CHAPTER 24

Schools of X-ray Structural Analysis in the Soviet Union

by A. V. Shubnikov

The discovery of X-ray diffraction coincided with the centennial celebration of the eviction of Napoleon from Russia. The Czarist government attempted to use this day for boosting the patriotic spirit of the people, but without much success. In 1911 a mood of opposition prevailed among students and professors which was brought about by mass discharges of students and professors from universities, the closing of a series of departments at universities, and other measures taken by the Minister of Public Education, L. A. Kasso. Among the creative workers in the field of crystallography who left the Moscow University were V. I. Vernadskii, A. E. Fersman, Ia. V. Samoilov, and G. V. Wulf. At that time I was finishing my studies at the Moscow (State) University, working under the guidance of G. V. Wulf on a paper on the symmetry of $K_2Cr_2O_7$ crystals, and at the same time acting as the unofficial assistant of my teacher at the Peoples' City University. The further research and teaching activities of G. V. Wulf continued at this Peoples' University, organized with great difficulties from private means in Moscow in 1908. A year before the described incidents in Moscow the well-known Russian crystallographer E. S. Fedorov, the Director of the Mining Institute in Petersburg named for Empress Catherine II, was discharged from his post (approval not granted by Minister Timashev after a second election by the Scientific Council of the Institute). This was the general picture of the political circumstances which befell Russian crystallographers in the year of Laue's magnificent discovery.

Despite the extremely unfavourable circumstances for the flourishing of the Sciences which prevailed in Czarist Russia at the beginning of the 20th century, crystallography in this country was developed to a rather high level. This was evidenced by the fact that at the time of Laue's discovery, a series of original textbooks had been written for the

teaching of crystallography at higher schools. Research in the field of crystallography underwent intensive development and was concentrated around two schools: the Petersburg school, headed by Fedorov at the Mining Institute, and the Moscow School, headed by Wulf at the Peoples' University. Their many similarities notwithstanding, these two schools essentially differed from each other in the purpose, the method, and the role of crystallography in the development of Natural Sciences.

In his renowned courses of crystallography, Fedorov treated crystallography as the 'base of all sciences of inorganic nature'. He placed theoretical crystallography 'on the same level with the most precise of the existing sciences'. Fedorov was of the opinion that theoretical crystallography could be built up, 'without the risk of even the smallest conflict with experimental data', from the 'initial experimental state of crystallography' and the 'immutable fact', which was that 'all particles of a crystalline substance are identical and arranged in parallel positions', that these particles—'crystalline molecules'—taken as a whole 'completely fill space', and that the 'parallelohedra should be considered as portions of space, belonging to separate crystalline molecules'. It is interesting to note that Fedorov remained faithful to this 'basic law' even after the completion of the space-group derivation (1900) which clearly indicated that a non-parallel arrangement of identical particles was possible. It should be added that Fedorov did not follow up his conclusion because he assumed that crystals belonging to asymmorphic groups could not exist in nature. His *Brief Course of Crystallography*, published ten years after the derivation of the space groups, does not even mention these groups.

My teacher Wulf held different views of crystallography. In contrast to Fedorov who over-estimated crystallography, considering it as the 'base of all sciences of inorganic nature', Wulf under-estimated crystallography, which, in his opinion was simply a 'chapter in physics', 'did not deserve to be called a separate science'. Combining forces with physicists (Voigt), Wulf identified crystallography with the 'study of a solid as a certain *medium*'. In this Wulf definitely set himself apart from mineralogists who, until recently, considered a crystal as an '*individual of inorganic nature*'. Wulf was disturbed because the idea of crystallography as a part of physics did not find unanimous acceptance; for this reason, our university does not include crystallography in its physics course.

Von Laue's discovery left very deep impressions on the two schools of

crystallography in Russia and brought with it different reactions from the leaders of these schools.

