

PREFACE

During the last decades crystallography has been considerably stimulated by the significant progress that has taken place in theoretical work, computer and software development, techniques for measurement and control, and instrumentation which in turn, has led to some remarkable results. X-ray crystallography continues to play its central role. This development can be illustrated by a few selected examples.



Nowadays crystal structure research is governed by the strategies of “direct methods.” From its early days in Germany I well remember a series of lectures given in 1960 by Herbert Hauptman at Erwin Hellner's laboratory in Kiel. His lecture notes were subsequently widely circulated amongst the young German crystallographers and introduced many of us to this field which showed promise of further development. In particular, Woolfson's work and his summer schools at Erice and York encouraged the world wide use of "direct methods" computer programmes. This ensured that this important technique of structure determination was readily available to the many practitioners in crystallography as well as in chemistry, physics, biology and medicine.

The least-squares method for structure refinement was further extended to take into account the temperature coefficients for anharmonic atomic motion, parameters for merohedral and pseudomerohedral twinning, expectations for interatomic distances, penalty functions and, following Zachariasen's theoretical treatment, extinction. Not only could the quality of structure refinement be improved, but also the results became much more informative. For instance, when investigating ionic conductors or structures with temperature activated atomic interchange of sites, one obtains evidence for paths of atomic motion from the calculation of probability density and potential maps. Often a powder is the only form in which a crystalline compound can be prepared, allowing only the X-ray powder pattern to be measured. Even under these conditions, many crystal structures have been successfully solved since the late 60's, when Rietveld introduced his least-squares optimization programme for fitting the complete measured and calculated diffraction profiles. When using the modern sophisticated programme systems on even the smaller, but tremendously efficient computers, one almost forgets all the effort that scientists had to expend in early times in overcoming the enormous computational problems in structure determination work.

Many years ago crystal phases such as NaNO_2 were found to exhibit superperiodicities in their X-ray patterns which were not integral multiples of their normal lattice translations. During my post-graduate years with Fritz Laves these so-called modulated structures and related phenomena were often the subject of our intense discussions. We learned much from our meetings with Heinz Jagodzinski and Masaaki Korekawa about the theoretical treatment of this subject in terms of transversal and longitudinal lattice distortions or as periodic density fluctuations. At that time practical crystal structure research tended to put such problems aside. Today we are aware of the fundamental importance of these effects in connection with phase transitions in many substances and that lattice dynamics and cooperative behaviour of atoms are responsible for these types of structures. In the meantime more and more compounds with modulated structures have been discovered, and during the last 15 years the literature on these so-called incommensurate phases has grown so that it now includes hundreds of publications. Practical structure determinations in this particular area of crystallography have been greatly facilitated by the application of aspects of the Landau theory for second order phase transitions and also by Janner and Janssen's concept of

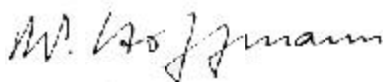
superspace groups. High-resolution electron microscopy has proved to be of great value as an additional method for studying incommensurate structures and commensurate-incommensurate transformations.

X-ray crystallographers are showing an increasing interest in investigations into the relationship between structural and physical properties. For instance a remarkable correlation exists between the mobility of implanted ions and the more or less open structured frameworks having permeable structural channels or layer type structures with interstices. The so-called super-ionic conductor Li_3N exhibits an extremely high value of three-dimensional ionic conductivity upon the application of an electric field. Similarly $\text{Li}_2\text{Ti}_3\text{O}_7$ or $\beta\text{-Al}_2\text{O}_3$ containing Na have high one- or two-dimensional conductivities respectively. At the present time many laboratories all over the world carry out research work in order to find efficient ionic conductors for technical applications while fundamental research endeavours to develop a better understanding of transport phenomena in crystals. Many important discoveries in this field can be expected in the future, particularly from the results of combining high precision X-ray structure analysis with inelastic neutron scattering investigations or spectroscopic methods that are sensitive to the dynamics of atomic events.

In the broad aspect, crystallographic research concerns itself with the manifold symptoms of phase transitions in crystalline solids. Likewise, another important aspect of this field of scientific work is the combination of X-ray diffraction with other techniques appropriate to the study of atomic movement and co-operative behaviour of atoms. Great efforts have been made to develop accessory equipment for varying both temperature and pressure over a wide range during diffraction, scattering or spectroscopic experiments. Temperatures ranging from that of liquid helium to in excess of 2000 K and hydrostatic pressures much higher than 100 kbar can be attained. Commercial devices having such capabilities are becoming much more common in many laboratories. Structural work in this field is still in its infancy despite the many impressive results that have already been obtained under conditions of extreme temperature or pressure. Instrumentation and experimental techniques will benefit greatly as more research projects are initiated.

In the above examples of X-ray crystallographic work, technical progress in industry and the requirements of scientific instrumentation act as a mutual stimulant. During my first years in crystallography I even learned how to replace home-made cathodes in demountable X-ray tubes, to use Beevers-Lipson strips as well as mechanical and optical Fourier synthesiser for my computational work. Comparing this bygone era with the present in which the design and manufacture of apparatus and instruments has undergone much change, it can be said that we have reached the High-Tec state. X-ray generators are very compact and highly stabilized. X-ray tubes have very high power ratings, especially those with a rotating anode. Some laboratories are even in a position to use synchrotron radiation which opens up new vistas to experimentalists in crystal structure research. Computer controlled automatic single crystal and powder diffractometers are now in a mature state of design and development. Resolution as well as precision for measurements made using highly monochromatic radiation have reached a very high standard. More and more laboratories will make good use of X-ray position-sensitive detectors. These will give them the opportunity to further reduce measuring time and they will be able to follow relatively fast transformation processes or chemical reactions between solids as they take place.

Many important tools have been provided by industry for the steadily growing field of experimental crystallography and I think that there has been a good response to this. Let us see what the future will bring.



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