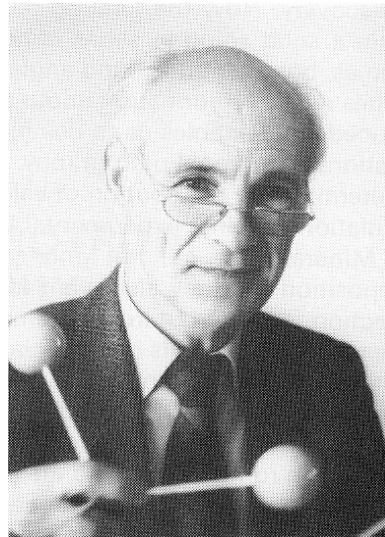


PREFACE

When I was invited to write about the application of X-ray diffraction in mineralogy I compared the X-ray methods available in 1950 when I started as research student with the methods now accessible. Our X-ray sources were rather weak and non-stabilized, Debye-Scherrer cameras with poorly designed collimators produced powder diagrams of low resolution and strong background intensity. The film carrier of our first Weissenberg camera was pulled by a wire that sometimes slid on the roll, giving rise to long streaks instead of diffraction spots. Single crystal diffraction intensities were estimated by comparing their photographic densities with those of a linear density scale. The rather limited and inaccurate experimental data were used to calculate Patterson projections from which a trial structure was derived. This structure was then refined by successively calculating structure factors and electron density projections. Calculations were done with mechanical desk calculators and Beevers-Lipson strips. Collecting as well as handling even such limited data sets were very time-consuming.



As a consequence the structures obtained were of rather low accuracy so that in general discussions about differences in bond lengths within a polyhedron were almost meaningless. In minerals where extensive isomorphous replacement between main elements such as magnesium, iron and manganese or calcium and sodium or, in particular, silicon and aluminum is very wide-spread it was usually impossible to determine the site distribution of the various cations and, therefore, the degree of order which is often the key to an understanding of the mineral's geological history. Although the structure types of most of the important rock-forming minerals were approximately known by 1950 this knowledge was in most cases based on the structure determination of just one more or less randomly chosen crystal.

Within the three and a half decades since then I witnessed and profited from an immense progress in all branches of X-ray crystallography, experimental as well as theoretical ones. Manufacturers competed with another for providing better equipment.

As a result the time necessary to record diffraction patterns has strongly been reduced by the newly developed rotating-anode X-ray generators, by improving the classical Weissenberg and precession cameras, by introducing new equipment for photographic data collection (e.g. densitometers and photoscanners), and in particular by applying counter methods for intensity measurements. Mainly thanks to the counter method we are now able to measure large 3-dimensional data sets very accurately and fully automatically within a few days with a four-circle diffractometer. Automation of these measurements as well as handling large data sets within reasonable time has been made possible only by the unprecedented development of electronic computers.

At the same time direct methods for phase determination have been developed and least-squares refinement procedures have been improved to such an extent that many routine structure determinations are nowadays done by the computer with little interference from the crystallographer.

As a result of this joint effort of scientists and engineers in industry as well as in research institutes the crystal structures of almost all known minerals have been determined, most of them with great accuracy. It is not seldom now that the crystal structure of a new mineral is published in the same issue of a journal as its discovery. Now the limiting factor for studying the change of structure with chemical composition within a solid solution series is not time but availability of suitable single crystals. From accurate cell volumes, bond lengths, bond angles and, in particular, from the knowledge of cation distribution in mixed crystals reliable information about the stability of a mineral and about its thermal and baric history can be deduced. This enables us to use high-accuracy single crystal studies to solve, for example, quite specific questions of regional petrography. If extreme efforts are made it is now even possible in favour-

able cases to determine the distribution of valence electrons and lone pair electrons and to check quantum chemical calculations against experimental values.

Mineralogists are not only interested in the structure of a substance and in its changes with composition but they also want to know how a structure changes with temperature and pressure. Data collection at liquid nitrogen temperatures has been developed mainly for organic crystals and the necessary equipment is commercially available. It can be used to distinguish between random distribution of atoms between slightly split positions (static disorder) and thermal vibrations (dynamic disorder) for example in feldspars. With greater effort, intensity sets can even be collected at liquid helium temperature.

In contrast, accurate single crystal structure determinations at temperatures above about 400°C are still far from routine work and are done at few laboratories only. This is only partly due to the fact that the interpretation of atomic distances and angles obtained from such high-temperature studies is not straightforward because bond lengths are masked by strong thermal vibrations; it is more due to the fact that satisfactory heating devices are not commercially available.

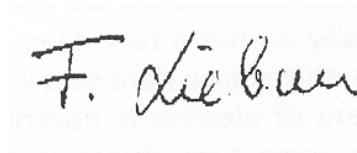
The experimental situation is not much different for structure determinations at higher pressures although no particular problems arise in interpreting their results.

Since high-temperature/high-pressure conditions exist in the interior of the earth and are responsible for the occurrence of the majority of minerals and mineral assemblages at the earth's surface which are thermodynamically unstable at ambient conditions, extensive structure determinations at high temperatures and pressures are the task of the future. This is even the more true since many technical processes are carried out at high temperatures and many materials are used under extreme P, T conditions. There is a real demand on commercially available high-temperature/high-pressure equipment for routine single crystal as well as powder diffraction studies in mineralogy as well as in materials science.

In the past, reliable and accurate crystal structure analyses were only possible when single crystals large enough for collection of 3-dimensional data sets were available. Within recent years the Rietveld method has been developed and improved to such an extent that good quality refinement can even be made if an approximate structure is known although only polycrystalline material is available. Current efforts to improve the hardware and software for high-resolution profile measurements as well as the structure refinement programs will soon make the Rietveld method a powerful supplement to single crystal structure determination.

Another field where progress is being made is the time-resolved measurement of X-ray diffraction data. At present the rate of data acquisition is just high enough to follow the dynamics of solid-state reactions by powder diffractometry. It is to be hoped that in the not too far future ordering processes and even phase transformations in single crystals can be followed with the aid of high-resolution position-sensitive detectors and high-intensity X-ray sources, hopefully other than synchrotron sources.

The history of X-ray diffraction is an excellent example to demonstrate that scientific progress is accompanied by progress in experimental methods and equipment. To the same extent as scientists approach new research areas, new and better apparatus is being developed which in turn leads us into new fields. The better the collaboration between researchers and manufacturers, the greater the progress that can be made. Good collaboration is, therefore, mutually advantageous.



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