When the news of the discovery of X-ray diffraction reached Wulf, he immediately expressed his desire to work in this field. Studying von Laue's equations to the very end, Wulf derived from them the relationship

$$\frac{\lambda}{2} = \frac{\Delta\varepsilon}{m},$$

which is of identical meaning with Bragg's well-known formula

$$n\lambda = 2d \sin\theta$$

The paper was published in *Phys. Zs.* 1913, *14*, 217. All of Wulf's further scientific work was largely determined by von Laue's discovery. In 1916 Wulf translated into Russian the book by W. H. and W. L. Bragg—*X-rays and Crystal Structure.*

Fedorov's reaction to Laue's discovery was quite different. Evaluating correctly the 'change brought about in crystallography by the application of X-rays to the study of crystals', Fedorov could not overlook the fact that new experimental data of the structures of diamond, rocksalt, and other crystals refuted the 'unalterable fact' (the unfailingly parallel distribution of identical particles in a crystal), which is contained in the 'basic law'. Compelled to acknowledge that 'under no circumstances can crystals be considered as simple space lattices of particles', Fedorov nevertheless attempted in various ways to change this law, but without success. Fedorov passed away in 1919, in Leningrad.

Fedorov's students at the Leningrad Mining Institute attempted to organize experimental research in the field of X-ray structural analysis. However, the difficult post-war days seriously impeded these attempts. Somewhat more favourable conditions existed in Moscow, where Wulf was in charge of studies by means of X-ray diffraction. It must be emphasized, however, that this work in Leningrad as well as in Moscow developed extremely slowly. It need be said only that until the death of Wulf (in 1925), the crystal structure of only one substance ($NaClO_3$) had been studied in our country, by Wulf himself. The next twenty years could be characterized also as a preparatory period for serious experimental research in the field of X-ray structural analysis.

The research in this field underwent an intensive development only after World War II and was localized in certain research centres in Moscow: the Institute of Crystallography of the Academy of Sciences,

USSR, under the supervision of N. V. Belov; the L. Ia. Karpov Physico-Chemical Institute, under the supervision of G. S. Zhdanov; the Institute of General and Inorganic Chemistry of the Academy of Sciences, USSR, and the Moscow University, under the supervision of G. B. Bokij; and the Institute of Organic Chemistry of the Academy of Sciences, USSR, under the supervision of A. I. Kitaigorodskii.

Belov devoted his studies to the structure of silicates. In collaboration with his numerous students Belov succeeded in deciphering a whole series of very complex silicate structures (ilvaite, epidote, zoisite, cuspidine, xonotlite, wollastonite, gadolinite, seidoserite, lovenite, lovoserite, epididymite, rhodonite, and hillebrandite). 'Direct' methods of X-ray structural analysis were, and still are, developing parallel to the experimental research in Belov's school. The complex methods of structural calculations are now carried out by machines. Belov is now rightfully accepted as the leading figure in the field of structural crystallography in our country and an outstanding expert of space groups.

Zhdanov is known here as the author of the first textbook on X-ray analysis. At the beginning of his independent scientific activities, Zhdanov had a somewhat limited choice in the selection of substances for his studies which had to be in the field of interest of the Karpov Institute. This resulted in studies of the crystal structures of a series of inorganic compounds (carbides, cyanides, rhodanides, borides, oxides), and organic substances (nitro and halogen derivatives of naphthalene and benzene, organometallic substances, and organic dyes). At the present time Zhdanov is interested in crystals with special physical properties (ferroelectrics, piezoelectrics, superconductors, and others). This research is being conducted at the Department of Solid State Physics of the Moscow University.

Bokij chose complex compounds as the object of his crystal chemical investigations. A new group of complex compounds with multiple bonds (within the molecule) was discovered and investigated recently. The crystal chemical theory of daltonides and bertolides was formulated. The Department of Crystallography and Crystal Chemistry was organized by Bokij under the Geological Faculty of the Moscow University. His scientific work has been conducted primarily at the Institute of General and Inorganic Chemistry of the Academy of Sciences, USSR. Bokij is the author of the book *Crystal Chemistry* (1960), and editor of the *Journal of Structural Chemistry*, in the founding of which he has been instrumental. Among Bokij's numerous students, M. A. Porai-Koshits deserves special mention.

Organic crystal chemistry is the speciality of A. I. Kitaigorodskii. The underlying idea of this science, according to the author, is the close-packing of nonspherical particles—molecules—, i.e. arrangements of molecules such that the 'protrusions' of one molecule fit into the 'depressions' of the other. This idea is developed in detail by A. I. Kitaigorodskii in his book, *Organic Crystal Chemistry* (1955), and is substantiated in studies by the author and his students and by thorough investigations of the structures of organic crystals according to data available in literature. Kitaigorodskii is known here as the author of basic textbooks on X-ray structural analysis.