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# 1913–2013 – The centennial of X-ray absorption spectroscopy (XAS): Evidences about a question still open

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### ABSTRACT

In 1913 J. Herweg first (June 30) and M. de Broglie slightly later (November 17) claimed the discovery of a series of spots and lines closely following the main absorption edges of heavy metals, which they interpreted as the proof of the existence of X-ray spectra analogous to light spectra. In the following year they documented their discoveries via photographic plates. However, they were both discredited: Herweg by G.E.M. Jauncey, who showed that his spectra, taken on Pt and W, did not obey Moseley's rule; de Broglie by W.H. Bragg, M. Siegbahn and E. Wagner, who showed that his lines were in fact the fluorescence lines of the Ag and Br constituents of the photographic emulsion. Consequently, W. Stenström's description (sent to publisher on July 2, 1918) of certain photographically recorded and graphically rendered modulations near the *M*-series edges of heavy metals may possibly be the first published evidence of true X-ray absorption spectra. Indeed, they were interpreted as such by W. Kossel (1920) in his seminal theoretical paper. Otherwise, H. Fricke's table, although printed in 1920, which exhibits the photographic plate of sulphur absorption dated October 1, 1918, and its graphical rendering by a photometric method, is the first unequivocally dated evidence of recorded modulations at a XAS *K*-edge.

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## 1. Introduction

Who should be credited for discovering X-ray absorption spectra and for initiating X-ray absorption spectroscopy (XAS) as a new branch of Physics? Did such a discovery occur by chance, as it was the case with W.C. Röntgen's X-rays, or was it the result of a lengthy, costly search like that for the Higgs' boson?

In 1913, the physicists dedicated to X-rays were in a high state of dismay. For more than a decade their studies on those highly penetrating rays had increased steadily without giving answer to such crucial questions as follows: (a) had they a wavy or corpuscular nature? (b) how would they fit with the quantum and photon theories introduced by M. Planck and A. Einstein? and (c) what will be their relationships with N. Bohr's newest atomic theory, then still under development? In point of fact, H. Haga had shown

them to undergo polarization, at least partially; C.G. Barkla had documented that they had characteristic emission lines in addition to a continuum; and also (with V. Collier) that they absorbed discontinuously along two series, which he named *K*- and *L*-series. Moreover, just in the previous year, the important role of the X-rays in science had been confirmed by W. Friedrich's and P. Knipping's experiments using the continuum emission (bremsstrahlung). They demonstrated that at least some of them are diffracted by solid matter. However, the explanation given by M. von Laue that diffraction is a property intrinsic in X-rays propagation in solids had been challenged by H.G.J. Moseley, who rather believed diffraction is inherent in the order of matter itself. Indeed, W.L. Bragg's suggestion of X-ray reflection by atomic planes, alternative to Laue's diffraction, seemed to fit the data so well as to make the way wide open to determining the regular distribution of atom in solid matter. The first determination of the diamond structure by W.H. and W.L. Bragg would soon follow and therefrom crystal structure determination would be born as a new branch of physics, as it involved chemistry, mineralogy, biology, metallurgy, etc. All these results, taken one by one, seemed to indicate that X-rays were a form of radiation similar to light and, consequently, that they were a

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portion of the electromagnetic spectrum envisaged by J.C. Maxwell, which H.R. Hertz had later experimentally demonstrated and J.R. Rydberg had mathematically fit for the case of light absorption and emission. However, some important information were still missing and, in particular, detecting an absorption spectrum for X-rays that would resemble the light spectrum was urgently needed.

## 2. First attempts

On June 30, 1913, while Bohr was still underway with elaborating his new atomic theory (which indeed drew some mathematics from Rydberg's work on light), [August] Julius Herweg, a lecturer at Greifswald University in Germany, submitted a short paper where he claimed having detected the X-ray absorption spectrum of platinum [1], using this metal as both the anticathode of the X-ray source and the absorber: it was, therefore, a self-absorption spectrum. His apparatus consisted in a discharge tube emitting a beam of X-rays, which were reflected over a wide angle by a gypsum crystal before reaching the photographic detector. The claimed spectrum was described to consist in a sequence of light and dark sharp lines following the main absorption band of Pt and superimposed on a continuously decreasing background.

