CHAPTER 19

The New Crystallography in France

by J. Wyart

19.1. The Period before August 1914

At the time of Laue's discovery, research in crystallography was carried on in France principally in two laboratories, those of Georges Friedel and of Frédéric Wallerant, at the School of Mines in St. Étienne and at the Sorbonne in Paris, respectively. Jacques Curie, it is true, also investigated crystals in his laboratory and, together with his brother Pierre, discovered piezoelectricity which soon found extensive application in the measurement of radioactivity; but he had few students and formed no school. Among the research of Georges Friedel that on twinning is universally known and accepted, as are his studies of face development in relation to the lattice underlying the crystal structure. Frédéric Wallerant's best known work was on polymorphism and on crystalline texture. In 1912 both Friedel and Wallerant were deeply interested in the study of liquid crystals, a form of aggregation of matter only recently discovered by the physicist in Karlsruhe, O. Lehmann. Friedel's co-worker was François Grandjean, Wallerant's Charles Mauguin. Laue, Friedrich and Knipping's publication immediately drew their attention, and Laue's remark that the diagrams did not disclose the hemihedral symmetry of zincblende prompted Georges Friedel to clarify, 2 June 1913, the connection between the symmetries of the crystal and the diffraction pattern. If the passage of X-rays, like that of light, implies a centre of symmetry, i.e. if nothing distinguishes propagation in a direction AB from that along BA, then X-ray diffraction cannot reveal the lack of centrosymmetry in a crystal, and a right-hand quartz produces the same pattern as a left-hand one. This remark is well-known among crystallographers as Friedel's Law, and its more thorough proof has given rise to a fair number of theoretical papers throughout the years. Though usually true, Friedel's Law does not hold generally, even for non-absorbing

crystals. But this does not impair the usefulness of the 11 classes of 'Laue symmetry' which Friedel enumerated.

Neither Friedel nor Wallerant had equipment for working with X-rays at their disposal. So it came about that in the hectic 1913/14 pre-war period Maurice de Broglie was the first in France to obtain X-ray diffraction. He was working in the laboratory of Paul Langevin at the Collège de France on the ionization of gases, so that he was well acquainted with the required technique. In his first communication to the Academy of Sciences (31 March 1913) de Broglie reports on results he obtained by the Laue-Friedrich-Knipping method with cubic crystals (ZnS, CaF_2, NaCl, magnetite). He studied the influence of temperature by cooling the crystals to liquid nitrogen temperature, and of magnetic fields (up to 10^4 gauss) in the case of magnetite. He finds that cooling neither increases the number of diffracted spots, nor sharpens them; that the magnetic field at right angles to the primary beam (which has the direction of a ternary symmetry axis) does not destroy the crystal symmetry; and incidentally, that the secondary rays which produce the diffracted spots, are not deflected by the magnetic field, as they would be were they electron beams.

In the following three months de Broglie continued using the Laue method and photographic recording; striations appearing in the diffracted spots were at that time under discussion both by de Broglie and others (Barkla, Hupka), because it was not clear whether they were to be explained as further diffraction fringes or as produced by irregular growth of the crystal.

De Broglie's first fundamental contribution came in his two notes of November and December 1913 introducing the rotating crystal method; this soon became one of the most useful methods for X-ray spectroscopy as well as crystal structure analysis. The first note announces a provisional camera in which the crystal was mounted on the drum of a recording barometer which gave it a rotation of 2° per hour. Evidently the clockwork was not running smoothly enough, for a number of lines appeared which had not been registered by W. H. Bragg or Moseley and Darwin. A double film technique was used for distinguishing by absorption between coincident first and higher order lines. In the second note successful double-sided registrations of the platinum and tungsten spectra are recorded, obtained on a variety of crystals. On rocksalt complete spectra were registered inside 15 minutes. An interesting remark in this paper is that the effect of temperature on the diffracted intensity depends on the order and not on the angle of diffraction.

