MILESTONES

MILESTONE 4

A new crystallography is born

The adrenaline rush accompanying the thrill of a scientific discovery was palpable in the summer of 1913 in the laboratory of William Henry Bragg in Leeds, UK. "It was a glorious time, when we worked far into every night with new worlds unfolding before us in the silent laboratory," recalls his son William Lawrence Bragg. In rapid succession, father and son solved the structures of several inorganic crystals and of diamond. Underpinning this flurry of activity was the intuition that X-rays were reflected from planes of atoms in crystals and the discovery of Bragg's law (Milestone 3). Also crucial was the development of an X-ray spectrometer.

W. H. Bragg, in his 50s at the time of von Laue's experiment (Milestone 2), had already been working on X-rays for several years and had become a master in handling X-ray tubes and ionization chambers. Although these pieces of equipment were extremely delicate to work with, he managed to assemble an instrument that became an essential tool for the nascent technique of X-ray crystallography. It was developed from an optical spectrometer, in which the diffraction element was replaced by the crystal under study. X-rays emanating from a tube were collimated to the sample and the reflected radiation was collected in an ionization chamber with a gold-leaf electroscope. The main difference of this design with respect to von Laue's photographic plate set-up was that the X-rays were measured in reflection rather than in transmission - a key advance that followed the discovery of specular reflection of X-rays from mica in 1912. This geometry gave the Braggs the flexibility to detect the reflected X-rays for different angles of incidence one at the time, and single out individual angles of reflection from the layers of atoms in the crystal. Using Bragg's law, the crystal structure of the sample could then be derived.

In the beginning, assigning a structure was largely a matter of imagining atoms in space; those that could be solved were the simplest ones, mostly limited to face-centred cubic crystals. Nevertheless, at a time in which even the notion of an ionic crystal was not well established, the structural characterization of a salt as simple as NaCl was of major significance. Perhaps the most striking demonstration of the power of the new analysis was the determination of the structure of diamond, which conclusively confirmed the tetravalency of carbon, as postulated for many organic compounds.

Bragg's X-ray spectrometer required fairly large crystals, often only accessible through the goodwill of mineralogist friends. In 1916–1917, however, Paul Debye, Paul Sherrer and, independently,



The X-ray spectrometer built by W. H. Bragg.

Alfred Hull showed that powder (polycrystalline) samples also diffracted X-rays, opening up X-ray analysis to many more types of crystal. Experiments with powders were conceived from the idea that the diffraction of X-rays was due to their interaction with the electrons of the atoms in the lattice. Because, according to the Bohr model, electrons are in a defined spatial location relative to the nucleus, diffraction should also occur in randomly oriented crystals (a coherent theory behind this phenomenon would be due to Arthur Compton). An important upshot of this insight was that powder diffraction spectra provided a means to directly compare scattered intensities coming from all crystal planes, something that was not possible using the Bragg spectrometer.

As more and more crystal types could be measured, the complexity of the data analysis increased. Already in 1915, W. H. Bragg had proposed to use Fourier transform to convert the two-dimensional crystallographic patterns obtained at different angles into a three-dimensional map of electron density, an idea that greatly assisted the blossoming of powder diffraction experiments (Milestone 15).

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