

# Liversidge Research Lecture

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MODERN STRUCTURAL INORGANIC CHEMISTRY

A. D. WADSLEY, D.Sc., F.R.A.C.I.



The Royal Society of New South Wales



**Arthur David Wadsley**

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### ARTHUR DAVID WADSLEY 1918-1969\*

**Arthur David** (David) **Wadsley** was born on 1 August, 1918 in Hobart, Tasmania. After secondary education at Clemes College (Hobart), he worked for one year as a laboratory assistant at the Research Laboratories of the Electrolytic Zinc Co. in Risdon, Tasmania. He then studied at the University of Tasmania, graduating B.Sc. in 1940 with High Distinction in Primary Metallurgy. During an 'Honours Year' he also studied Secondary Metallurgy at Hobart Technical College, and graduated with Honours (2nd class) in 1941. Under the supervision of Professor E.E. Kurth, he then worked on the preparation of magnesia and magnesium chloride from Tasmanian dolomite; he completed the requirements in mid-1941, and graduated M.Sc. in 1942. His first professional position was as a Physicist/Grade I at the Munitions Supply Laboratory, Maribyrnong, Melbourne. He subsequently became Tutor in Chemistry at Queen's College, University of Melbourne, and early in 1943 he was appointed as a chemist at the Minerals Utilization Section of the CSIRO Division of Industrial Chemistry (Melbourne). His most important research work there commenced with a review article "The crystal chemistry of non-stoichiometric compounds" (A.D. Wadsley, *Revs. Pure and Appl. Chem.*, 1955, **5**, 165-193) - which marked the beginning of his life's work on this topic. In it he observed, described and discussed the phenomenon of "crystallographic-shear (*CS*) structures" - then rather recent, but now well-known. This paper, together with his earlier ones on the structures of various manganese oxides (lithiophorite, psilomelane and chalcophanite) were the basis of his thesis, for which he was awarded the degree of D.Sc. from the University of Tasmania in 1956.

In 1958, in his remarkable Liversidge Research Lecture, (reproduced below) he further developed his ideas, briefly summarizing his speculations about the ways in which non-stoichiometry could be structurally accommodated, especially in *CS* structures. As an alternative to the prevailing "random point defect model" of non-stoichiometry he proposed an alternative for which there was already some supporting experimental evidence, but which was generally dismissed as a "special case": he pointed out that inhomogeneities in some oxide systems could not be attributed to "vacancies" or "interstitials", but to "crystallographic shear" along planar faults. His hypothesis was widely disseminated - and accepted - at an American Chemical Society meeting in Washington in 1962, at which the two opposing viewpoints were (intentionally) pitted; and he became known for originating the only advance in the field in 30 years. In the next six or seven years his work provided substantial and detailed confirmation of the ideas propounded in his Liversidge Lecture.

This work comprises: (i) a flood of detailed, X-ray, structural evidence (in collaboration with, particularly, Sten Andersson in Stockholm and Bob Roth visiting Melbourne from the U.S. National Bureau of Standards) stemming from his discovery of the first "block structures" (with two sets of *CS* planes at about 70 - 80°); (ii) his

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\*The author is very grateful to Professor B.G. Hyde who made a major contribution in the writing of this biographical sketch of A.D. Wadsley. See also item (4) Biographical Sources

development (with John Snaders and John Allpress of the CSIRO Division of Tribophysics) of the first application of electron microscopy (*EM*) to the structural nature of stoichiometric - and the "texture" of nonstoichiometric" - crystals. An important key to the "block structures" was his determination (with B.M. Gatehouse in 1962) of the structure of H-Nb<sub>2</sub>O<sub>5</sub> (one of the many polymorphs of Nb<sub>2</sub>O<sub>5</sub>, which had defied crystallographic solution for more than a decade). The structures of TiNb<sub>24</sub>O<sub>62</sub> and PNb<sub>9</sub>O<sub>25</sub> were determined, and then a host of more complicated structures with various block sizes and modes of block connection were solved. The *EM* work revealed nonstoichiometry resulting from planar faults (corresponding to shear planes) due to intergrowth of one phase with another, and other phenomena - exactly as he had predicted more than a decade earlier. The composition of non-periodic blocks differed from that of the host crystal; this fact led Sten Andersson to propose (just after Wadsley's death, in 1960) that these be called 'Wadsley defects'.