This first paper on X-ray spectra by de Broglie opened up a long series of spectroscopic papers. Together with F. A. Lindemann, the later Lord Cherwell, he introduced the method of secondary excitation of the emission spectra of substances from which targets inside the X-ray tube could not be formed, by irradiating them with harder X-rays. He could hereby complete the systematic exploration of X-ray spectra throughout the periodic system, except for the elements of order below 30. On this occasion the absorption edges of the silver and bromine in the photographic emulsion were also observed for the first time (May 1914). Whereas the atomic weight of Te is smaller than that of I, the X-ray spectra show that Te has the higher atomic number.

Among the other papers by M. de Broglie focussing devices by reflection on bent mica flakes and diffraction obtained with thin metallic sheets, a precursor of the powder method, should be mentioned. This most fertile activity came to an abrupt end with the outbreak of war in August 1914 which put a stop to all research in this field in France for five long years.

19.2. The Period 1918–1950

M. de Broglie's Laboratory

When scientists went back to the laboratories after the end of the First World War, Maurice de Broglie was the first to organize X-ray research. He did this by transforming his private mansion in central Paris, not far from the Étoile, into a makeshift laboratory where he, together with a brilliant group of young collaborators ran their X-ray tubes in rooms still panelled with oak or hung with gobelins. The main line of de Broglie's own work remained X-ray spectroscopy which at that time was one of the chief sources of evidence for the correctness of the rapidly developing ideas of atomic structure.

Alexandre Dauvillier was M. de Broglie's first helper in establishing the new laboratory. During the war he had been in the army medical corps operating a motorized radiological field unit. He stayed with de Broglie for twelve years, from 1919 onward, and extended the technique and knowledge of X-ray spectra to the long-wave region where tube, grating, and plate had to be kept in the same vacuum in order to eliminate unwanted absorption. A. H. Compton wrote of his work in the *J. Optical Society of America* 1928: 'Dauvillier was making rapid strides, working from the soft X-ray side of the gap (between light and

X-rays). First, using a grating of palmitic acid, he found the Kα-line of carbon of wave-length 45 Å. Then, using for a grating a crystal of the lead salt of melissic acid, with the remarkable grating spacing of 87.5 Å, he measured a spectral line of thorium as long as 121 Å, leaving only a small fraction of the interval to the shortest ultraviolet lines. The credit for filling-in the greater part of the original gap must thus be given to Dauvillier.'

Soon after Dauvillier, Jean Thibaud, Jean-Jacques Trillat and Louis Leprince-Ringuet joined de Broglie.

As far as his X-ray work is concerned, Jean Thibaud is mainly known for his measurement of X-ray wave-lengths by means of a ruled grating in 1927, a method which originated with A. H. Compton and R. L. Doan in 1925. From his measurements Thibaud expressed X-ray wave-lengths directly in terms of the standard meter and thereby related Siegbahn's X-unit, which was based on crystal diffraction, to the Angström unit which is 10^{-10} of a meter. This work, and subsequent measurements of even greater precision, led to the revision of one of the most fundamental constants in physics and chemistry, Avogadro's number.

In the first period of the eight years that J. J. Trillat worked in de Broglie's laboratory, he investigated long-chain organic compounds by means of X-ray diffraction. These studies, which paralleled those of A. Müller of the Royal Institution in London, were of twofold interest: paraffins and fatty acids were among the very limited group of organic compounds for which the full structure could be determined with the means of discussion then available; besides, they were suitable crystals for the spectroscopy of very soft X-rays. Trillat studied their orientation on glass or metallic supports and invented the 'method of the tangent drop'. In this method a drop of the melt is allowed to solidify in air, whereby the surface layers form a structure of equidistant curved sheets which reflect locally according to Bragg's law. The diagram obtained from a tangentially incident X-ray can be compared to a wide-angle diagram with ordinary crystals and gave Trillat and his co-worker Dupré La Tour information about the structure of the surface layer.

When in 1927 Davisson and Germer in U.S.A., G. P. Thomson in England, and little later Maurice Ponte in France confirmed Louis de Broglie's idea of the wave nature of electrons by diffraction experiments it was natural that Trillat, being in close contact with the latter, should take up electron diffraction. He became the inventor of many ingenious methods and applied the new technique to the study of the

oxidation of metals and alloys, the cementation of iron and the kinetics of other chemical reactions, especially of the surface type.

