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100 years of X-ray diffraction: from Röntgen's discovery to top-of-the-art synchrotron source applications

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The paper invites the reader to recall the 100 years long history of X-rays diffraction discovery, advancement and achievements with great impact on our daily life. Let us pay a tribute to the founders of X-ray diffraction and emphasize the importance of their work for our modern understanding of matter. Special honor has to be given to Max von Laue, who discovered in 1912 that X-rays are electromagnetic in nature, with wavelength short enough, to cause diffraction when passing through a periodic crystal medium. Shortly afterwards, the importance of his work was recognized and he received Nobel Prize two years later. Other distinguished researchers are Sir William Henry Bragg and William Lawrence Bragg, who were awarded a Nobel Prize in 1915 "for their services in the analysis of crystal structure by means of X-rays". Bulgarian history of X-ray diffraction analysis started around 1939, when Ivan Stranski and Rostislaw Kaishev performed the first experiments. One of the very first publications by Bulgarian authors on this topic belongs to Strashimir Dimitrov in collaboration with Kaishev.

At present, the X-ray diffraction is irreplaceable, unique method for structural investigation of inorganic and organic materials, biomolecules, including human DNA, nanocomposites and many others, especially after the development of more than 40 X-ray synchrotron sources worldwide.

Key words: X-ray diffraction history, Bulgarian X-rays science history.

INTRODUCTION

Since the discovery of X-rays not only the scientific community, but the entire society have recognized their importance for our daily life. X-rays are employed in structural investigation of inorganic and organic materials, for chemical elemental analysis and biological imaging.

Hundred years of X-ray diffraction analysis, is a good occasion to recall the people, whom we have to thank for our achievements today. The article invites the reader to recall the significant moments in the 100 years long history of advancement and achievements since the scientific discovery of X-rays diffraction.

Prehistory

Before dealing with the essentials of X-ray diffraction applications, let us recall the story of the X-ray discovery, marked with at least 5 related Nobel Prizes in a period of only 10 years.

The very first Nobel Prize, in the remote 1901, was awarded to Wilhelm Conrad Röntgen "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays, subsequently named after him" [1]. At the time of his discovery, Röntgen was appointed Professor at the University of Würzburg. His scientific interests since then were far from that field, but since the investigations on cathode rays were very new and modern, he decided to perform some experiments similar to those of Herz and Lenard. In the autumn of 1895 he assembled equipment, consisting of Ruhmkorff's coil and evacuated Lenard's tube covered with paperboard. What he observed amazed him [2]! In the dark room, a barium-platinum-cyanide screen, located 2 meters away from the equip-

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ment, was fluorescencing. Röntgen was famous for his diligence, so he closed the door of his lab and spent six weeks repeating and trying different experiments to convince himself that the observation came really from the experiment and is not a fiction. He even did not speak to his assistant or his wife, who started to worry about him.

The amount of work he performed in this period is indeed impressing! The first results were published as a short communication in the local scientific journal [3], where as a footnote to the main text Röntgen wrote *"for shortcut I would like to use the expression „rays" and more precisely, to make the difference with all other rays, I will use the name X-rays"*. The communication was sent as a Christmas present to almost 90 scientists all over the world and it actually became the Christmas present to the humanity as well.

The first communication was followed by a second one, issued a month later. There was only one more communication written by Röntgen on this topic, published a year later in Berlin [4]. So, the new X-rays were born and described in only 30 pages!

The main part of the experimental work of Röntgen aimed on proving the properties of the "agent", if it was really rays, if they differed from light and cathode rays and in which way. It has to be mentioned here, that he also tried to observe diffraction but did not succeed. His achievement had a profound effect. Researchers worldwide could experiment with X-rays as Röntgen refused to patent his findings, convinced that his inventions and discoveries belong to the entire world.