Other important areas that illustrated the importance and relevance of his "intergrowth principle" were his continuing interest in oxide bronzes of vanadium, titanium, molybdenum and niobium. In the late 1960s he collaborated with A.F. Reid and A.E. Ringwood on a study of the structural behaviour of silicates under high pressure with the aim of shedding light on phase relations deep in the earth's mantle.

David Wadsley was appointed Chief Research Scientist in 1964 and Assistant Chief of his CSIRO Division in 1967. He was the invited plenary lecturer at the IXth Coordination Chemistry Symposium (held in St. Moritz in September, 1966), "*Composition, Coordination and Valency in Lattice Compounds*". This meeting commemorated the centenary of the birth of Alfred Werner - an inorganic *coordination chemist* (not a solid state chemist) - and the invitation recognised the impact of Wadsley's work on inorganic chemistry as a whole. He died at the relatively young age of 51, at the height of his eminent career.

### Awards and Honours

- 1956 D.Sc., University of Tasmania
- 1957 H.G. Smith Medal, R.A.C.I.
- 1958 Liversidge Research Lecture, Royal Society of N.S.W.
- 1965 H.G. Smith Medal, R.A.C.I.
- 1991 Dedication of the A.D. Wadsley Laboratory, CSIRO Division of Mineral Products, Port Melbourne, Victoria

### Biographical Sources

1. Andersson, S., addendum in *The chemistry of extended defects in non-metallic solids*, ed. L. Eyring and M. O'Keeffe (Amsterdam: North Holland, 1970), (Proceedings of an "Advanced Study Institute", Casa Blanca Inn (Scottsdale, Arizona, April 16-26, 1969); also, Andersson, S., *J. Solid State Chem.*, 1970, **1**, v-vi.
2. Anon. (I.E. Newnham), obituary 'Dr A.Wadsley', *Nature*, 1969, **222**, 101.

3. Anderson, J.S., 'The microstructure of nonstoichiometric compounds; David Wadsley's influence and recent work', *Revs. Pure Appl. Chem.*, 1971, **21**, 67-82.
4. Professor B.G. Hyde, personal communication: Bruce Hyde has written a detailed scientific biography of David Wadsley entitled 'David Wadsley's Science', (218 pages, 33 figures), that is yet to be published

#### **Scientific Publications by A.D. Wadsley**

A list of the 69 scientific publications by A.D. Wadsley, compiled and kindly supplied by Professor B.G. Hyde, is given in the Appendix.

## MODERN STRUCTURAL INORGANIC CHEMISTRY\*

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### Introduction

By any standards, the late Professor Archibald Liversidge was a very great man, who exercised a profound influence upon science in Australia as well as in the United Kingdom. His long association with the Royal Society of New South Wales and the Australian and New Zealand Association for the Advancement of Science, in both of which he held high office, is perpetuated by means of special lectures, and I am very proud of being asked to deliver one of them. In fact it is a challenge of a unique kind. Generalities and reviews are not enough to justify the conditions under which it is offered, but "it will be such as will primarily encourage research, and not by giving instruction in what is already known". This is no easy task, offering as it does an invitation to evaluate some field with emphasis on what still needs to be done.