Jean Perrin's Laboratory

Jean Perrin, Nobel laureate and professor of physical chemistry at the Sorbonne, was one of the most spirited and stimulating teachers of Science in France. His 'Laboratory of Physical Chemistry' might well have been named better so as to indicate its main field of research more precisely, namely the structure of matter. Typical of the fundamental simplicity of Perrin's work are his determination of Avogadro's number from the microscopic observation of the density gradient of emulsified droplets, and his observations of the colours of patches of uniform thickness in films of fatty acid soaps from which he deduced the lengths of the soap molecules before the days of their X-ray determination. Similar observations of the uniformly coloured patches on thin mica flakes between crossed nicols led his co-worker René Marcellin (killed in September 1914) to a correct value of the cell length of the mica structure.

X-ray spectroscopic work began in this laboratory when Miss Yvette Cauchois constructed, in 1931, the first of a series of spectrographs using a bent crystal for intensifying weak spectral lines and increasing the resolving power by focussing the rays diffracted by the crystal. From that date onwards there was a steady flow of X-spectroscopic results, often under the common authorship of her and H. Hulubei (later professor of physics and rector of the University in Bucharest, Rumania), which made this laboratory rank in this field second only to M. Siegbahn's laboratory in Stockholm.

Her own work, and that of her pupils Manescu, Despujols, Barrère and others, covers the details of emission and absorption spectra of the K and L series of a very large number of elements, including some, like krypton and neon, in the gaseous state. Working with a wide source, obtained by secondary excitation of the samples outside the X-ray tube, she overcame the difficulties of low intensity and high absorption. The results, collected in 1947 in a book by Cauchois and Hulubei, are about to be published in a revised and enlarged second edition. The details of both emission and absorption spectra contain a great deal of information about the electronic states of the atoms in the crystal medium, but to find a simple interpretation for them is still a major problem of solid state physics. Professor Cauchois' work included ultra-soft X-rays and γ-rays besides the more usual X-ray range.

Georges Friedel's Laboratory

When the University of Strasbourg became French at the end of the First World War, Georges Friedel was appointed in 1919 to the chair of mineralogy. Being particularly interested in clarifying the nature of liquid crystals, he asked his son, Edmond Friedel, to investigate the hypothetical stratified structure of the smectic phases with X-rays. Since there was no suitable X-ray equipment in Strasbourg, Edmond Friedel performed his experiments in the laboratory of Maurice de Broglie. He confirmed the stratified structure and followed ethyl azoxybenzoate and ethyl azoxycinnamate through the temperature range from crystalline to mesomorphous to liquid state. In the temperature interval of smectic ethyl para-azoxy-benzoate he was able to measure the sheet thickness of 19.9 Å. He also found for sodium oleate a sheet thickness of 43.5 Å, thus refining the value which Perrin and Wells had obtained by their optical methods.

When X-ray equipment became available in Strasbourg, Louis Royer was in a position to check some of the basic data on which his theory of the mutual orientation of different kinds of crystals is based, a phenomenon he called 'epitaxis'. Raymon Hocart similarly used the equipment for the study of the twinning which is a standard feature in some minerals, such as boleite, pseudoboleite, cumengite, boracite; he and his group of students also investigated epitaxis.

The Laboratoire de Minéralogie et Cristallographie in Paris and its Spread

In 1919 Frédéric Wallerant succeeded to get Charles Mauguin appointed as Associate Professor and helped him to set up his X-ray equipment. Mauguin became the first in France to be interested in the analysis of individual crystal structures rather than in general physical problems associated with the crystalline state. After a first checking of the known quartz and calcite structures (1921 and 1925), Mauguin determined independently the structure of graphite (1925) (A. W. Hull in 1917 had found it already, and in 1924 other independent determinations by Hassel and Mark, and by J. D. Bernal appeared). He found unknown structure types in investigating cinnabar (1923) and calomel (1925). After that he devoted several years of study to the various kinds of micas, without, however, solving their structures. In his teaching, Mauguin developed a simplified presentation of space-group theory, including a symbolism which was later combined with that of Carl Hermann to form the Hermann-Mauguin notation now universally used. As early as 1924 his book *La structure des cristaux* appeared which

presented an introduction and survey of the methods and results of X-ray diffraction backed by Mauguin's own experience.