On November 17, 1913, a similar short communication [2] was submitted by [Louis-César-Victor-] Maurice de Broglie, an independent researcher at Paris Collège de France. He had used a new type of spectrometer (a precursor of the XRD rotating crystal method), where a rock salt crystal fixed on a cylindrical barometer that turned at constant angular speed was set to reflect all X-rays incoming under different angles onto a photographic plate. After the main absorption line, de Broglie noticed a series of fine as well as diffused reflected rays, bands, etc. overlapping a continuous background.

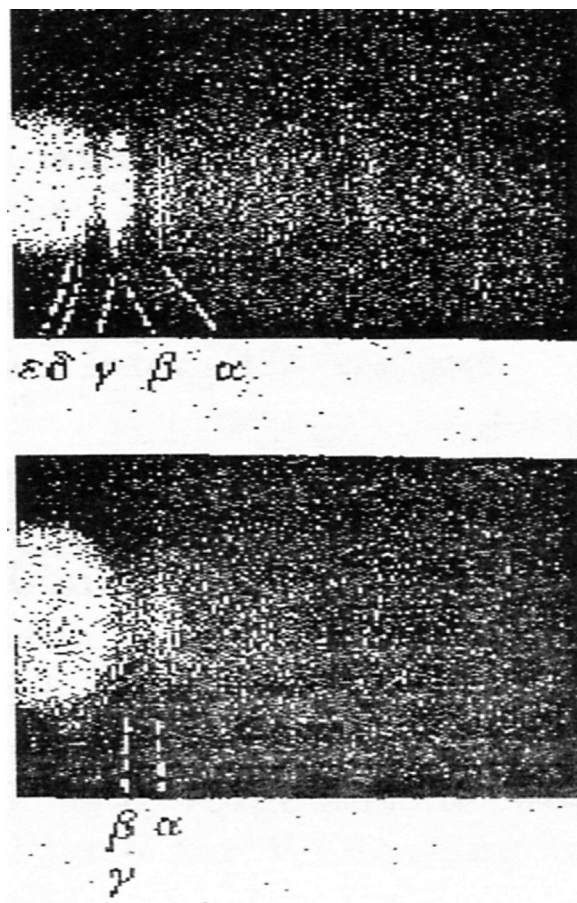
The two results, obtained on vastly different setups and essentially confirming one another, seemed to show that the X-ray spectrum had been eventually detected and properly recorded. Unfortunately, this was not so.

Early 1914, Herweg published the plates displaying his “spectra” of Pt and W [3]: indeed there were spots following the main absorption edge (Fig. 1). Slightly later also de Broglie, together with A.F. Lindemann [4], published plates that were even better and clearly showed the alternation of lighter and darker bands forming their Pt “spectrum” (Fig. 2). Therefore, the evidences were on display for the peer-reviewed process, and such a process disproved both results.

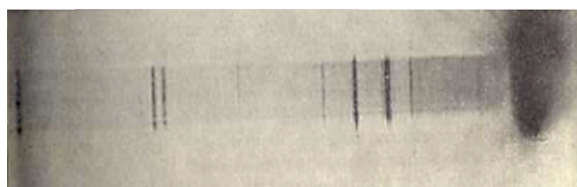
On one side, Herweg's Pt and W identical images were criticized by G.E.M. Jauncey, then a young demonstrator at Toronto University, who showed that there had been an error, as two different metals cannot absorb at the same frequency (or energy). He recalculated the glancing angles given by Herweg for Pt and showed them to coincide with the calculated ones for W [5], thus disagreeing with Moseley's law, by that time already well established. On the other side, de Broglie and Lindemann's images were re-interpreted, independently, by W.H. Bragg and M. Siegbahn, who both came to the same conclusion: the dark lines were the fluorescence emission lines of Ag and Br in the photographic emulsion, which superimposed on a background rapidly decreasing in darkness after the Pt absorption edge. Herweg gave up. By contrast, de Broglie tried other experiments to support the correctness of his “spectrum” and drew interesting contributions on other points, but eventually E. Wagner's extremely well-resolved photographic plates [6] convinced not only the reviewers but also de Broglie himself and, correctly, he admitted that he had been mistaken [7].