In the solid state chemistry is three-dimensional, and structural chemistry is concerned primarily with the arrangements of atoms, their motions relative to one another and the forces which exist between them. It deals with organization rather than with transient phenomena. Two ideas represent turning points in the history of chemistry, and it is significant that in each the third dimension was introduced. Organic chemistry became a science after van't Hoff and le Bel introduced the concept of the tetrahedral carbon atom, and subsequently the architecture of molecules could, in principle, be established by chemical means. The first major advances in the systematic study of salts were due to Werner's theory of coordination number, the ligands to a metal atom being disposed in a definite geometrical pattern. Various chemists experimented with chemical models which were based upon the repetitious packing of spheres, but it was not until the introduction of X-ray diffraction analysis that these matters could be proved and extended. The chief triumphs of this most elegant discipline attended the introduction of the mathematical techniques of Fourier analysis in which, systematically if laboriously, the centres of scattering matter could be accurately deduced and the configuration of even the most complicated of molecular or ionic systems established. It is still, however, an impossible task to find direct evidence of chemical bonds, and as solid-state chemistry is based ultimately upon the bond-forming characteristics of atoms one must still, in the best traditions of science, rely upon speculations and theory. As data accumulate and laboratory techniques improve, the laws of chemistry undergo continuous revision. Theory must give way before facts, which may be regarded as the experimental verification of ideas. This method of successive approximation is the essence of research work and it is seldom that any problem, no matter how trivial it might appear, could not be expected to throw a shadow of uncertainty upon chemical principles.

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\* Liversidge Research Lecture delivered before the Royal Society of N.S.W., 29th July, 1958. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1958, **92**, 25-35.

At the present time, structural inorganic chemistry may in one sense be regarded as very well documented. We have only to turn to books such as W. L. Bragg's "The Atomic Structures of Minerals", A. F. Wells' "Structural Inorganic Chemistry" and "The Nature of the Chemical Bond" by L. Pauling to realize the extent of facts which are known. As a field of research work, one might well take the view of bringing these volumes up to date by filling in the gaps or by the inclusion of newer or refined data. But this would not be in the spirit of the Liversidge lecture. Rather, different avenues of experimental chemistry must be sought, and this could be done in several ways.

One could explore a new field of solid-state chemistry if the experimental methods by which simultaneous high pressures and temperatures are achieved were made available. The synthesis of diamond, cubic boron nitride and a high-density form of silica (coesite) is known. But many ionic substances, not in the most compact form under ordinary conditions, could be expected to have other structures which are the most stable at high pressures. If these revert rapidly to the normal forms on the release of pressure, techniques of X-ray analysis at high pressure could be developed. The valency states which exist at high pressure must also be the subject of future studies.

Alternatively, one may expect much new research work in structural chemistry in another direction. Reaction between solids is initiated by heating, which supplies the necessary energy. Heat may often change the total chemical composition, particularly if hydrogen, fluorine, the alkali metals or some other volatile component is present. Will other forms of energy, such as fast neutrons, be capable of inducing chemical changes at low temperatures? Or can they bring about transformations into disordered or polymorphic forms?

Possibilities such as these are a matter for conjecture with the present state of knowledge. Tonight, instead, I propose to examine a path in which, at the present, ideas of structure are slowly developing, and which may lead ultimately to the reassessment of much of the data at present taken for granted in certain chemical systems.

Solid-state chemistry is a name now largely used to describe compounds of the metals with the non-metals of the first, second, third and fourth periods of the periodic table. It also includes compounds formed between these elements. It embraces many of the disciplines of mineralogy, metallurgy and solid-state physics as well as of chemistry. Compounds in this definition are regarded as ionic, although in many cases covalent bonds are formed. The structures are formed by networks of atoms coordinated together which terminate only at the boundaries of the crystal or at some other discontinuity. If the metal ion can adopt two different valency states in the one phase, there is no reason why the compounds it forms should conform to the earliest quantitative laws taught in chemistry, the laws of constant and of multiple proportions. A *non-stoichiometric compound*, in J. S. Anderson's definition (1946), is a homogeneous phase with a range of composition, and in which the maxima or minima of properties - melting point, conductivity, lattice order - do not coincide with a rational atomic ratio of the components.

The reasons for variation of composition are threefold:

(a) Ions of either sort or both simultaneously may be absent from the network of atoms.

(b) Additional ions may occupy positions which are normally vacant.

- (c) The grouping of ions in certain crystallographic planes may alter so as effectively to reduce the numbers of one kind.

