RECENT TRENDS IN CRYSTALLOGRAPHY

THE experimental determination of a crystal structure consists of two distinct steps : (i) the determination of the symmetry of the crystal, i.e., the type of its lattice and its space group and (ii) the determination of the atomic arrangement which is consistent with this symmetry and which will satisfactorily account for the intensities diffracted by the different "atomic planes" inside the crystal. The determination of the space group is not altogether a straightforward procedure. Some of the symmetry elements which incorporate the operation of a translation like the screw axis or the glide plane can be recognized by systematic absences in the X-ray reflections. Even here an ambiguity may be introduced because it may happen that extinction in a more general class of spectra may automatically imply extinctions in a less general class. Apart from this there is an inherent difficulty in the determination of space group because X-ray diffraction being of the Fraunhofer type cannot normally detect the presence or absence of a centre of symmetry. However, the expectation expressed by M. J. Buerger that the intensities themselves should provide the information necessary to unambiguously specify the space group has proved essentially correct. Wilson has shown that the presence or the absence of the centre of symmetry can be detected from the study of the distribution of intensities or by computing the average intensities in any particular zone. This statistical method works out most satisfactorily when there are a large number of light but equal atoms in the unit cell. A number of studies on the effect of heavy atoms on the intensity distribution curves have been made. It is now established that the method of local intensity averages can be used to detect such symmetry elements like two-fold axes, mirror planes, etc., which cannot be unambiguously determined from the direct inspection of X-ray diffraction photographs.

The other approach to the problem of the determination of the symmetry elements is through the information obtained from the concentration of peaks in certain planes in the three dimensional Patterson synthesis or in Harker sections. The possibilities of this procedure have been worked out. It is claimed that using these techniques it is now possible to identify 215 out of 219 non-enantiomorphous space groups. The enantiomorphous space groups can theoretically at least be distinguished from crystal morphology or by the use of anomalous scattering techniques. It must be remarked, however,

that while small ambiguities in the space group "have not proved to be a serious obstacle in the determination of crystal structures there is no doubt that the unequivocal determination of the space group at the outset may lead to more rapid and certain progress" (Lipson and Cochran).

Knowing the space group the crystal structure determination cannot, in general, be direct because the information regarding the relative phases of the reflection is lost during the recording of the diffraction spots. However, many complicated structures have been solved by the method of trial and error. Perhaps the most direct method of solving crystal structures would be the isomorphous substitution method. The solving of the structures of the phthalocyanines by J. M. Robertson is perhaps one of the most outstanding successes of this method. The extension of this method to non-centro-symmetric cases by Bijvoet and the development of the double isomorphous substitution method by D. Harker and others are expected to prove extremely fruitful in the determination of complex structures. Another direct method which has been so successfully developed and exploited by Buerger, Robertson and others is the vector set method. This method uses the Patterson synthesis or the method of auto correlation where every available observed datum is incorporated, there being no necessity for the inclusion of such doubtful quantities like the relative phases of the reflections. The principle of the method depends on the fact that when the vector set of points (the Patterson) of a fundamental set (the structure) is known, it is possible by "image seeking" methods, to recover from the vector set the original fundamental set. However, various techniques have been suggested to overcome the difficulties which arise on account of the physical fact that atoms having a spatial extension are unlike the fictitious mathematical points of a fundamental set.

A very important step in the analytical method of direct phase determination was made when Harker and Kaspar discovered that inequalities long known to mathematics (like that of Schwartz) could be applied to the problem of phase determination in at least centro-symmetric structures. Such an application is possible because the density of the scatterer at all points in any crystal (for X-ray diffraction) is always positive, a condition similar to that on which most of these mathematical inequalities are

based. This has been followed by a series of investigations but perhaps the most significant amongst these is the squared atom method of Sayre. This is based on the fact that in a structure of equal, well resolved atoms, if one considers an electron density function which is the square of the normal function, the resultant function would not be very different from the original one. except for a difference in the shape of the peaks. This concept leads immediately to product relationships such that if the structure amplitudes F_{pq} and $F_{h-p,k-q}$ are both large then F_{hk} is almost definitely the sign of their product. The most effective methods of utilising these relationships for the correct assignment of phases have been explored.

As yet no routine method seems to have been found for the solution of the phase problem. But such a claim has been made for the statistical method of Hauptman and Karle. It consists in applying the method of statistics—joint probability methods, to the observed amplitudes and intensities. *A priori* if the atoms whose positions are not known are assumed to be randomly distributed the probabilities of the sign of a reflection are equal. But given a certain set of observed intensities or amplitudes, these probabilities become different from one half each and depend not only on the observed intensities but also on certain quantities called mixed moments solely dependent on space groups. The solution of the structure of dimethoxybenzophenone recently may be said to be one of the outstanding successes of this method.

There is, however, an approach to crystallography which is completely different from the procedures given above. This is based on the pioneering work of Federov and Barlow who speculated about the structures of crystals based on simple packing considerations. The work of Federov on the filling of space with identical polyhedra having the same orientation is well known. He found that this was possible with five types of polyhedra. Later workers have considered the problem of filling space with regular and semi-regular solids either alone or in combination but without the Federov restriction on orientation. Further developments in this method have been associated in recent years with Goldschmidt, Pauling and Wells. These attempts at explaining crystal structure on the basis of packing, rather than the conventional methods of lattice and symmetry, are based on the following considerations, *viz.*, that it is possible to calculate quite generally the field of force around each atom

or other structural unit; it would then be possible to know its bonding requirements and hence one could proceed to compute the spatial arrangement of the lowest potential energy. This would normally be a compromise between the requirements of different kinds of atoms, if more than one kind are involved. If, for example, the field of force is spherical, one could expect the structural unit to form a closed packed structure. But one cannot directly predict which of the closed packed structures—cubic, hexagonal or the more complex varieties —will have the least energy.

A serious attempt to understand the principles underlying the structure of crystals on this basis has been made by Dr. A. F. Wells* and he has presented the experimentally determined crystal structures from the point of view of topology rather than the conventional approach of lattices and symmetry. The procedures adopted by him are somewhat on the following lines. When considering the structure of a substance having a particular formula instead of following the conventional practice of discussing all the known structures of substances of similar formula-type, an attempt is made to derive all the simple structures possible for this formula consistent with the requirements of the atoms involved (like co-ordination number, number of bonds per atom, etc.) and then to discuss the observed structure against this background of crystal geometry. To do this a very careful survey has been made by him of the basic geometry underlying the structure of crystals, the nature of periodic network of connected points, etc. It has even been necessary also to develop the theory of three dimensional networks. Wells not only considers the cases of space filling polyhedra but also those of open packings of polyhedra, close and open packing of equal and unequal spheres. It would be very difficult to give a brief summary of Wells' work but it is indeed most impressive to note how many of the so-called complicated structures make use of extremely simple structural themes. There can be no doubt that this approach to crystallography would prove so fruitful that it should form the subject of intensive study by every serious crystallographer.

S. RAMASESHAN.