## 3. First positive results

By 1918, the question of the X-ray absorption spectrum had gone back to its pristine state, although in the meanwhile W. Kossel [8]



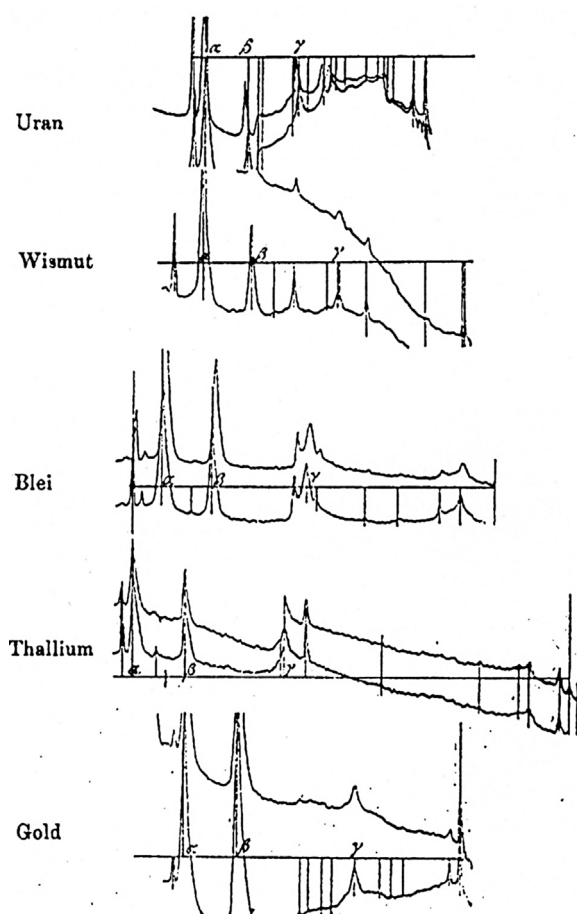
**Fig. 1.** The “spectra” of platinum and tungsten recorded by Julius Herweg (*Verh. Dtsch. Phys. Ges.*, **16**, 1914, 76, Table Nr. 1, Figs. 3 and 4) showing the range around the main absorption edge and the lines of “second order” additional to those of “first order” detected by Moseley and Darwin (1913). Their coincidence provoked G.E.M. Jauncey's criticism.



**Fig. 2.** The platinum absorption “spectrum” according to Maurice de Broglie and Frederick Alexander Lindemann (*Verh. Dtsch. Phys. Ges.*, **16**, 1914, 195, Fig. 1). The additional lines are the fluorescence lines of silver and bromine present in the plate photographic emulsion, as suggested by W.H. Bragg and M. Siegbahn, and demonstrated by E. Wagner.

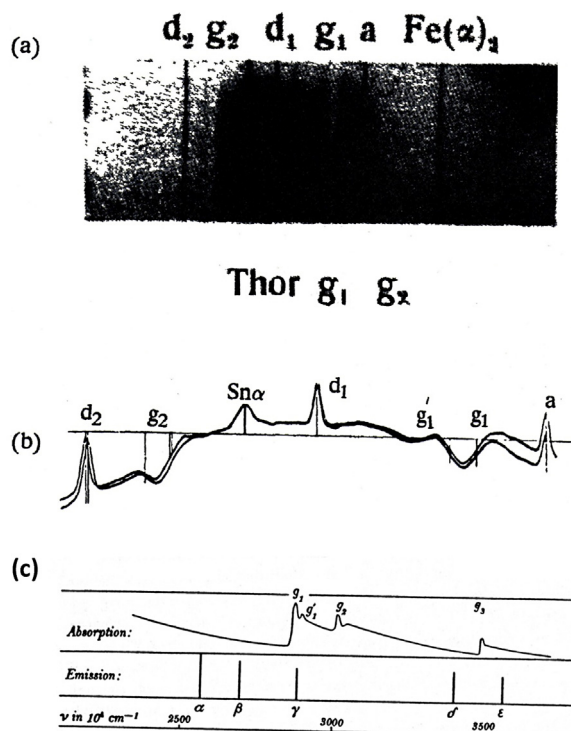
and M. Siegbahn [9] had discovered another series of absorption discontinuities: the *M*-series, which added up to those discovered by Barkla and Collier. This new finding made the need for a clarification of the entire matter even more urgent. Actually, it was by studying in depth the *M*-series of 16 heavy elements from Dy to U that the evidence for the unquestionable existence of an absorption spectrum, in the modern understanding of this term, finally arose.