It is difficult, except in the briefest way, to discuss all of these matters in the time which is available, and I propose to limit my remarks to the first and third of these mechanisms. The second has been dealt with elsewhere (Wadsley, 1957a).

### Phase Systems where Metal Vacancies Occur

In a classic investigation Hägg (1935) showed that  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{Fe}_2\text{O}_3$  represented the limits of one particular non-stoichiometric phase with the spinel structure. Based upon the crystallographic data,  $\gamma\text{Fe}_2\text{O}_3$  more properly had the formula  $\text{Fe}_{22/3}\text{O}_4$ . Variability of composition was proved to be due to the removal of iron atoms from  $\text{Fe}_3\text{O}_4$  in which they were all present, and charge deficiencies were adjusted by changes of valency of the metal ions remaining. It should therefore be written  $\text{Fe}_{22/3}\text{vac}_{1/3}\text{O}_4$ . The structure was a continuous variable giving rise to the term "subtractive solid solution".

It has been shown by subsequent studies that in different preparations of  $\gamma\text{Fe}_2\text{O}_3$  having substantially the spinel lattice, the vacancies could be ordered (Braun, 1952; David and Welch 1956). This takes the form of weak additional lines in an X-ray diffraction pattern due to a superlattice, which is a repeat unit indicating the loss of some of the elements of symmetry.  $\gamma\text{Fe}_2\text{O}_3$  could vary between the limits  $\text{Fe}_8[\text{H}_4\text{Fe}_{12}]\text{O}_{32}$  to

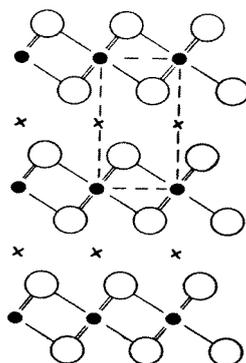


FIGURE 1

In the NiAs-like grouping, the metal atoms (drawn both as small black circles and as crosses) are each bonded to the non-metals (large open circles); the removal of the metals marked by crosses results in the  $\text{CdI}_2$ -type arrangement (in projection). The unit cell for both is drawn in broken lines.

$\text{Fe}_8[(\text{Fe}_{11/3}\text{vac}_{22/3})\text{Fe}_{12}]\text{O}_{32}$  for any one unit cell. The hydrogen ions replace iron atoms and vacancies which together form a set of octahedral sites strictly defined by the diffraction data. More recently still there is evidence (van Oosterhout *et al.*, 1958) of another superlattice three times larger than the spinel unit cell, in which the formula is  $\text{Fe}_{24}[(\text{Fe}_4\text{vac}_8)\text{Fe}_{36}]\text{O}_{96}$ .

It now appears that there are at least three possible arrangements for this one substance in which the vacancies are randomly distributed, partly ordered, or fully ordered over a

limited number of the metal positions. Only one end member of a system in which the iron content is variable has been considered, and it is by now evident, if vacancies (or hydrogen atoms) adopt a definite structural role as they appear to do, that the system is no longer a two- but a three-component one. The term "solid solution" has little meaning. Classical methods of phase analysis are difficult to apply in cases such as this, the evidence having been collected by and large as the results of chance experiments. Methods of systematic study need to be developed, and hydrothermal techniques will undoubtedly assume great importance, particularly where hydrogen plays a structural role. The pH potential phase diagrams used by Pourbaix (1949) in the field of metal corrosion have been used effectively in geochemical studies of uranium and vanadium (Garrels, 1955; Evans and Garrels, 1958). By introducing the temperature variable as well, with its associated hydrothermal pressure, this would develop into a most powerful tool.

Until not very long ago, the system chromium-sulphur was regarded as homogeneous within the range CrS-Cr<sub>2</sub>S<sub>3</sub>. This was supposedly due to the random removal of metal atoms from CrS which had an atomic arrangement usually referred to as the NiAs type. This is widely believed to be a very common mechanism for the sulphides, selenides and tellurides of the transition metals, and in favourable cases the complete removal of half the cations results in the CdI<sub>2</sub>-like structure (Fig. 1). Often this elegant transition is found only within limited ranges.