The next, very important person in our story is Charles Glover Barkla, who devoted his life to the investigations on X-rays. His extraordinary work, honored with Nobel Prize in 1917, is described on the Nobel Prize site as follows [1]: *"His discovery of homogeneous radiations characteristic of the elements showed that these elements had their characteristic line spectra in X-ray and he was the first to show that secondary emission is of two kinds, one consisting of X-rays scattered unchanged, and the other a fluorescent radiation peculiar to the particular substance. He discovered the polarization of X-rays, an experimental result of considerable importance for it meant that X-radiation could be regarded as similar to ordinary light. Barkla made valuable contributions to present knowledge on the absorption and photographic action of X-rays and his later work demonstrated the relation between the characteristic X-radiation and the corpuscular radiation accompanying it. He has also shown both the applicability and the limitation of the quantum theory in relation to Röntgen radiation ...Barkla's discovery of the characteristic X-radiation has proved to be a phenomenon of extraordinary importance as regards physical research, a fact which has been made increasingly manifest by the subsequent researches of other investigators..."*

Once upon a time in Munich

Now the time line goes to Munich, where Röntgen had moved to in the beginning of the 20th century. The scientific community there had good traditions. One of them was that every day professors and students were discussing modern scientific topics at the Café Hofgarten. Under discussion were crystallography, X-rays and their polarization, different new theories, ideas mostly inspired by the interests of the appointed at that time professors at the University of Munich and on the first place by professor Röntgen, of course.

On the second place – Professor Groth, who was the Director of the Institute of Crystallography. He used to invite famous crystallographers from all over the world, which gave the possibility to the students and professors for real and spontaneous transfer of knowledge and generation of new ideas. Although at that time some facts were already known, for instance the existence of 32 symmetry classes and 230 Space Groups, and the theory of "molécular intégrantes", according to which crystals were supposed to be a periodic arrangement of identical particles, crystallography was still rather a mathematical exercise. This was also the time when the theory of the atoms and their inner structure did not exist yet. Knowing this, Groth's great contribution can be highly appreciated. In 1876, he wrote "Physical crystallography", which became a leading book in Crystallography for decades [5]. The most famous book, written by him is "Chemical crystallography" (1906, in 5 volumes), where he classified crystal forms according to their chemical structure. This way he established for the first time the connection between physical shape and chemical nature of the crystals.

Another very important person in our story is professor Sommerfeld. At the time when Röngen invited him for the position of a Director of the Theoretical institute at the University of Munich, Sommerfeld's scientific interests had been connected with the theory of diffraction in the optical range. Curiously, Sommerfeld stated that his condition to accept the position was to have a laboratory with appropriate equipment for proving his theories. Professor Sommerfeld was easy going, charming and open person who soon became the center of all scientific meetings at the Café Hofgarten. About his extraordinary scientific capacity one could judge from the success of his students such as P. Debye, P. Ewald, W. Pauli, W. Heisenberg. All these students participated in the café and some of the students of Röntgen like P. Knipping, J. Brentano, R. Glocker, and Joffe can be added to this list.

All mentioned students are renowned scientists of course but we will pay special attention only to Paul Ewald (1888–1985). In one of his books Ewald wrote [6]: "*Towards the end of summer semester of 1910 the present author, Paul Ewald, had belonged to the group of students centered about Sommerfeld for about two years, and he felt that he could venture to ask his teacher to accept him as a doctorant.*"

Ewald chose a thesis problem with the working title "To find the optical properties of an anisotropic arrangement of isotropic resonators", the basic idea of which he explained as [6]: *"...If the same type resonators were placed in a lattice array, with perfect regularity but different distances along the three coordinate axes – would the dispersive and refractive properties of this medium be those of a crystal?"*

Almost ready, Ewald met some difficulties explaining his calculations. According to Munich university traditions, he asked the newly appointed assistant Max von Laue for help. Laue was actually the favorite student of Max Plank in Berlin, but he insisted to move to Munich and in 1909 he was appointed in the Theoretical institute under the supervision of Sommerfeld. Laue invited Ewald for a supper at home. They met (in late January 1912) and took a walk in the English Garden (near the University), where Ewald started explaining his problems. Ewald wrote [6] about this walk: *"Meanwhile they were entering the park, when Laue asked: "what is the distance between the resonators?". To this Ewald answered that it was very small compared to the wave-length of visible light, perhaps 1/500 or 1/1000 of the wave-length, but that an exact value could not be given because of the unknown nature of the "molecules integrantes" or "particles" of the structure theory; that, however, the exact distance was immaterial for his problem because it was sufficient to know that it was only a minute fraction of the wave-length."*