[Karl] Wilhelm Stenström [10,11], a doctorate student at Lund University in Sweden, received from Siegbahn (then the acting professor of physics during the final years of Rydberg's illness) the assignment of studying in detail the photographic plates of the heaviest elements absorbing at  $\lambda$  from 4 to 10 Å that Siegbahn himself had begun studying, but could not bring to an end. To fulfil



**Fig. 3.** Modulations across the  $M$ -series edges of the absorption spectra of various heavy elements recorded photographically by Wilhelm Stenström and redrawn as graphics by him (*Ann. Phys.*, **57**, 1918, 360, Fig. 5a).

his duty, Stenström was allowed to use a special type of spectrograph operating under vacuum previously set up by Siegbahn together with E. Friman [12]. Stenström took the matter very seriously and introduced several of his own technical improvements [10]. He increased strongly the power of the source (up to 10 kV and 15 mA, using a 0.2 mm hot W rod electrode), making it so stable as to be able to operate continuously for 1 h and even more; he increased the transparency of the membrane and reduced the width of the slit leading to the spectrograph in order to minimize dispersion; he perfected by adjusting the absorbing crystal up to 0.01 mm accuracy; finally, he fitted 13 plates all along the half-circle of the apparatus so as to obtain detection over a wide angle, with an accuracy estimated to be 0.2–0.3% from 45° to 15°. As for the detection system, he made a comparison among three types of photographic plates and selected for his measurements against a German-made type and a French-made one, as the first assured best recording of the strong lines and the other of the weak ones. A final problem was in the selection of the monochromator crystal, which he eventually compromised to be always gypsum, so as to have all data comparable, although certain organic crystals had appeared to work better, but also deteriorated faster. Stenström published his results in the form of extensive numeric tables and of graphic renderings of the darkening observed on several of his plates (Fig. 3), but he only described most of them without entering into fine details, as his major goal was at determining the wavelengths of the three major lines he thought the  $M$ -series



**Fig. 4.** The absorption spectrum of thorium at the  $M_3$  edge photographically recorded (a) and graphically rendered (b) by Wilhelm Stenström (dissertation, 1919, 33). All indications shown are the same, but for the absorption edge of reference, which is  $Fe_{\alpha}$  in (a) and  $Sn_{\alpha}$  in (b). In (c) is the interpretation of the same spectrum made by Walther Kossel (*Zeitschr. Phys.*, **1**, 1920, 124, Fig. 2) for what concerns the modulations across the major absorption discontinuity.

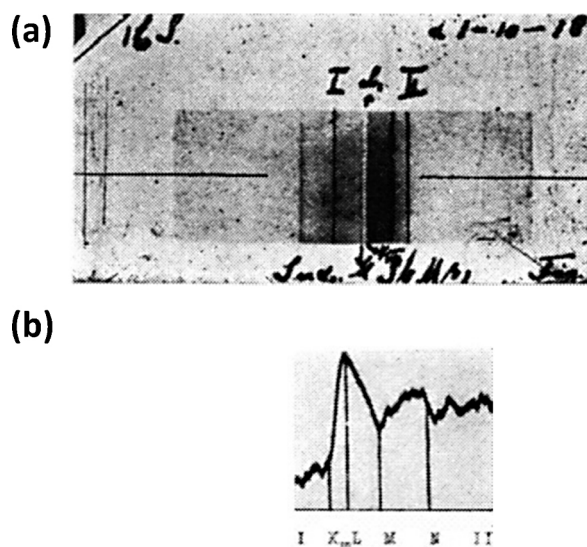
was made of.<sup>1</sup> Nevertheless, he pointed out that most absorption lines were asymmetric and diffuse, with a long tail towards the short wavelength side. He also pointed out that each diffuse line he was measuring at a 0.01 mm resolution was presumably made up of groups of individual finer lines, i.e., that it was in fact a band of lines that needed to be better resolved both in position and in structure. However, he did not progress further in this direction, because he could reasonably guess that a number of the extra-lines he was measuring on his plates may be due to chemical impurities in his starting materials.