Jellinek (1957) has shown quite conclusively that this is an oversimplification, and that there are six recognizable compounds which exist within the limits given above. These are CrS, Cr<sub>7</sub>S<sub>8</sub>, Cr<sub>5</sub>S<sub>6</sub>, Cr<sub>3</sub>S<sub>4</sub> and Cr<sub>2</sub>S<sub>3</sub> in two forms. All are distinct phases with no range of composition and with no solid solution between them; they are strictly stoichiometric. In Figures 2 (a) and 2 (b) the structures are shown diagrammatically, the metal atoms alone being drawn. In each case vacancies which occur are confined to each

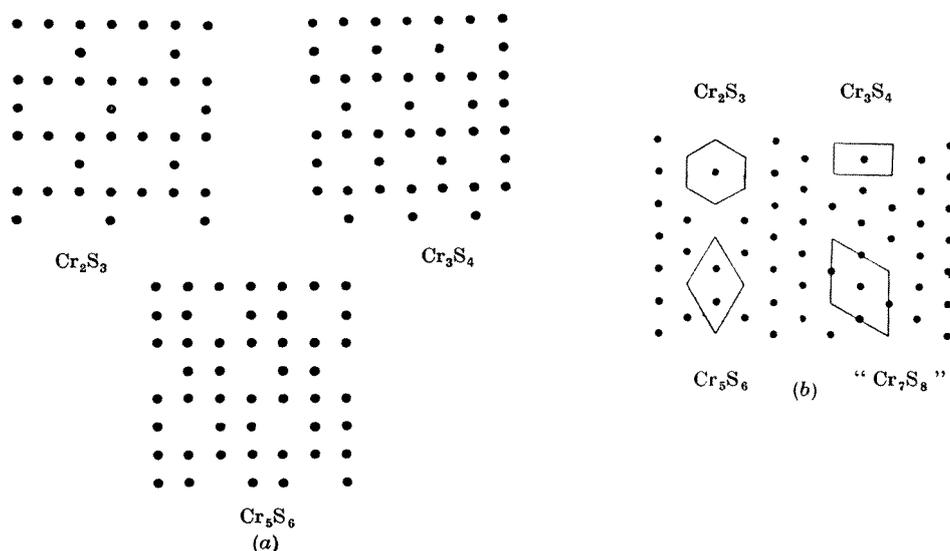


FIGURE 2

- (a) The structures of Cr<sub>2</sub>S<sub>3</sub>, Cr<sub>3</sub>S<sub>4</sub> and Cr<sub>5</sub>S<sub>6</sub> drawn in projection, the sulphur atoms being omitted for clarity. In each case the vacancies are confined to alternate metal atom layers and form a regular sequence, both in each sheet and between "defective" sheets.
- (b) A single sheet of metal atoms. The geometrical figures show how the vacancies form regular patterns of different kinds. For a particular phase the appropriate pattern is regularly distributed over the whole of each defective sheet. "Cr<sub>7</sub>S<sub>8</sub>" is modelled upon Fe<sub>7</sub>S<sub>8</sub> (Bertaut, 1953).

alternate layer of metal atoms. Different arrangements of the vacancies are characteristic of the different phases. In  $\text{Cr}_7\text{S}_8$  they are random, and the structure is therefore only partly ordered; in  $\text{Fe}_7\text{S}_8$  they are ordered (Bertaut, 1953), and the grouping of vacancies is included in Figure 2 (b) for comparison. This system may again be considered a ternary one in which a vacancy assumes the role of a lattice component.

The possibility exists that there are additional phases within the range  $\text{Cr}_7\text{S}_8$ -CrS. If based upon the scheme elucidated by Jellinek, their structures would be based upon other methods of arranging hexagonal or rectangular networks of holes. If these are too far apart, it is likely that the holes or vacancies are clustered together as in the defective layers of the  $\text{Cr}_2\text{S}_3$  or  $\text{Cr}_3\text{S}_4$  kind, and these groups, regular in themselves, are disordered in any one layer. This, with the evidence of a two-phase region, seems unlikely. But additional experimental variables have not been studied systematically - temperature of formation or temperature of annealing. Furthermore, since the segregation of structural units is a rate-controlled process, the time of heat treatment must also be considered. The examination of the phase system by X-ray diffraction was made at normal temperature and pressure (N.T.P.) which, on an absolute scale, is a purely arbitrary point and as a reference has little meaning.

