a system. As will be discussed below, there had been some indications of such shifts already in 1958. However, the first conclusive result was published 50 years ago, in 1964.

2. About the authors

One of the authors, Evelyn Sokolowski (ES), was a member of the pioneering group. The group consisted of Prof. Kai Siegbahn (Nobel Laureate 1981) and his two research students Carl Nordling and ES. ES was the first one to present a doctoral thesis on this subject. The thesis "*Investigations of inner electron shells by spectroscopic studies of photo- and Auger electrons*" was presented in 1959.

After the promotion to Doctor in Physics, ES left the field and became heavily engaged in building up the Swedish competence in nuclear technology. In connection to the HArd X-ray PhotoElectron Spectroscopy conference (HAXPES 2013) in Uppsala ES was interviewed at a special session dedicated to the discovery of the Core Level Chemical Shifts. Before the interview she presented a summary of the work in the pioneering group. In this report we have chosen to include certain parts from this document in its original form. Those parts are given in italics.

The other two authors, Svante Svensson (SS) and Nils Mårtensson (NM), entered the field of electron spectroscopy in the 1970s. At this time the field was established worldwide. SS and NM have been active in the field since then and they have in particular been involved in synchrotron radiation research in Sweden and elsewhere.

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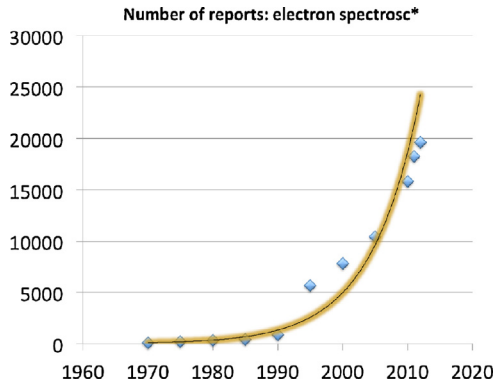

Fig. 1. Number of reports/year for searching for *electron spectrosc** in Web of Science.

3. The early days of electron spectroscopy

Kai Siegbahn (See Fig. 2) was a professor at the Royal Institute of Technology (KTH) in Stockholm when he got the chair in Uppsala, where he started the pioneering electron spectroscopy experiments. As described above he had two research students in the group: Evelyn Sokolowski (ES) and Carl Nordling. ES had a background in nuclear physics and beta spectroscopy, whereas Carl Nordling had been working with X-ray spectroscopy. In order to understand the environment around this group in the middle of the 1950s (ES) summarizes first her experience of working in Stockholm:

> *I spent my first months as research student at the cyclotron in Stockholm, and found the research there somewhat exotic: there was an international race going on, which lab would be the first to produce ELEMENT 100! Many trans-uranium elements had already been identified, with progressively shorter half-lives, but element 100 would be special – the winner of the race could expect international attention, apart from his name being for ever inscribed in the Periodic Table.*

When she was head-hunted by Kai Siegbahn to Uppsala she had a very clear understanding of Kai Siegbahn's plans and ambitions:

> *Kai Siegbahn had started his academic carrier in low-energy nuclear physics. In my opinion Kai's outstanding talent was his ability to design ingenious precision instruments, mainly used for measuring the energy levels in a variety of radioactive nuclei. The result was probably important to the theorists, refining their core models (like Aage Bohr or Maria Goeppert-Mayer who both got the Nobel Prize around this time). But at the Nobel Institute and in Kai's group the experimentalists prevailed, and eventually our work boiled down to strictly empirical monotonous data collection, somewhat cynically called "nuclear botany".*
>
> *The transitions between nuclear energy states showed up as discrete gamma lines in the radioactive decay, and could be analyzed in a gamma spectrometer. But in some of the events the gamma ray would transfer its energy to an atomic shell electron which would then leave the atom – the internal photo effect. With Kai Siegbahn's magnetic beta spectrometers the electron energy could be determined with greater accuracy than the corresponding gamma energy. But there was a little hitch: the binding energy of the electron before it was set free in the spectrometer, which must be taken into account before the nuclear transition energies could be derived. But Kai had a solution to the problem. The relevant binding energy ought to be the same, irrespective of what had kicked the electron out of its system, so if the radioactive gamma source was replaced by an X-ray source (with an accurately known line spectrum), the equation could be solved.*
>
> *In the autumn of 1954 Kai had reached a new milestone in his career by getting a professorship in Uppsala – not only one of the most prestigious universities in Sweden but also his childhood home since his father had been a professor in the same department. Many of Kai's instruments had already been shipped to Uppsala, but few of his assistants had followed him. I was very astonished when – for the first time – he addressed me at the Nobel Institute, offering me a job as "research assistant" (without teaching duties).*
>
> *Another young graduate student had just been recruited – Carl Nordling – and together we would be in charge of the iron-free beta spectrometer where new branches of physics, such as ESCA, were eventually born. But at the beginning what lay before us was "nuclear botany", and particularly an auxiliary detail of it – the routine correction for electron binding energies. It took some thinking before I accepted Kai's offer, but the privilege of working with an experimentalist of his standing decided the matter.*
>
> *The laboratory with the iron-free beta spectrometer (see Fig. 3) was a few meters across the corridor from Kai's office, and he was a frequent visitor in our quarters. It was a one-way road, however, for there was a cardboard sign on his door with the inscription: "IF YOU HAVE NOTHING TO SAY, DON'T SAY IT HERE!"*
>
> *From the windows of our lab we could look into Kai's house – and vice versa. Practically every night after dinner he would return to us by the back stairs, always with the same satisfied greeting: "I saw the lamp of diligence is still shining". By and large we got on well together, but I never felt I knew him, and I only remember one time he spoke to us of a private matter. That morning he looked rather harassed and apparently felt he must give us an explanation: he had spent the night awake, huddled on his pillow, since the other end of his bed had been invaded by – a mouse.*
>
> *Experimental research in those days was still in the era of "scotch tape and chewing gum" which did not always withstand the ambitions of our cleaning woman. It took some time before we found a remedy: a piece of paper with the text "WARNING: 100 000 OHMS". After that the copper coils were perhaps less shiny but our measurements more predictable.*

Fig. 2. Professor Kai Siegbahn (1918–2007, Nobel Laureate 1981).

The first modern core photoelectron spectrum, showing photoelectron lines was published in Physical Review in 1957 [2]. The first core electron line, studied by the group, was Cu1s and its binding energy was determined with high precision, see Fig. 4. In this figure we observe two structures corresponding to photoelectrons excited by MoKα_1 (17.479 keV) and MoKα_2 (17.374 keV), respectively. Based on these lines they obtained binding energies