Actually, Stenström had another important piece of evidence up his sleeves, which he just hinted at in his major paper [10, pp. 364 and 366], but presented in full in his dissertation [11]: in addition to U, which he had published [10, p. 367], he had recorded a plate on Th and had made its preliminary graphic rendering (Fig. 4). Possibly, he may have written a special essay on it, but early in 1919 he was granted a post-doctorate position in USA, which he spent first working with W. Duane at Harvard, then at Chicago University under R. Millikan. Eventually, he decided to settle permanently in USA (1921), where he dedicated his technically acquired skill to set up powerful sources for curing cancer by X-ray applications, and created a school of biophysics.

Stenström had worked very carefully, although he had missed two absorption edges of the  $M$ -series, he had been able to give only a first glimpse at the modulations occurring near the main  $M_3$  one. As a matter of fact, he did not make all his evidence available to everybody's satisfaction. It is due to the efforts of Hugo Fricke, for the  $K$ -series, and Gustav [Ludwig] Hertz, for the  $L$ -series,

<sup>1</sup> These two were discovered by E. Hjalmar [13], another Lund doctorate student, who is also credited of discovering the first lines of the  $N$ -series.

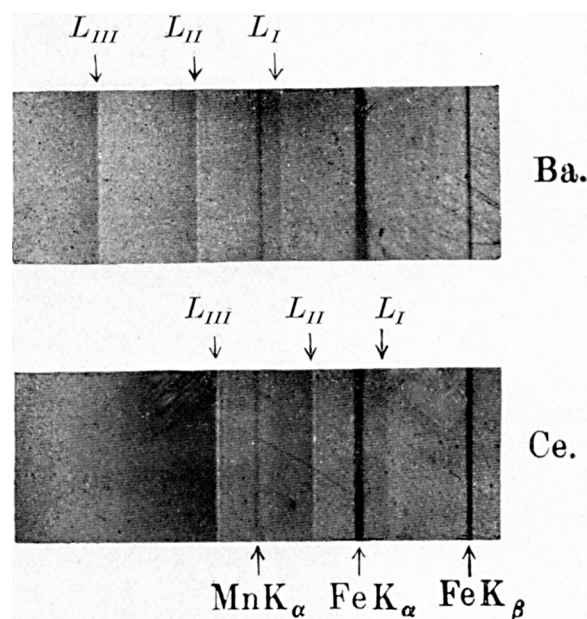




**Fig. 5.** The K-edge absorption spectrum of sulphur as photographically recorded (a) and graphically rendered (b) by Hugo Fricke (*Phys. Rev.*, **16**, 1920, 212, Table 1, Figs. 9 and 3): the printed letters at the bottom of graphic (b), although slightly magnified, correspond to the hand-written letters in plate (a). Note the date of photograph recording on the upper right side of plate (a): October 1, 1918.

in documenting their respective absorptions that everybody was finally convinced that such modulations existed, and this opened the way to accept XAS as a major branch of physics.

Fricke had joined Siegbahn's laboratory at Lund University in 1918, after earning his doctorate at Copenhagen University under Bohr. More or less at the same time and concurrently with Stenström, he took over the detailed study of the X-ray absorption in the K-series, and used the same apparatus, but he developed a setup of his own that was appropriate for light elements and innovative as for experimental data analysis and presentation [14]. His experiments were carried out at a  $10^{-4}$  accuracy in angle resolution and  $10^{-3}$  in energy resolution. He took over the sample preparation method from R. Glocker [15] so as to obtain the best absorption conditions: calculated weights of the chemicals containing the absorber were spread on the paper to obtain layers of such a thickness (from 7 to  $10\ \mu\text{m}$  [14, p. 205]) as to assure the plate best blackening conditions (equivalent to present-day optimizing the signal-to-noise ratios). As for the crystal analyser, he used sugar for the lighter atoms and rock salt for the others, and had both crystals turned by  $1.5\text{--}2.0^\circ$  during exposure to X-rays so as to be certain that the proper wavelength range would be intercepted. Recording was by the usual photographic method, but the details were examined by photometry under the microscope at an accuracy of a few 0.01 mm in width. Fricke's major conclusion was that "the limit is never a sharp discontinuity in the blackening of the plate, ... but it presents a rather complex structure" [14, p. 206]. Indeed, the plate images and their graphic rendering in the tip-in table [14, p. 212] clearly show modulations after the main absorption discontinuity. The most evident ones are those recorded on Ti and S, for which not only the graphic renderings but also the plates were exhibited. The plate for sulphur deserves particular attention: on its upper right limb it is marked with the numbers 1-10-18, to mean October 1, 1918 (Fig. 5). It is the oldest dated evidence of modulations recorded at any absorption edge to be found in the published literature. However, Stenström had been operating long before Fricke and, as a matter of fact, his paper was sent for publication on July 2, 1918 [10, p. 375]. Thus, despite the date written on it, we cannot deem Fricke's plate to date the day when XAS was born.



