

New concepts of crystal structure

As is well known, the theory of crystal structure was worked out by Sohncke, Schoenflies and Federov in the 19th century on a purely geometric basis long before the discovery of the diffraction of X-rays by crystals opened up the possibility of the physical exploration of their atomic structure. The results of the geometric theory are embodied in the statement that any crystal must belong to one of the 230 possible space-groups, which in their turn are derivable from the 32 possible point-groups or symmetry classes to which a crystal can be assigned; these symmetry classes can be grouped together so as to yield the well known classification of crystals into six (or seven) divisions. The theory of space-groups rests on the premise that the structure of a crystal exhibits the translational symmetry of a space-lattice or three-dimensional network of equally spaced points; a number of such lattices similar and similarly situated but not coincident interpenetrate each other, and the structure of the crystal is obtained by locating a set of atoms of the same kind at all the points of each such lattice. The enumeration of the possible space-groups is based on a consideration of the various types of symmetry which could be exhibited by such a structure. In passing from the point-groups to the space-groups, some additional types of symmetry become possible, viz., glide-plane reflexions and screw-axes, the effect of which is to multiply the number of lattices which are occupied by atoms of the same kind and to locate these atoms within the unit cell of the structure at equal intervals which are integral submultiples of the lattice spacings. The theory of space-groups is complete in itself and its conclusions are fully borne out by the results of the X-ray investigations made with crystals. The determination of the space-group to which a crystal belongs is possible by X-ray study, the so-called absent reflexions giving the clue to the existence of glide-plane reflexions and screw-axes as elements in the symmetry of the structure. Indeed, assignment in this manner of the crystal to the space-group to which it belongs is a necessary step in the task of completely elucidating its structure.

While the complete generality and utility of the theory of space-groups are unquestionable, the nature of the approach which it makes to the subject of crystal structure is purely formal and geometric, and hence the theory cannot take us far towards a physical understanding of the facts of crystal structure. It only tells us what combinations of the various elements of symmetry are possible and the results of such combination, but is not concerned with the reasons for their appearance. A characteristic feature of the theory of space-groups is the introduction, in all except some special cases, of undetermined parameters in the

description which it affords of crystal structure. The appearance of unknown quantities in the description of a structure characterised by perfect order and symmetry must be considered a disturbing and unsatisfactory feature and is an indication that the foundations of the theory have not been laid deeply enough in the groundwork of physical reality.

An alternative approach

It is proposed in the following to put forward tentatively a concept of crystal structure which, while it is radically different from that forming the basis of the theory of space-groups, does not come into conflict with the results of that theory, but on the other hand, affords a physical interpretation of them, and also explains many facts known regarding the structure of crystals which have hitherto remained without adequate explanation. The concept proposed may be stated in the form of four propositions or postulates.

- I. All the atoms in a crystal whether of the same or of different kind are located at the points of a common space-lattice: but not all the points of the lattice are necessarily occupied.
- II. The locations of the atoms at the points of the common space-lattice with respect to each other are determined by fixed rules derived from their mutual affinities.
- III. The unit of the structure which results from the grouping of the atoms around each other at the points of the common space-lattice is of the same species as the cells of that lattice, but its dimensions are integral multiples of the cell dimensions.
- IV. The valence directions in the crystal structure obey the law of rational indices.

We shall now proceed to comment upon each of these postulates in turn, offering some sort of justification for each of them and pointing out their interrelations. The first postulate contains the kernel of the proposed new concept of crystal structure. Various considerations may be urged in favour of its acceptance. In the first place, it removes all uncertainty or arbitrariness in the specification of crystal structure, and has thus a purely philosophical or a priori justification. Secondly, it may be remarked that for a variety of atoms of different kinds to settle down to form the regular arrangement in space which we call a crystal, it is clearly necessary that they should all take up places in a common plan and the simplest assumption which we could make regarding the nature of this plan is that it is a three-dimensional network or space-lattice, the points of which provide locations for all the atoms. It is also evident that the existence of such a plan does not necessitate that all the points in the lattice should be filled. *Per contra*, the existence of unfilled places would, in general, be necessary if atoms of

different kinds and, therefore, of different sizes are all to be accommodated in the same lattice.

