CHAPTER 25

The World-wide Spread of X-ray Diffraction Methods

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In the foregoing chapters the development of centres and schools of X-ray diffraction has been described in some detail for the leading countries. Early work has, however, not been restricted to these countries, and the spread of the application of these methods to new countries and to new laboratories took place in the twenty years between the wars and continues today at an even increased rate. This is a natural development for a method of such general importance for problems in many sciences and in technology, and the present chapter can not and need not go into the often repetitive detail of the development in all countries.

In collecting material for this chapter, the author sent out a questionnaire form to the sub-editors of the 1960 edition of the *World Directory of Crystallographers*. The 19 forms brought back 10 answers, most of them with very complete and interesting information, and the author wishes to acknowledge his great obligation to those who assisted him in collecting the material. It was essential in compiling the short passages following below; at the same time it should be made clear that the author in many cases has added material from his own knowledge or recollection, and mistakes which may have crept in through him should not be blamed on his informants.

We follow the alphabetical order.

Argentina

Probably the first Argentine scientist to get in contact with an X-ray diffraction laboratory was Dr. Horacio Damianovich. He travelled to Paris in 1929 taking with him some platinum electrodes that had been working for many hours in helium-filled discharge tubes. Prof. Trillat took some Debye-Scherrer patterns, but the results regarding a possible Pt-He interaction were not conclusive (Damianovich and Trillat, 1929).

In 1933 Prof. E. E. Galloni of the Natural Sciences Faculty in Buenos Aires worked for five months with a fellowship grant with Prof. J. Palacios in Madrid (space group of gypsum), but it was not until 1938 that a powder camera could be installed in the Institute of Experimental Medicine (Director Dr. A. H. Roffo) and the structure of platinum oxide studied (Galloni and Roffo, 1941).

In 1941 the Science Faculty of the University in Buenos Aires purchased a General Electric diffraction unit including powder and rotating crystal cameras. Work on metallic oxides and mineral identification was done with this unit up to 1952, and a similar unit purchased at about the same time for the Physics Institute of the University of La Plata was in use there.

The Argentine Atomic Energy Commission in Buenos Aires uses powder and Laue methods in its metallurgical Department and electron as well as X-ray diffraction in its diffraction laboratory which is directed by E. E. Galloni. This Commission has recently acquired Weissenberg, small-angle, and microcameras from the Navy Medical Institution.

Several more installations can be found at the Solid State Physics Institute at San Carlos de Bariloche (founded in 1954) and in academic physics and geology departments.

A National Committee of Crystallography was founded in 1959. A rapid increase in research is to be expected thanks to scholarships which enable students to study in well-known laboratories, and to visiting lecturers. The first meeting of the Ibero-american Association was held in Corboda Province in 1960; twenty papers were read on that occasion.

Austria

The first serious attempt at establishing structure analysis seems to have been made by Prof. Fr. Raaz of the Department of Mineralogy of the University in Vienna. Raaz had been studying the subject with Rinne and Schiebold in Leipzig and used Seemann equipment in 1929. Before that, from 1927 onwards, F. Halla and M. C. Neuburger used the powder method for studying metal oxides, alloys, and the lattice constants of metals at the Department for Physical and Inorganic Chemistry of the Technical University in Vienna. A considerable amount of work on light and X-ray scattering was done at the First Chemical Institute of the University of Vienna while H. Mark had the chair there (1932–38) in connection with the nature of liquids and of high-polymers. The mineralogical department, now under Prof. F.

Machatschki, and the chemical department of the university are still the centres of Austrian structure analysis. O. Kratky in Graz together with G. Porod devoted much work to the technique and interpretation of small-angle scattering by colloids and high-polymers. The main industrial laboratory using X-ray diffraction is that of the Planseewerke in Reuthe which specialize in powder metallurgy.