**Fig. 6.** The barium (above) and cerium (below) L-edges recorded by Gustav Hertz (*Zeitsch. Phys.*, **2**, 1920, 21). The lower spectrum marks in addition the K-series emissions of iron and manganese, present as impurities in the hot-rod anticathode, which can be seen also in the upper spectrum, although unmarked. In between the three dark major L-absorption edges  $L_{III}$ ,  $L_{II}$  and  $L_I$  of barium and cerium, one notices lighter lines and bands, which unequivocally document the existence of a structure at each L-edge for both elements, but which are especially evident in the cerium spectrum.

Fricke earned a fellowship for USA in 1919, worked for a while at Columbia University, and then at Harvard University under T. Lyman. In 1921 he was invited to use his X-ray knowledge on behalf of clinical medicine, and developed dosimeters for the rest of his active life, also founding a company of his own.

#### 4. XAS is definitively born

Despite the great bulk of evidence gathered at Lund University, it seems that the physical international community was still uncertain and needed additional confirmation of XAS existence.

Hertz was not especially devoted to study X-rays, and indeed the work by which he co-earned the 1925 Nobel Prize with James Franck had been performed in 1914 on a completely different subject, but he thought best entering the X-ray field for a while "to contribute to clarify the question" [16, p. 19]. In 1917 he was released from the German army after a two-year illness due to gas poisoning [17, p. 156] and resumed his position as "Privatdozent" at the Technical University of Berlin. In 1920 he published the results of his studies in two papers [16,18], which were conclusive for XAS recognition and seminal for its future developments. In the first one, he demonstrated beyond any doubt ("ohne Zweifel": [16, p. 22]) that in the L-series there existed the same fine structure of the absorption edges as that Stenström had detected in the M-series. To reach such a result, Hertz made use of all the methods tested till then and found to be the best available. He increased strongly the power of his source (up to 10 kV and 55–60 mA) as well as its duration ( $5\text{--}6\frac{1}{2}$  h); he built a new type of spectrograph under high vacuum with rock salt as the analyser crystal split according to the method proposed by H. Seemann [18]; he prepared his absorbing materials as slurries on paper according to Glocker [15]; and he used the German type of photographic plate that Sandström had estimated to be the best for strong recording [10]. The results were up to the expectation: very sharp lines over a uniform, continuous background containing a sequence of weak light lines of shorter

wavelengths (Fig. 6). Furthermore, in order to estimate details best he analysed his plates under a microscope at 30× magnification.

On the basis of all this new evidence Hertz hinted [16, p. 22] that there must be a dependence upon the chemical bond; that each X-ray emission line has a corresponding absorption line, although this is much weaker; finally, that any absorption edge must show a fine structure of the extension suggested by Kossel's theory and also agree to the frequency relationships that Kossel had suggested. Indeed, Hertz himself demonstrated this, because he could extrapolate his reciprocal frequency data measured for the *L*-series three edges and the *M*-series three major lines measured by Stenström and plot all of them as a function of *Z* [16, p. 24, figure], thus giving strong support to the validity of the selection rule also for X-rays [16, p. 25].