Our second postulate scarcely needs detailed justification. The atomic interactions would obviously determine the manner in which the atoms would take up positions in the postulated common space-lattice, and unless these interactions are of such a nature that they result in specific types of grouping of atoms of the same kind or different kinds about each other, anything like the regular order characteristic of a crystal would clearly be impossible.

Our third postulate may be regarded as consequential on the first two. If we postulate definite types of grouping of the atoms about each other in a common space-lattice, the final result of such grouping should exhibit the various types of symmetry shown to be possible by the theory of space-groups. In the first place, the structure would repeat itself in three dimensions at regular intervals, which are integral multiples of the spacing of the primitive lattice. In other words, the resulting structure would be such that the atomic co-ordinates in the unit of the structure would all be integral multiples of the spacing of the primitive common lattice, and, therefore, either rational sub-multiples or rational fractions of the dimensions of the structural unit. Thus, our postulates would lead naturally to the appearance in all cases of a translational symmetry in the structure of the crystal and also in appropriate special cases, to the types of symmetry recognised in the space-group theory as arising from glide-plane reflexions or screwaxes. But the existence of rational relationships between the atomic co-ordinates and the dimensions of the structural units is a general consequence of our postulates and is not restricted to such special cases.

Our fourth postulate is not an independent one but is merely consequential on our first and second postulates. But it appeared worthwhile to put it forward as a distinct postulate because of its obvious importance in relation to the views of crystal structure here considered, and also because it appears possible to find an independent justification for it. The idea of a directed valence is a fundamental notion of chemistry and is stressed in organic chemistry with reference to the so-called "tetrahedral" valence directions of the carbon and silicon atoms. But one has only to recall cases like cyclo-propane or cyclo-butane to stress the fact that even in saturated carbon compounds. The valences of carbon are not necessarily tetrahedral and that their directions are influenced by the structure. Thus, if the notion of valency has any meaning at all in relation to the crystalline state of matter, we may expect to find the directions in which it is exerted, in other words, the directions of the lines joining neighbouring atoms to bear some simple and specific relations to the structure of the crystal. If such relationships exist, their nature should be of the law of rational indices which one naturally regards as the most fundamental fact of crystal architecture. Thus, if our fourth postulate is regarded as having an independent theoretical justification, our first postulate would be a consequence of it, and vice versa.

Lest it be thought that our present approach to the theory of crystal structure is

hypothetical and speculative, it may be pointed out that a great many inorganic crystals, both of an elementary and of a compound nature, whose structures have been determined with some assurance of finality may be described in terms of our present concepts. Indeed, all crystals in which the atomic co-ordinates have been found to be simply related to the lattice spacings, either as a rational sub-multiple or as a rational fraction thereof fall naturally into the present scheme of thought. Many such structures may be found on an examination of the tabulated results of X-ray analysis. Particularly significant are those cases in which atomic locations of this kind are not demanded by the results of space-group theory.

Some outstanding questions

Before concluding, it may be worthwhile to reply briefly to some criticisms which may be urged against the present point of view. The most likely criticism that might be urged is that there are apparently well-attested cases of crystals in which the atomic co-ordinates are *not* expressible as rational sub-multiples or rational fractions of the structural cell-dimensions. The answer to this criticism is that such cases deserve careful re-examination with regard to the facts or their interpretation. The atomic co-ordinates here considered are the positions of the atomic nuclei, while the co-ordinates determined from the study of X-ray reflexion-intensity represent the optical centres of the electronic clouds surrounding the nuclei. If the electronic clouds are not spherically symmetrical, the locations determined from the X-ray intensities would not necessarily be those of the atomic nuclei. Another possible source of error in the X-ray studies is the thermal agitation of the atoms which may be considerable and not necessarily symmetrical about the nuclear positions. Not until these and other possible sources of error in the X-ray studies are carefully considered and eliminated in various simple cases which appear to conflict with the present point of view could their evidence be considered to outweigh the significance of the large number of cases in which it does fit with the facts and offers an intelligible explanation of them.

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