Chile

The application of X-ray diffraction dates entirely from after the Second World War. In the initial period, 1951–53, such work was begun in the physics departments of the universities in Concepción with English, and in Santiago with German (Siemens) equipment. Further X-ray facilities are to be found at the Technical University at Valparaiso and the State Geological Institute in Santiago. At the university in Santiago N. Joel applies X-ray diffraction to the physical problems of thermal vibrations as well as to structure analysis, and E. Grünbaum is paralleling this with electron diffraction. At all three universities the work is being done in the physics departments. The number of scientists trained in these methods is still small—about 12 in 1960—but as the methods now penetrate into the teaching curricula, a rapid advance seems likely.

Czechoslovakia

A first independent start with X-ray analysis was made at the Charles University in Prague in 1923 in a joint effort between the theoretical physicist K. Teige and the mineralogist B. Ježek. In 1923–25 F.Ulrich received a training under V. M. Goldschmidt in Oslo. A year or two earlier V. Dolejšek had gone to Lund in order to study X-ray spectroscopy with Manne Siegbahn. Two important papers resulted from this in 1922: the first measurement of the lines of the N-series; and, together with Siegbahn, the improvement of the accuracy of line measurement and its application to the K-spectra of elements from 17 Cl to 30 Zn. On his return to Prague, Dolejšek established a school of X-ray spectroscopy of great precision.

In the period between the wars, G. Hüttig did interesting work as Professor of Chemistry at the Charles University on 'vagrant constituents' in crystals using X-rays in conjunction with other methods. More recently, active schools of X-ray crystallography are to be found in Prague (Praha) and Brno in academic laboratories and in the industrial laboratory of the Skoda works.

Israel

At the Weizmann Institute in Rehovoth X-ray crystal analysis was from its beginning (1948) in the hands of the chemists. G. M. J. Schmidt in particular studied the effects of 'molecular overcrowding' on the structures of organic crystals. J. Gillis at the same institute is interested in the mathematical and computational problems of crystal structure analysis.

In the Physics Department of the Hebrew University in Jerusalem (Prof. E. Alexander) problems of X-ray optics and spectroscopy are being studied. Further laboratories using X-ray diffraction are those of the Atomic Energy Commission (governmental) and of Tadir, Ltd. (industrial).

Italy

In spite of the great tradition in mineralogy and crystallography which in Italy goes back to the 17th century, the first X-ray work came from the *chemical* institute of the Polytechnic in Milan and was directed to problems of analytical and physical chemistry. A very viable school, which still persists, was created here in 1924 by G. Bruni, G. R. Levi and G. Natta with many co-workers. Their investigation of oxides, hydroxides, fluorides, carbonates, etc. was based on powder diagrams, the technique of which G. R. Levi had been studying with Debye and Scherrer in Zürich. In the course of time, single-crystal methods were adopted, and now the use of Weissenberg and precession cameras, optical and machine summation leads to single-crystal work of high quality and chemical significance.

Among the mineralogists, E. Onorato was the first to enter the field (1927) by his determination of the space group of gypsum from Laue diagrams during his studies with Rinne-Schiebold in Leipzig. In the same laboratory V. Montoro received his training; he later devoted most of his work to analyses of metallurgical interest.

The lack of equipment which was largely responsible for the relatively small amount of work coming from Italy in the period between the wars was overcome in the last decade; the number of well equipped laboratories has doubled and a large group of young and well trained X-ray crystallographers is now at work in academic, industrial and governmental laboratories on chemical as well as physical and mineralogical problems. Fluorescence analysis and electron diffraction are also being used.

