100-Year anniversary of X-ray crystallography

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1. International Year of Crystallography 2014

Solid materials in the crystalline state are characterized by a periodic structure, which acts as a diffraction grating at an atomic scale for incident X-rays. The famous experiment of X-ray diffraction, using a zinc-blende crystal, was suggested by Max von Laue at the University of Munich, Germany and was conducted by W. Friedrich and P. Knipping in 1912. The Nobel Prize in Physics was awarded to Max von Laue in 1914 for his discovery of the X-ray diffraction phenomena, which verified the wave nature of X-rays. Discovery of X-ray diffraction changed the field of mathematical crystallography in the 19th century to an experimental science.

X-ray crystal structure analysis is a reverse process of X-ray diffraction. Intensities at individual diffraction spots recorded on the surface of a detector in reciprocal space are converted into their frequencies, and then inversely Fourier transformed into the crystal structure in real space. The X-ray diffraction method provides us the information about the spatial arrangement of atoms in the crystal lattice together with precise data concerning interatomic distances and bond angles. The three-dimensional information and the highly quantitative nature of the data distinguish X-ray crystallography from other analytical sciences such as microscopy or spectroscopy.

A proposal for celebrating the 100-year anniversary of X-ray crystallography since the discovery of X-ray diffraction was approved at General Assembly of the United Nations, and the year 2014 was assigned as International Year of Crystallography 2014 (IYCr2014). It is our great pleasure that X-ray crystallography has been used as one of the most important tools for materials characterization for more than 100 years.

2. Crystal structure analysis toward more complex structures

A year after the discovery of X-ray diffraction, the crystal structure of NaCl was analyzed by W. L. Bragg[1]. It turned out to have a quite simple structure, having a face-centered cubic lattice. Fourier methods, first suggested by W. L. Bragg in 1929[2], were demonstrated to be efficient for determining more complex structures. Fourier series, used for calculating the electron density distribution function, is a sum of a number of sine and cosine terms. Hand calculation with patience for calculating Fourier series was relieved by the use of Beevers-Lipson strips in the 1930s–1950s[3].

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M. F. Perutz had chosen Haemoglobin as a research subject for his doctoral thesis in 1937 when the modern electronic computer was not available. It was 1960 that he reported a final result of the three-dimensional structure analysis of Haemoglobin[4]. Nowadays, structure analysis of small molecules can be achieved in minutes. Even for the crystal structure analysis of proteins, it can take roughly ten minutes for a moderate sized structure using a notebook PC and one week or more for more complex structures if the quality of diffraction data is of good quality. The improvement of computing performance contributes to shorten the time required for the data analysis, and it has been a rate-determining factor in the development of X-ray crystallography as well as in other fields of the science. Nowadays, the standard procedure of single crystal structure analysis is considered as an established technique, and it is used almost routinely as a tool at every laboratory. People, who are interested in the investigation of materials themselves, can easily learn the technique due to today's easy to use software and intuitive graphical interfaces.

3. The advent of modern powder diffraction method

Some people are more interested in the development of tools rather than materials investigation. In the early days of the modern powder diffraction method, a common was problem that single crystals with adequate volume size for the diffraction experiment were difficult to obtain, in particular, for neutron powder diffraction. The powder diffraction method was the only means for the structure analysis of crystals with micro-meter size, although it was considered to be much less reliable compared to the single crystal diffraction method. However, many crystallographers as well as mathematicians and physicists were enthusiastic about solving and refining crystal structures under difficult conditions, that is to use one-dimensionally collapsed diffraction data from the powder specimen. Evolution of the modern powder diffraction method had been started by "a small step", which changed from using integrated intensities as the observed data and instead to use the profile intensities as described by H. M. Rietveld in his retrospect[5].

In the late 1960s, the Rietveld method was first proposed as a technique of crystal structure refinement using neutron powder diffraction data[6]. In the late 1970s, it became more widely known by people after it was applied to structure refinement using X-ray powder diffraction data[7],[8]. The proposal by G. S. Pawley[9]

in 1981 would also be a key step, which enabled the decomposition of a powder diffraction pattern into individual Bragg reflection components by least-squares fitting of the whole-powder-diffraction pattern. Once the integrated intensity dataset could be obtained with the Pawley method, it would be quite natural to use it for the crystal structure determination by direct methods in the manner similar to the single crystal technique. In the whole-powder-pattern decomposition, however, severely or intrinsically overlapping reflections remain undecomposed, and the degree of overlapping is generally higher for the powder diffraction patterns of organic materials. Global optimization techniques such as the Monte Carlo method, simulated annealing, genetic algorithms[10] were introduced in 1990s, and these techniques once again enabled researchers to solve crystal structures without decomposing the diffraction pattern. These methods are called "direct-space methods" in opposition to direct methods in "reciprocal-space approach". Charge flipping[11] proposed in the 2000s is the method, which travels between reciprocal and direct spaces.