Around Mauguin grew a school of crystallographers of the new type. Jean Wyart, Stanislas Goldsztaub, Jean Laval, and Pierre Chatelain were the first of these.

Jean Wyart, in 1926, determined the structure of a basic zinc acetate which he had synthetized. Later (1929) he studied several zeolites and more particularly 'chabazite', working out the position of atoms and following with X-rays the changes of their positions when the percentage of zeolitic water varies, or water is replaced by mercury or ammonia, or when the nature of the alkaline or alkaline-earth ions is changed by diffusion. He worked out the atomic structures of paratoluidine and leucite and studied several cases of polymorphism. When Charles Mauguin succeeded in 1933 to Frédéric Wallerant, Jean Wyart became his Associate Professor. With his students, he used X-rays chiefly for determining the atomic structure of minerals, and as a mean of identification of finely crystallized products formed during the hydrothermal synthesis of silicates. He remained permanently with Charles Mauguin, and succeeded him in 1948, when Mauguin retired.

St. Goldsztaub, while he was working with Mauguin, studied the iron oxides and determined the atomic structure of lepidocrocite. After the Second World War, he took over the former laboratory of Georges Friedel at the University of Strasbourg, and became engaged mainly in electronic optics and crystal growth.

Jean Laval investigated the diffuse scattering of X-rays. Using monochromatic radiation, he measured accurately with an ionization spectrometer the intensities of the incident and the scattered beams. He showed that diffuse scattering was essentially a temperature effect, and he established experimentally the laws for different crystals, in particular for sylvine. As these results were not in good agreement with the theories of Debye, Waller and Born, he worked out a quantitative theory which is generally adopted nowadays and which is based on Born's work on harmonic vibrations in solids. The diffuse scattering of X-rays is interpreted as selective reflection from the elastic wave-planes. From this theory and his X-rays measurements, he was able to obtain the coefficients of elasticity and the speeds of the acoustic waves in crystals such as sylvine. These remarkable results have since been widely confirmed, in France first by Philippe Olmer for aluminium; for iron Hubert Curien was able to determine only from X-ray data the atomic oscillation spectrum in iron crystals, the binding forces between an atom and 26 of its neighbours, and the specific heat curve.

Further confirmations of Laval's theory were found by D. Cribier regarding fluorine and P. Mériel regarding sodium chloride. Theoretical and experimental research of Laval and his students on the Compton effect in crystals should also be mentioned.

Since 1950 Laval occupies the chair of Theoretical Physics at the Collège de France and his research, mainly on the fundamentals of crystal elasticity, has moved there.

Pierre Chatelain, while working at the laboratory of Mauguin, took up once more the optical study of liquid crystals. To begin with, he rarely used X-rays, but during recent years in his laboratory at Montpellier, he and his co-worker J. Falgueirettes obtained important results on the structure of these substances by means of X-ray diffraction.

A large number of scientists have since studied at the Laboratory of Mineralogy and Crystallography at the Sorbonne, amongst the earliest and the best known, are C. Kurylenko, known for his studies on X-ray absorption; J. Rose for improvements of the X-ray spectrometer and methods of determining crystal structure; J. Barraud for his research on X-ray optics; Robert Gay and his group for his determinations of the atomic structures of organic compounds; M. M. Herpin, Rimsky, for their determination of crystal structures. André Guinier, though he never worked in this laboratory, is also one of Charles Mauguin's students. His thesis on the small-angle scattering methods made him known in the world of crystallographers, and the curved monochromator which he introduced, and his focussing powder cameras are used in every laboratory. These methods allowed him to study small-angle scattering in much greater detail and he clearly recognized what a powerful tool this was for the study of the first stage of a transformation of an alloy; the slight disturbance of the initial lattice does not change appreciably the diffraction pattern, but has a striking effect on diffuse scattering. He has studied binary alloys like Al—Cu, Al—Zn, Cu—Be, in which the scattering power of the two atoms is widely different and which are obtainable as single crystals. In these alloys he could prove the segregation of solute atoms. Among his early students, Fournet has applied the small-angle scattering to hemoglobin and given a theory of X-ray scattering in an order-disorder assemblage and in liquids; Devaux and Brusset have studied the hole size in various charcoals. Castaing is very well known for the perfecting of his 'Sonde' which permits him to determine, by the X-ray emission spectrum, the chemical composition of microscopic inclusions of the order of one micron. Guinier's work was done at the laboratory