In the simplest case the continuous structural variation between CrS and  $\text{Cr}_2\text{S}_3$  could be expected to occur as a high temperature sequence, and this could be examined either by using high temperature diffraction techniques or by "quenching in" the high temperature structure. If it exists it is then a special idealized case. What could one expect to find in the structures of layer lattices of this kind as a consequence of controlling these sundry variables?

Polymorphous forms may arise as the result of different stacking sequences in the non-metal layers. This is found for  $\text{Ti}_2\text{S}_3$  (Wadsley, 1957*b*) and  $\text{Zr}_2\text{Se}_3$  (McTaggart and Wadsley, 1958).

For the vacancies in the metal positions there are several methods of distribution:

- (a) Randomly distributed over all the octahedral positions and not confined to every second layer.
- (b) Randomly distributed in every second (or third, etc.) layer.
- (c) Ordered in alternate layers but with no three-dimensional ordering.
- (d) Confined to layers, either ordered or disordered, but with these having no regular sequence.
- (e) Ordered layers of two or more kinds.

The list of possibilities is immense, but there is good reason to suppose that they will eventually be found, if not by X-rays, then by electron diffraction. The literature on the crystal chemistry of layer silicates, clays, the lamellar compounds of graphite, on the polymorphism of silicon carbide and zinc sulphide, the bismuth oxyhalides (Wadsley, 1955) provide much evidence in support. The systematic examination of order-disorder transitions in sulphides or oxides has been limited to one or two examples (Frueh, 1950).

No relationships between transition temperature and structure, or some other parameter, have been established. The literature contains much conflicting evidence which arises from an inadequate appreciation of these matters. There are little or no thermodynamic data despite the obvious need for a measurement of an *order* term.

If we accept the abundant evidence that vacancies do exist and that, energetically and structurally, it is most probable that they tend to a system of order, one may well ask why they are present in the first instance. Schottky and Wagner (1930) worked out the conditions of equilibrium for lattice defects in a real crystal, and this has been useful in the subsequent application to problems of solid-state physics. But when the concentration of defects, of one kind or another, is large, a different approach is required in which the emphasis is upon energetics rather than upon statistical methods.

Each metal atom, in all the chromium sulphides which were previously discussed, has seven or eight nearest neighbours, six being sulphur atoms in an octahedral grouping; the others are metal atoms close enough to be regarded as forming a metallic type bond. Can solids of this kind be called intermetallic compounds? Many of them have some of the properties of metals - lustre, electrical conductivity or semi-conductivity, and ductility. The electron theory of metals, or some modification of it, could be expected to play an important part (Frueh, 1954), not only in terms of rate processes on the surface, but in the study of the solid itself which is our immediate objective. The Brillouin zones represent locations of discontinuities in the energy states which are permissible to free electrons in the periodic field of a crystal structure. A recent determination of the zones for AgCuS (the mineral stromeyerite) proved that a fractional number of silver ions gave a better electron-to-atom ratio than a whole number (Frueh, 1955). Any electrons in addition to these would need to be at a considerably higher energy level. Rather than attempt to accommodate these, some atoms were omitted. This is according to fact. Stromeyerite always has a deficit of sulphur; careful preparations of the composition AgCuS always contained free sulphur, and it was proved that the stable phase had the composition  $\text{Ag}_{0.9}\text{CuS}$ .

This approach, properly applied and extended, could give reasons why non-stoichiometric compounds may exist, and could, with refinement, give composition limits. Yet this is the only example in which it has been tried. Properties such as low temperature heat capacity, thermal and electrical conductivity, Hall effect, will also be fruitful sources of information when they are more widely accepted by the chemist and the geologist.

