One Day at Crystallography

September 25th, 2014

Tirana, Albania
One Hundred Years of Crystallography

Aldo F. Craievich
Institute of Physics, University of Sao Paulo, Brazil, craievich@if.usp.br

In April 1912, the physicist Max von Laue, with the collaboration of Walter Friedrich y Paul Knipping, discovered the effect of diffraction of X-rays by a crystal of copper sulphate. The results of this experiment evidenced simultaneously (i) the undulatory characteristics of X-rays - consisting of electromagnetic waves such as visible light but with much shorter wavelengths - and (ii) the periodic nature of crystalline structures composed of atoms with inter-atomic distances comparable to the wavelength of X-rays. Two years later, in 1914, William Henry and William Lawrence Bragg (father and son) determined the first structure of a crystalline material (sodium chloride) by means of X-ray diffraction. For these important discoveries, von Laue and the Bragg's received the Nobel Prize in Physics in 1914 and 1915, respectively. Later on the structures of many other crystals and more complex materials were determined by means of the same technique, thus allowing for a better understanding of their properties. Crystallographers have also significantly contributed to the discovery of a number of novel materials with many important applications to industry and medicine.

The first determination of an atomic structure using X-ray diffraction in 1914 is considered to be the initial milestone of Crystallography, which was from then continuously developing until now-days. Among many important achievements in the research field of Crystallography during the last 100 years, a few of them, listed below, were selected and will be briefly described:
-First use of the small-angle X-ray scattering technique, by André Guinier, in 1939, which explained the observed variations in mechanical properties of aluminium alloys, of paramount importance for aeronautical industry.
-Determination of the structure of the deoxyribonucleic acid (DNA), a nucleic acid that carries the genetic information in the cells and is capable of self-replication, by Francis Crick, James Watson and Maurice Wilkinson (1962 Nobel laureates in Medicine).
-Discovery and physical characterization of graphene, which consists of a two-dimensional graphite single layer, by Andre Geim and Konstantin Novoselov (2010 Nobel laureates in Physics).

This presentation will also describe the main features of the X-ray sources used in X-ray diffraction experiments over the last 100 years: (i) X-ray generators equipped with Coolidge tubes, in operation from 1915 and still been used nowadays in many laboratories of physics, chemistry, biology and geology, among others, (ii) high intensity synchrotron-based X-ray beam lines, in most cases installed at national laboratories, from 1970 circa, and (iii) X-ray lasers that yield very short photon pulses, only available nowadays in a few laboratories around the world, which allowed for, in 2011, the first determination of a (extremely short) time resolved atomic structure of a protein nanocrystal.

After a century lasted from the first determination of an atomic structure in 1914, 2014 was declared by UNESCO to be the International Year of Crystallography. In order to commemorate this centennial, the International Union of Crystallography is organizing many activities (workshops, schools, talks, competitions, etc), at different levels and open to scientists, students and other interested people. The whole program of events to be held all around the world is available at the www.iycr2014.org webpage.
Basic Aspects of Crystallography

Aldo F. Craievich
Institute of Physics, University of Sao Paulo, Brazil, craievich@if.usp.br

This presentation describes (i) the relevant features of the structures of different types of materials, and (ii) the basic theory of X-ray diffraction and scattering applied to the determination of the structure of materials. The talk will include the following topics:


Experimental instruments: Single crystal and powder X-ray diffractometers, and small-angle scattering and reflectivity setups.
The phase problem is notorious in x-ray crystallography. The x-ray detector can only record intensities but not phases of the electromagnetic waves. Each reflection on the diffraction pattern or structure factor corresponds to a wave consisting of an amplitude and a phase. The amplitude is easily calculated by taking the square root of the intensity, but the phase is lost during the data collection. However, the phases contain vital information for the determination of the electron density distribution in the crystal.

Crystal structure determination, especially for macromolecules, via X-ray crystallography is still a complicated multi-step process which involves the availability of different types of data (e.g., diffraction data at atomic resolution, or isomorphous derivative data, or data affected by anomalous dispersion effects, or a molecular model suitable for molecular replacement), and the combination of different tools (e.g., density modification techniques, efficient crystallographic FFT routines, same probabilistic approaches for substructure determination and for subsequent phase extension, restrained least squares procedures). There is a large ensemble of programs which are in use of the crystallographic community: their combinations into integrated program packages (e.g., AUTO-RICKSHAW (Panjikar et al., 2005; AUTOSHARP (Blanc et al., 2000), BnP (Weeks et al., 2001), CCP4i (Potterton et al., 2003), SOLVE-RESOLVE (Terwilliger, 2000)) have considerably advanced the automation and reduced the human intervention in the structure determination process.

Crystal structure determination: the road map
The interpretation of powder diffraction pattern is not straightforward: peaks corresponding to different diffraction effects systematically and/or casually overlap; the background is often difficult to be evaluated; the non-random distribution of crystallites can produce preferred orientation effect. As a consequence, the experimental diffraction intensity cannot be accurately estimated. This problem limits all the steps of the structure solution process [1].

Up to twenty-five years ago, the role of powder diffraction was relegated to studies of qualitative and quantitative analysis. Nowadays powder technique is widely adopted for the characterization of new materials: organic, inorganic, metallorganic, biological, pharmaceutical. Such a progress depends on the advances in computing power and experimental equipment as well as the development of innovative theories, methodologies and computing programs aiming at overcoming the typical problems of powder solution: peak overlap, background estimate, preferred orientation occurrence. The scope of modern research in powder diffraction is to attain structure solution in a way as possible as automatic, efficient and fast. In spite of great improvement, powder solution is still a challenge.