Spain

Within a year after Laue's discovery F. Pardillo gave a report on it and on the first work of the Braggs to the Royal Society of Natural History (*Bol.* 1913, *13*, 336), and two years later (1915) Blas Cabrera wrote a similar report in the *Anales Soc. Esp. Fis. y Quim. 13*, 7. It took, however, another ten years before the new experimental technique was actually introduced in Spain, first at the Physics Department of the University in Madrid, but soon after, and on a larger scale at the Instituto Nacional de Física y Química which had meanwhile been established with the help of the International Education Board (Rockefeller) in Madrid. Here J. Palacios assembled a group of keen young workers to whom he lectured and for whom he invited guests from abroad. A Weissenberg camera was built in the workshop of the institute from the drawings which Hengstenberg had provided, and he and Wierl, both from H. Mark's laboratory in Ludwigshafen, initiated electron diffraction which was taken up by L. Brú. J. Garrido, O. Foz, L. Rivoir and R. Salvin worked together with Palacios on structure determinations of inorganic and organic crystals and on the perfection of the Fourier methods of analysis. The Civil War brought all this to a near standstill from 1935 onwards. The same is true for the work which F. Pardillo had inaugurated quite independently and without external help in the mineralogy department of the university in Barcelona.

A revival took place after the Second World War, and there were considerable shifts of location of the scientists. L. Brú who had no X-ray instrumentation as long as he was professor of physics at La Laguna in the Canaries, was appointed to the physics chair at the University of Sevilla in 1949, and there, gathering some of his former collaborators around him, he began work on structure problems. In 1956 he came in the same capacity to the University of Madrid and is continuing both X-ray and electron diffraction there with an increasing number of co-workers.

L. Rivoir heads the X-ray department in the converted Instituto Nacional de Física y Química, now Instituto de Física 'Alonso de Santa Cruz'.

The most active among the Spanish crystallographers is J. L. Amoros who after graduating at the university in Barcelona in 1942 worked there in the Instituto Lucas Mallada of the Higher Research Council (CSIC) before becoming the professor of crystallography in Madrid. Together with his numerous co-workers he is investigating structures as well as physical properties of crystals and the methods of their

analysis. Interesting and useful publications have been issued by this group which provide the new generations of students with texts to study.

It should be mentioned that also J. Garrido and J. Orland published in 1946 a book *Los rayos X y la estructura fina de los cristales* which forms a good introduction to the subject and contains some methods developed by the authors.

A Crystallographic Society was formed in 1950 with some 35 members; in 1960 membership had risen to 60. In 1960 an Ibero-American Association for Crystallography was founded with the intent of tying together crystallographic research in Argentina, Chile, Uruguay and Spain.

Switzerland

The development of diffraction methods in this country was shaped mainly by the prominent men in Zürich: P. Debye, P. Scherrer, and P. Niggli. They came to Zürich in 1920, the former two to the Physics Department, the latter to that of Mineralogy and Petrography of the E.T.H. In neither of these places did much interest evolve in crystal structure determination as such, although Niggli analysed tenorite, and under Scherrer the structures of ferroelectric crystals like Rochelle salt were investigated. In Niggli's institute the emphasis lay on the general laws of crystalline architecture in a rather abstract, geometrical and classifying sense; E. Brandenberger's important analysis of the laws of extinctions, and H. Heesch's extension of the theory of space groups to include anti-symmetry elements should, however, be mentioned.

Crystal structure analysis in the accepted sense was used on a large scale from 1930 onwards by the physico-chemist W. Feitknecht in Bern, initially in conjunction with W. Lotmar. Systematic chemical surveys of series of compounds, such as the basic salts of bivalent metals, double hydroxides, and hydroxy salts were carried through mainly using powder diagrams, and led to extensive series of papers; Lotmar later turned to high-polymer and protein diffraction. In the department of mineralogy of the same university, Bern, W. Nowacki has built up an active and well equipped centre of structure analysis. A great variety of crystals, ranging from minerals to sterines and other organic crystals of high molecular symmetry have been determined here. The principles of crystalline structure, and the statistics of the distribution of structures among the space groups have drawn the particular interest of Nowacki (for the latter see Donnay and Nowacki, *Crystal Data, Memoir 60*, Geological Soc. of America, 1954).

In the years 1932–38 (approximately) a very active school of X-ray optics flourished in Geneva under the physicist J. Weigle. In a number of papers Weigle and his co-workers tested the validity of the dynamical theory of X-ray diffraction, and also laid the foundations for the understanding of the moiré patterns which are very revealing in electron diffraction and microscopy. This school came to an end when Weigle turned his interest to genetics and settled in U.S.A.