4. Promotion of scientific activities

Setting the table is also an important issue for the promotion of science. The IUCr Commission on Powder Diffraction (CPD) was established when the Congress and General Assembly of IUCr were held in Perth, Australia in 1987. It first organized a Workshop on the Rietveld method at Reactor Centrum Netherland in Petten, Netherlands in 1989. Then the European powder Diffraction Conference was organized, the first meeting of which was held in Munich in 1991. Many schools and workshops, co-sponsored by local committees and CPD were successively held all over the world for learning these new techniques. Knowledge and computer software of Rietveld refinement and related methods were gradually spreading from university professors and students to materials researchers in private companies. Today, the powder diffraction methods, derived from the Rietveld method, are widely used not only for scientific research but also for industrial purposes such as quality control on production lines.

Hardware and software developments are another factor supporting the promotion of scientific activities. Powder diffraction using synchrotron radiation produces higher resolution and thus less overlapping peaks. High quality synchrotron radiation data also stimulated the improvements of laboratory systems: one example is the use of high flux and brilliant X-ray sources, coupled with graded multi-layer optics for beam-tailoring and the other is the development of fast one- and two-dimensional detectors. Developments of mathematical tools for data analysis could not be achieved without the improved performance of computers, and wide spread use of these techniques with low cost/high performance PCs. From the 1960s to 1980s, researchers used mainframe computers, and they could only have the chance of crystallographic computation a few times a day when punched cards were used as storage media. Nowadays, people can incessantly manipulate the PC for the data analysis at his/her own desk.

5. Accumulated knowledge and experiences in crystallography

The modern analysis system of X-ray crystallography is built on the bases, each of which consists of accumulated results of scientific research and hardware-software developments during a century. As we understand, the diffractometer used for intensity data collection is a complex system, consisting of X-ray generator, the multi-layer optics, the detectors, goniometers etc. Behind the hardware, software is always working for system control. After the intensity data collection, data processing software begins to work for data correction, and after that the data are transferred to the data analysis software. Mathematical functions are used for subtracting background intensities and modeling the diffraction profile in extracting integrated intensities. Intensity formulae used for the data correction are based on kinematical and dynamical diffraction theories. Mathematical crystallography defines crystal system and crystallographic symmetry at the beginning of the crystal structure determination, and various algorithms are used for structure solution and refinement.

Now X-ray crystallography looks like a complex of tall buildings. The single crystal building is consolidated, consisting of two main parts of small and macro molecules. The powder diffraction building has a long tradition. But in the neighborhood, the building of modern powder diffraction has been constructed for more than 40 years. A nano material building is under construction, one of the columns of which is the classical pair distribution function based on the Debye equation[12] proposed 100 years ago. Some buildings are renewed by introducing new techniques as in the case of the whole-pattern-fitting technique for microstructural analysis. Someone can go up to the top of the building with an elevator, but he/she will lose the chance to see and grasp a whole view of the building. Of course, it is practically impossible for him/her to visit every room. Knowledge of basic theories, used for the analysis, is, however, very important and required for understanding and properly evaluating results of analysis. It will also be necessary to create new tools and to participate in new building construction. It may be unfortunate for X-ray crystallography if the chance of studying X-ray crystallography is decreased at universities.

6. Mission of Rigaku Corporation

Rigaku Corporation (RC), established with the name Rigaku-Denki Corporation in 1951, celebrated its 60-year anniversary three years ago. Yoshihiro Shimura, a founder of RC, had been engaged in X-ray analysis since the time of World War II when he was studying at the university. After the war when he had to determine his career, it was natural for him to be deeply interested

with the fabrication of X-ray analytical instruments. It was his experience at that time that X-ray analysis techniques were used for very important subjects of studies. X-ray analytical instruments were, however, not easy to use, and moreover, their performance was not high enough to obtain the best observed data. These concerns in his mind bore fruit in the form of his first commercialized XRD instrument with an automatic-recording function.

Hikaru Shimura, a successor to the former president Y. Shimura, followed his father's philosophy. He also focused on the development of basic technologies in order to meet the requirements of a higher intensity X-ray beam, more sensitive detection of X-ray, faster data acquisition and data analysis for advanced studies of materials. Some basic technological elements of RC are the rotating anode X-ray generator, graded multi-layer optics for parallel and convergent X-ray beams, imaging plate, CCD, one-dimensional strip detector, two-dimensional hybrid pixel detector, high-precision goniometers etc. Rigaku continues to develop higher performance hardware and software by incorporating advanced scientific research results in X-ray crystallography into the products. It is our mission to produce X-ray analytical instruments, which are more useful and easier to handle to help advance X-ray crystallography.

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