EXPO2013 is a well-known computer program devoted to structure solution of small molecules by powder diffraction data and able to automatically perform [2]:

a) cell parameters determination;

b) space group identification;

c) extraction of the integrated diffraction intensities from the experimental profile and structure solution working in the reciprocal space;

Direct Methods are applied for solving the phase problem and providing the electron density map chemically interpreted. Then the optimization of the map, by using procedures combining Fourier transform calculations and weighted least squares, is carried out.

d) structure solution working in the direct space;

The solution in direct space (effective in case of organic compound) can be alternatively applied to the solution in reciprocal space, in particular when the quality of the experimental data and/or the structure complexity prevent for estimating reliably the integrated intensities extracted from the experimental profile. In this case, a casual structure model (compatible with the expected molecular geometry) is considered and driven towards the correct solution by Simulated Annealing based technique.

e) crystal structure refinement by the Rietveld method.

The main solution strategies of EXPO2013 and examples of successful structure solutions are reported.

Crystallography applied in mineralogical sciences
Dr. Francesco Capitelli, CNR-IC, Rome, Italy. francesco.capitelli@ic.cnr.it

In the present topic, after a short introduction on the multidisciplinarity of the crystallography in the actual scientific context, the role of single crystal diffraction in geology and in particular in mineralogy is discussed, highlighting the contributions from other techniques, such as X-ray powder diffraction and vibrational spectroscopy (IR and Raman), and starting from micro-chemical analyses, in order to explain how does a structure solution of a natural phase works, illustrating some possible fall-out on (isostructural) synthetic compounds with applicative interests, and presenting some examples of minerals (natural phosphates and borates) solved and published in the last years.

X-ray microscopy with small/wide X-ray scattering (SAXS-WAXS) contrast.
Dr. Davide Altamura, CNR-IC, Bari, Italy. davide.altamura@ic.cnr.it

The emergence of ultra-brilliant synchrotron photon sources and efficient x-ray focusing optics (mainly Kirkpatrick-Baez, mirrors, zone plates, and compound refractive optics) have opened unprecedented opportunities in microscopy techniques, based on hard X-rays, to analyze solid, soft and liquid matter. Although synchrotron light sources are unique for brilliance and available beam spot to investigate the structure of matter, the advent of novel superbright laboratory X-ray microsources allowed the development of laboratory facilities, showing relevant potentialities for a detailed material analyses in ex-situ experiments [1,2,3]. Indeed, such micro-sources, used in combination with X-ray scattering techniques (Small and Wide Angle X-ray scattering (SAXS/WAXS)), proved to be efficient in probing matter at different length scales providing a structural, microstructural and morphological characterization of the specimens in a non-invasive way, with nanometer (SAXS) and atomic (WAXS) resolution.
Here a brief introduction to the scanning diffractive microscopy with SAXS/WAXS contrast will be given along with relevant examples in biomedical science:
- residues of exosomes’ drops from healthy epithelial colon cell line and colorectal cancer cells [4]
- collagen/human elastin artificial scaffolds developed for vascular tissue engineering applications [5]
- coxarthrosis-affected bone biopsies taken from patients, aged 62–87 years, during hip prosthesis implant surgery [6]

5. Sibillano T., De Caro L., Altamura D., Siliqi D., Ramella M., Boccafoschi F., Tirinato L., di Fabrizio E. and Giannini C., Small angle X-ray scattering – an unveiling tool for diagnostics in nanomedicine (submitted)

FIGURE: COXARTHROSIS-AFFECTED BONE BIOPSY: (a) Two-dimensional scanning SAXS data, with each pixel containing a two-dimensional SAXS frame. (b) An azimuthally integrated SAXS profile, with a zoom on the first meridional reflection of collagen in the inset. (c) An azimuthally integrated WAXS profile, with a zoom of the 002 and 210 reflections of HA in the inset. (d) Two-dimensional SAXS microscopy mapping the first meridional reflection of. (e) Two-dimensional WAXS microscopy mapping the 002 peak of the HA component; (f) Two-dimensional WAXS microscopy mapping the 210 peak of the HA component. The scale bar length in the microscopy images is 1 mm. The color wheel designates the SAXS orientation for each pixel of the maps in (d), (e) and (f). Reprinted from C. Giannini et al, J. Appl. Cryst. 47 110-17 (2014)

Atomic Resolution Electron Microscopy Methods in the Study of Inorganic Matter

Elvio Carlino
Center for Electron Microscopy IOM-CNR Laboratorio TASC
Area Science Park Basovizza Bld.MM-34149 Trieste-Italy

Transmission electron microscopy (TEM) enables to obtain atomic resolution information on specimen morphology, crystal structure, chemistry, electronic structure and magnetic properties. Furthermore, as the electron probe can be focused on sub-Ångström areas, it enables to achieve information from extremely small volume of a specimen. The features of TEM equipment enable to obtain at the same time images and diffraction patterns of the specimen, tuning the illumination condition and the experiment geometry to highlight the features to be studied [figure 1].
The combination of electron diffraction and atomic resolution electron microscopy, allowing the measurement of diffracted intensities but also phases, combined with crystallographic oriented methods results in electron crystallography, which represents a powerful and fascinating tool for structure analysis. Here we will show some examples of how electron diffraction obtained in different electron optical geometries can be used to study the crystal structure. Moreover we will show how electron diffraction and atomic resolution phase contrast electron images can be used in synergy to achieve detailed crystallographic information on single nano-particles of inorganic materials shedding light also on the crystallography of disordered, partially disordered or defective material systems.