of the Conservatoire des Arts et Métiers from 1940 to 1960. It has now moved to the new research centre of the Faculty of Science of Paris University at Orsay (S. & O.).

Urbain's Laboratory and its Spread

The first *chemical* laboratory in France to obtain X-ray equipment was the laboratory of Georges Urbain at the Sorbonne. Here Delaunay obtained his X-ray tube at the same time as Charles Mauguin, and he soon had as assistant, later as successor, Marcel Mathieu. The latter had already worked in 1925 and 1926 at the Royal Institution of London, in Sir William Bragg's laboratory. He applied X-ray analytical methods to several chemical problems, to what he called the topo-chemical reactions, such as the gelatinization of nitro-cellulose. He studied solid catalysts and found that catalytic activity is related to the existence of holes in the solid phase. In some cases he was able to estimate the shape and size of these holes. His laboratory rapidly became very active and was attended by numerous scientists, a number of which have become renowned crystallographers. One of the first of these was Jacques Mering whose work deals with X-ray scattering by highly imperfect crystals, such as charcoal and clay. For several years the lamented Miss Rosalind Franklin worked with him.

E. Grison specialized in the determination of atomic structures and V. Luzzati was initiated by him to X-ray techniques. After several years spent in Mathieu's laboratory, the latter, well known for his researches on the phase problem and for his determinations of the atomic structures of nitric acids, organized an X-ray laboratory for biology at Strasbourg.

With Georges Urbain, G. Champetier also used X-rays to study the properties of macromolecules, for instance the mechanism of the nitration of cotton by nitric acid vapour.

Among the first students of Mathieu was Miss Cécile Stora. She remained in charge of his laboratory when he left thbrnonee So with his whole group to get installed in larger laboratories, first at the Institut de Recherches Appliquées, and later at the Office National d'Études et de Recherches Aeronautiques. The structures which Miss Stora studied by means of X-rays are those of organic dyes, derivatives of triphenylmethane and of Indigo (Mrs. von Eller-Pandraud). G. von Eller, besides for publishing interesting memoirs on the phase problem, is well known for his much used photosummation machine for Fourier synthesis, which was first constructed in Stora's Sorbonne laboratory.

Other Laboratories

Another chemical laboratory using X-rays is that of Professor Chaudron in Vitry. He and his first students Benard, Faivre, Lacombe, Michel, nowadays directors of important laboratories, have perfected the methods of precise lattice parameter measurement in particular by the back-reflection method. Much of their work deals with very pure metals, alloys, and the mechanisms of oxidation and of corrosion as linked to crystal defects.

During the Second World War, Mathieu's associate Mering, having taken refuge at the University of Grenoble, set up there an X-ray laboratory and was joined by F. Bertaut. The latter remained in charge of this active laboratory after the end of the war, when Mering returned to Paris. Bertaut and his coworkers have determined the structures of mineral compounds, more particularly of iron and rare earth garnets. Bertaut also published important memoirs of a theoretical character on the direct determination of atomic structures from X-ray data alone.

Needless to say, X-ray diffraction methods have penetrated, slowly but irresistibly, into many more governmental and industrial laboratories in France. Among the first, mention should be made of Mrs. Adrienne Weill's X-ray section of the Navy Research Laboratory, of the National Telecommunications Laboratory, and the National Nuclear Research Laboratories. Important industrial X-ray laboratories are to be found in the steel and mining industries, the tire manufacture and in photographic works. There is room for expansion here, and it may be hoped that as more students are now getting a training in crystallographic methods, so will the use industry makes of X-ray diffraction continue to rise.