Let us now draw our attention to Laue and his point of view. In his Nobel Prize lecture he explained how much all professors at Munich University influenced him [1]: *"It turned to be a matter of great good fortune that Sommerfeld passed to me the article "Wellenoptik" at that time to work upon for the Encyclopedia of Mathematical Science. For it was during that object that I was obliged to seek a mathematical presentation of the lattice theory... On my arrival in Munich in 1909 my attention was drawn constantly – first owing to the influence of Röntgen's work at this University and subsequently by Sommerfeld's active interest in X-rays and γ-rays, which he had also testified in several works-back to the question of their actual nature ... it was Groth who expressed his defense of it (the space-lattices model), both orally and in writing, and I, also thus learned from him."* and then concluded [1]: *"Such was the state of affair as, one evening in February 1912, P.P. Ewald came to visit me... he was faced at that time with certain difficulties and came to me with a request for advice."*

Through the memories of Ewald [5] and Laue [1] one can reconstruct the remarkable conversation on that day. Laue said that during the conversation with Ewald in his mind was: *"...lattice spectra have to be ensued. The fact that the lattice constant in crystals is of an order of 10^{-8} cm was sufficiently known from the analogy with other interatomic distances in solid and liquid substances, and in addition, this could easily be argued from the density, molecular weight and the mass of the hydrogen atom which, just at that time, had been particularly well determined. The order of X-ray wavelengths was estimated by Wien and Sommerfeld at 10^{-9} cm, so ..."*

Ewald explained about the time after the supper: "*When this time came, he found Laue listening in a slightly distracted way. He again insisted on knowing the distance between the resonators and when he received the same answer as before, he asked: "what would happen if you assume very much shorter waves to travel in a crystal?"*..."

Ewald was on a hurry finishing his thesis, so he only copied the calculations to Laue. After finishing his PhD, Ewald got a job and forgot about this issue. However, the interest of Laue and respectively of the other scientists at Munich University continued. Meanwhile, Ewald continued working on X-rays and became later the father of the dynamic theory of the X-ray diffraction.

In 1912 during the Easter holydays, completely in accordance with the good university traditions, a group of professors, assistants and students were skiing in the Alps. During the vacation, Laue shared his idea with Sommerfeld, Wien and other scientists, but encountered a strong disbelief in a significant outcome of any diffraction experiment based on the regularity of the internal structure of crystals. On the other hand, Walter Friedrich, who was newly appointed as an experimental assistant in Sommerfeld's group, immediately expressed his willingness to carry out a relevant test. Also Paul Knipping, who had just finished his thesis in Röntgen's institute, volunteered for assisting in the experiment. Finally, the opinion prevailed that experiment was safer than theory and that since the diffraction experiment required no sophisticated set-up, it should at least be tried.

Friedrich and Knipping performed series of experiments with $CuSO_4$ and they had success when experimented on transmission. Visiting the scientific café, Laue was informed about that progress and was so excited that he even remembered the house, where he solved the equations. He wrote [1]: "*Only shortly before this, when writing an article for Enzyklopaedie der matematischen Wissenschaften, I had given the old theory of diffraction by an optical grating, which went back to Schwerd (1835), a new formulation in order that by applying the equation of the theory twice over, the theory of diffraction by a cross-grating could be obtained. I had only to write out this equation three times, corresponding to the three periodicities of the space lattice, so as to obtain the interpretation of the discovery. In particular the observed rings of rays could thus be related to the cones of rays demanded separately by each of the three conditions of constructive interference.*"

The last events happened in 1912. The results were then presented (8.06.1912) by Sommerfeld at the Bavarian Academy of Sciences. Meanwhile Laue delivered a lecture in Berlin, presenting the results to his former colleagues and the scientific society in Berlin. On his way back to Munich, Laue went to visit Professor Wien and introduced the recent achievements to the group there and a professor from Göttingen. The presentations were followed by publication of the significant results. The first publication was written by Friedrich, Knipping and Laue [7], followed by another one written by Laue [8]. These publications gave the birth of X-ray diffraction science. Shortly, the importance of Laue's work was recognized and he received the Nobel Prize in 1914 "*for his discovery of the diffraction of X-rays by crystals*" [1].

Practical application

The theory of Laue for the diffraction of X-rays by crystal lattice and its mathematical formulation was a ground breaking discovery a ground breaking discovery. However, as Professor Granqvist explained [1]: "*...calculating the crystal structures, from von Laue's formulae, was an exceedingly complicated one, in as much as not only the space lattices, but also the wavelengths and the intensity-distribution over the various wavelengths in the spectra of the X-rays, were unknown quantities.*"