A re-activation has taken place in the mineralogical institute in Zürich since the appointment of F. Laves as professor of crystallography; an interesting program of research into the relations of structural and physical properties is developing on a broad front. A. Niggli has further extended the mathematical theory of space groups.

Needless to say that in a highly industrialized country like Switzerland X-ray diffraction is being used in the chemical, metallurgical, electrical industries and in the special Laboratoire suisse des Recherches horlogères in Neuchâtel.

Yugoslavia

The first paper to be published was a powder diffraction study for the identification of bauxites by M. Karšulin, A. Tomič and A. Lahodny and dates from 1949. But the introduction of single-crystal methods and of Beevers-Lipson strips is due to D. Grdenić (1950) who received his training with A. I. Kitaigorodskii at the Institute for Organic Chemistry in Moscow. The centres of research are the physical, physico-chemical and mineralogical institutes at the universities in Zagreb and Belgrade, the Institute for Nuclear Science in Belgrade and the industrial institute for light metals in Zagreb. In Prof. Grdenić' chemical institute 'Ruder Boščović' of the University in Zagreb inorganic and organo-metallic compounds are being investigated, while in the physics institute small angle scattering is applied to colloid systems.

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The above discussion represents a fairly good sampling of the growth of diffraction methods in countries with a long tradition in crystallography and mineralogy, and in those where research is only recent. Among the countries not mentioned above are Belgium and India; Poland, Pakistan, Korea; and the Chinese Peoples Republic.

Of the last, too little is known, except for the fact that there are first

rate crystallographers (for instance S. H. Yü, see Reminiscences of Lipson and Wilson); this is counteracted by the fact that in the planned programme of education and research of this country X-ray diffraction has not yet reached a high priority. Once this stage is reached, an outburst of structural work may be expected.

In Korea and Pakistan there are well trained research workers and useful equipment, but the entire educational work has first to be carried out before a group of research people can be brought together —and experience shows that isolation of a single, or only a few scientists usually squashes research. In Poland there are X-ray laboratories at the six universities and some more at state or academy instituions, but the output seems not to be high.

India has been included in the survey of the British and Commonwealth Schools (Chapter 17), and the same holds for Canada, Australia, New Zealand and South Africa. Some additional information will be found for India and South Africa in the Personal Reminiscences of K. Banerjee and R. W. James, respectively.

In Belgium, X-ray diffraction goes back to H. Brasseur, who in 1930 worked on malachite and azurite first in Manchester, and then in Pasadena. Back in Liège at the mineralogical laboratory, he and his co-workers investigated the structures of double cyanides, like the hydrated barium-platino-cyanide. Apart from this laboratory, X-ray methods seem not to have aroused much active interest in Belgium until in the 1950's. Then J. Toussaint in Liège, and later H. van Meersche in Louvain, a student of Bijvoet's, took up organic structure work, and H. J. Lambot, who had studied with Guinier, made careful studies at the Université Libre in Brussels of the precipitation mechanism in the ageing of duralumin. X-ray methods were also introduced in several industrial laboratories.

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There are a number of other countries where X-ray diffraction methods are being taught and used, though in a rather isolated way, such as Greece, Egypt, Bulgaria, Rumania, Brazil and other South American countries. Experience shows that the development of the subject is usually a cooperative one. As long as the chemists, both in academic and industrial laboratories, are not actively interested, the group of crystallographers remains small, and from the point of view of the student the special training required does not hold promise of a well paid and interesting employment. Once this first stage of indifference

is overcome, it takes not long to prepare a good seed-bed for the subject to develop and take root. The sending abroad of suitably prepared students to well-established teaching laboratories, or the invitation of workers from such laboratories for a visit of a few months, has proved to be the most efficient means for getting the subject established in good form and without avoidable experimentation.

It is interesting to note the important effect which the problems of agriculture have had on the spread of these methods in the less industrialized countries. 'Clay minerals' is usually one of the first subjects tackled after the establishment of the first X-ray diffraction machines.

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