Hertz' second paper [19], although extremely brief (2 pages only), summarizes the matter conclusively: Kossel's theory [20,21] is correct; there is indeed a fine structure superimposed on each one of the three edges of the *L*-series, which consists of very narrow lines (c. 0.002 Å); the same fine structure occurs in the *K*-series, or at least in a Mn absorption spectrum he had taken by chance (Hertz was not aware of Fricke's work); the lines correspond to transitions from the *K*- and *L*-shells to the first unoccupied states at the surface of the atom; they undergo some influence of the valence and chemical bond between the atom and its next-near ones. All these are properties of XAS that are currently acknowledged as definitive. Of an even greater interest, for the history of XAS, is the discussion that follows the series of statements, since three major physicists (A. Sommerfeld, W. Kossel – speaking also on behalf of M. Siegbahn and E. Wagner) agreed in praising Hertz' conclusions: thus, XAS had been validated to everybody's satisfaction.

Nevertheless, at Lund University the school on X-ray absorption spectroscopy was dismembered. The end of WWI had made Lund's function of scientific go-between between German and British physicists no longer needed, and the emigration of some of its own best scholars had deprived it of a large enough critical mass of people to develop this branch of science further. M. Siegbahn himself moved away to Uppsala, and brought with him A.E. Lindh, his latest brilliant pupil. During late 1923 he summarized twelve years of results – not only those attained at Lund by him and his students, but also those made elsewhere by others – in a book titled *Spektroskopie der Röntgenstrahlen* [22], which is the first book that ever appeared on this subject (1924). It was immediately translated into English [23], which was on the way of replacing German as the international language of science. In the same year 1924, M. Siegbahn was granted the Nobel Prize in physics “for his discoveries and research in the field of X-ray spectroscopy”: eventually, XAS had received its final acknowledgement as a significant branch of physical science, and the Nobel Prize granted to G. Hertz (together with J. Franck) in the following year, although officially for another type of research, put the final seal on it. It is indeed very strange that A. Sommerfeld [24,25] and W. Kossel [21], whose works had deserved such a prize just as well, never received the Nobel Prize: possibly, the reason is that they concentrated their efforts on the theory of XAS, and performed no experiments. Indeed, experiments were the requisites in Nobel's will, a requisite frequently forgotten or bypassed in the following years.

## 5. Discussion and conclusion

The search for the X-ray absorption spectrum had started with unsuccessful attempts mainly due to the far too weak sources used as well as, to a minor extent, to the photographic method of recording, which did not warrant adequately resolved results. Indeed, what Herweg, de Broglie, Rohmann, Wagner and other early researchers had been able to detect were the major absorption

discontinuities (lines or, later, edges), which correspond – albeit much weaker, and all shifted to lower wavelength – to the major emission lines, thus lending support to Kossel's first interpretation model. When the energy of the source increased, the photographic method of recording became better resolved (or, alternatively, the blackening in the photographic plates started being transferred to graphs plotting the extent of blackening versus distance from the major discontinuity or edge), it turned out that the discontinuities had a complex structure, consisting of several fine lines having different intensities; in other words, superimposed upon the major edge there were modulations, as Kossel had forecasted to be, when suggesting his model of electron removal from the various shells and transition to unoccupied state outside the atom. Indeed, XAS was born, and the first sure evidence of the newborn branch of physical science is dated, apparently, October 1, 1918. Furthermore, it was beginning to be felt that an atom absorption structure does not depend on the atom impinged by X-rays alone, but on a variety of reasons that are both internal to the atom (valence, chemical bond) and external to it (geometric relationships with the surrounding atoms, i.e., crystal structure). In later years, XAS developed to become a completely different science [26]: no longer the precise position of the edges, but the shape and modulations after the edges became its field of study.

Yet, to grow and keep gathering better and better insight into the structure of matter, XAS required X-rays of greater and greater energy and detection methods of higher resolution, and covering wider angles. Then the “secondary structure”, several hundreds of eV above the “fine structure” at the edge, was discovered and a new theory had to be developed: the “Kronig structures” joined the “Kossel structures”, and Ralph Kronig incorporated in his theory everything Kossel had theoretically developed, up to the change of paradigm imposed by the synchrotron and by Lytle's group new theoretical approach. Then, again, nothing was lost of both theories, but two branches developed independently: the EXAFS algorithms superseded Kronig's theoretical approach, and the XANES software packages superseded Kossel's simple theory.

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