This is the reason why Ewald defined [5] the beginning of the real X-ray diffraction analysis as follows: "*Crystal Structure Analysis began in November 1912 with the first papers of W. L. Bragg, then still student in Cambridge, in which, by analysis of the Laue diagrams of zink blende, he determined the correct lattice upon which the structure of this crystal is built. Soon afterwards he obtained the first complete structure determinations, namely of NaCl, KCl, KBr, KI, a series of alkali halides having similar structures. By this determination a scale for measuring of atomic distances in crystals and, simultaneously, of X-ray wave-lengths obtained.*"

The real progress was possible due to the subsequent discovery of W. L. Bragg, who found out that the phenomenon could be treated mathematically as a reflection by successive parallel planes that may be placed so as to pass through the lattice points, and that in this way the ratio between the wavelengths and the distances of the said planes from each other can be calculated by a simple formula from the angle of reflection [1]. The other very important event was that W.H. Bragg and W. L. Bragg constructed the first X-ray spectrometer, based on reflection principle, which admitted a definite, even though initially unknown, wavelength being made use of. Exactly this spectrometer allowed the Bragg's to gain the first, extremely important insights into the structure of crystals. The rays falling on the crystal were produced by X-ray tubes, platinum being at first used for the anticathode while consequently anticathodes were produced from palladium and rhodium. In order to take practical advantage of those different X-rays W. L. Bragg developed a method for calculating their intensity in the case of a complex space lattice.

If one has to summarize the contribution of the Bragg's to science, one has to mention that these two investigators determined the crystal structures of various materials, the wavelengths of the X-rays and the distances between the successive planes, placed with such exactitude, that the error, if any, is probably at most some few units per cent. Thanks to the methods that the Bragg, father and son, have devised for investigating crystal structures, an entirely new world has been opened and has already in part been explored with marvelous exactitude.

In recognition of the great practical importance of their method, the Nobel Prize in Physics in 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg "*for their services in the analysis of crystal structure by means of X-rays*".

Bulgarian contribution to X-ray diffraction science

In the book of Ewald, devoted to the 50 year anniversary of X-ray diffraction [5], the author makes a comprehensive review of historical developments in the field, pretending to cover all achievements over the world. Somehow the Balkan region is scarcely mentioned. He describes only an experiment on a mineral, employing the Debye method, performed in Yugoslavia in 1947. In the same text, Ewald admits that for countries like Romania and Bulgaria there is nothing to be said because of their isolation.

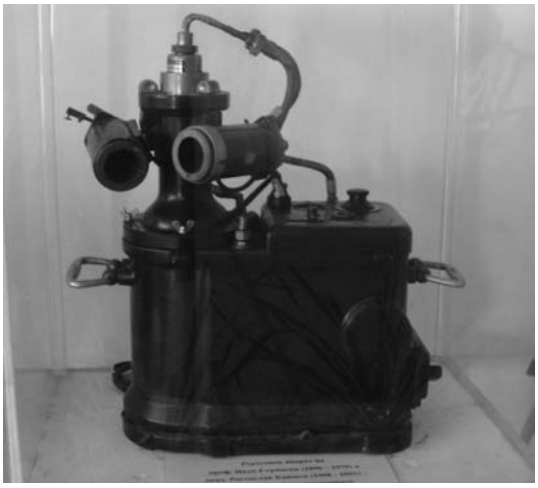

Fig. 1. First X-ray diffractometer, used for research purposes in Bulgaria

The very first experiments, performed in in Bulgaria, date back from the time before World War II. Bulgarian X-ray diffraction analysis is closely connected with one very prominent and distinguished scientist – Iwan Nicolá Stranski, who brought from abroad the first X-ray apparatus, made by the "Siemens" company (Fig. 1). At that time, Stranski was appointed professor at the Institute of Physical Chemistry, belonging to the Bulgarian Academy of Sciences.

Actually Iwan Nicolá Stranski [9] (Fig. 2) left a profound imprint on the world science record with his famous theory of crystal growth (theory of Kossel-Stranski) and he is the father of the Bulgarian school of physical chemistry. He studied chemistry and graduated in Sofia in 1922, but he got his doctorate in 1925 in Germany (at Physikalisch-chemische Institut of the University, Berlin). His doctoral research was devoted to X-ray spectroscopic analysis. He started his career as lecturer in Physical Chemistry at the Department of Physical Chemistry Sofia University in 1926, becoming the first teacher in physical chemistry in Bulgaria. In 1937 he was the first elected Professor there. In 1941 Stranski moved to Germany. During the years 1941–44 he was visiting professor at the University and the TH Breslau (now Wroclaw, Poland). In 1944 he became a scientific fellow of the Kaiser-Wilhelm-Institut für physikalische Chemie und Elektrochemie (Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry) in Dahlem, Berlin, becoming its associate director in 1953. The TU Berlin made him the successor to Max Volmer as professor of Physical Chemistry in 1946. He taught at the Free University of Berlin as an honorary professor until 1963. Two research institutes in Germany have been named after him: the Iwan N. Stranski Institute of the TU Berlin and the I. N. Stranski Institute for Metallurgy in Oberhausen.

Rostislaw Kaishev [10] (Fig. 2) was appointed as assistant to Stanski in 1933. Both are the co-founders of the contemporary theory of crystal nucleation and growth. They both were connected with Germany (Kaischew obtained his PhD in 1932 under the supervision of the famous F. Simon) and their fruitful cooperation continues also by working on the first X-ray diffraction experiments. In 1958 Kaischew became the founder of the Institute of Physical Chemistry, within the Bulgarian Academy

Iwan Stranski **Rostislaw Kaischew** **Strashimir Dimitrov**

Fig. 2. Bulgarian pioneers in X-ray diffraction analysis

of Sciences, named after him today, and held the position of director there until his retirement in 1989.

The first publication with Bulgarian contribution, devoted to X-ray diffraction experiments dated from 1939, on clay material, provided by Strashimir Dimitrov, and were performed by Kaischew. Dimitrov (Fig. 2) graduated in 1914 from Sofia University. He made a specialty of mineralogy and petrology in Heidelberg, Germany in 1927. His career is closely connected with Sofia University, where he became a professor in 1941. He was the Dean of the Department of mineralogy and petrography. In 1947 Dimitrov became one of the founders and director of the Geological Institute of BAS, named today after him. His great contribution to the Bulgarian science was recognized by naming a mineral after him (*Strashimirite* $Cu_8(AsO_4)_4(OH)_4{\cdot}5(H_2O)$).

Advancement and achievements

If one can use the Nobel Prizes as a measure of the recognition and significance of any scientific field, here is the place to state, that since 1901, more than 24 Nobel Prize holders belong to the family of researches, connected with X-ray diffraction [1]. Even the Nobel Prize in chemistry for 2012 is evidence of the great impact of the Laue's discovery on our daily life. Most of the recent progress is due to the development of synchrotron sources, starting in 1970. Nowadays there are more than 40 such sourced all over the world. Thanks to the extended possibilities, X-rays diffraction analysis is applied in biology, earth and environmental science, soft matter, polymers, complex and nanostructured materials sciences, in investigations of semiconductors, surfaces, and interfaces, in chemical dynamics, for ultrafast/time-resolved studies, etc. [11, 12].

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100 ГОДИНИ РЕНТГЕНОВА ДИФРАКЦИЯ: ОТ ОТКРИТИЕТО НА РЬОНТГЕН ДО МОДЕРНИТЕ ПРИЛОЖЕНИЯ НА СИНХРОТРОННИТЕ ИЗТОЧНИЦИ

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(Резюме)

Статията приканва читателя да проследи 100-годишната история от откриването на рентгеновите лъчи, напредъка и достиженията при тяхното използване и ефекта върху нашето ежедневие. Отдаваме почит на откривателите на рентгеновата дифракция и подчертаваме важността на техните усилия за съвременното ни познание при изследване на материята. Специално уважение трябва да отдадем на Макс фон Лауе, който през 1912 година установи, че рентгеновите лъчи са електромагнитни по природа с достатъчно къси дължини на вълните за да предизвикат дифракция, когато преминават през една периодична кристална среда. Скоро след това важността на неговата работа беше оценена високо и след две години той бе удостоен с Нобелова награда. В същата сфера работят и други авторитетни учени като Сър Уилиам Хенри Брег и Уилиам Лоуренсе Грег, които получават Нобелова награда през 1915 „за техния принос за анализ на кристални структури с рентгенови лъчи". В България стартирането на рентгено-дифракционния анализ води началото си от 1939 г., когато Иван Странски и Ростислав Каишев правят първите експерименти. Една от най-първите публикации от български автори по тази тема принадлежи на Страшимир Димитров в колаборация с Каишев. В днешно време рентгеновата дифракция е незаменим, уникален метод за структурни изследвания на неорганични и органични материали, биоматериали, включващи човешкото ДНК, нанокомпозити, особено стимулирани след разработването и пускане в действие на повече от 40 рентгенови синхротронни източника по света.