### **Systems in which Changes of Polyhedral Grouping, or Shears, Occur**

Originally it was supposed that the oxides a metal could form were based upon the valency of ions in the dissolved state. Since  $\text{Ti}^{4+}$ ,  $\text{Ti}^{3+}$  and  $\text{Ti}^{2+}$  were believed known, it was assumed that titanium could form three oxides,  $\text{TiO}_2$  (three polymorphous forms of which were known in mineralogy),  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}$ . These were proved to exist by preparation and by chemical analysis. A tensimetric X-ray study later showed that more phases than these could be formed (Ehrlich, 1939, 1941); moreover, they were non-stoichiometric and could be represented as single-phase regions by the formulae  $\text{TiO}_2$ - $\text{TiO}_{1.9}$ ;  $\text{TiO}_{1.8}$ - $\text{TiO}_{1.7}$ ;  $\text{TiO}_{1.56}$ - $\text{TiO}_{1.46}$ ; and  $\text{TiO}_{1.35}$ - $\text{TiO}_{0.6}$ . This particular phase system was confirmed in most respects by several workers, and a "not impossible" phase diagram was constructed to summarize the work up to 1954 (De Vries and Roy, 1954).

Very recently, however, the same system has again been examined with great attention to detail, and at least seven previously unnoticed phases were found to exist within the range  $\text{TiO}_{1.75}$ - $\text{TiO}_{1.9}$ . It was shown that they could all be represented by a general formula  $\text{Ti}_n\text{O}_{2n-1}$  having whole number values between 4 and 10 (Andersson *et al.*, 1957). Each of these substances is strictly stoichiometric and was prepared by melting, and then annealing, mixtures of titanium metal and the dioxide in the appropriate proportions. They should therefore have been found in the previous phase studies. Can these two sets of careful work be reconciled?

The crystal structure of  $\text{Ti}_5\text{O}_9$  has now been worked out in detail (Andersson, MS. 1958)\*. It consists of the rutile structure in the form of blocks which are separated by regular discontinuities. At the junction of the blocks (in which the octahedra which constitute the structure share edges and corners) some octahedra share faces as well as edges (Fig. 3). The net result is the loss of oxygen in the unit cell, which now has a complex formula. It is to be expected that other members of the series  $\text{Ti}_n\text{O}_{2n-1}$  will have structures of a closely related kind.

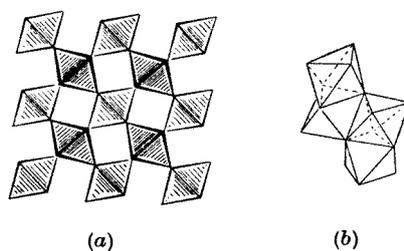


FIGURE 3

- (a) The structure of  $\text{TiO}_2$  (rutile) represented as octahedra viewed in projection down the edges. The octahedra share corners, as well as edges above and below the plane of the paper.
- (b) Discontinuity in  $\text{Ti}_5\text{O}_9$  (drawn in perspective) which joins blocks of the normal rutile structure. Faces as well as edges are now shared.

A series of oxides is known which has the general formula  $(\text{Mo,W})_n\text{O}_{3n-1}$ ,  $n$  having values between 8 and 14 inclusive. The structure of each is based upon that of  $\text{WO}_3$  which consists of W-O octahedra sharing all six corners with similar ones [Fig. 4 (a)]. In the series, blocks of this structure are separated by discontinuities or shears in which the octahedra of adjacent blocks share edges with one another, again resulting in a loss of oxygen [Fig. 4 (b)]. Differences between individual members of the series are restricted only to the widths of the unchanged  $\text{WO}_3$ -type blocks, the discontinuity for all members being identical. The numeral  $n$  in the general formula can be used as a measure of the distances between the discontinuities (Hägg and Magnéli, 1954).

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\*The author is grateful to Dr. Sten Andersson, University of Stockholm, Sweden, for allowing him to quote this work prior to its publication.

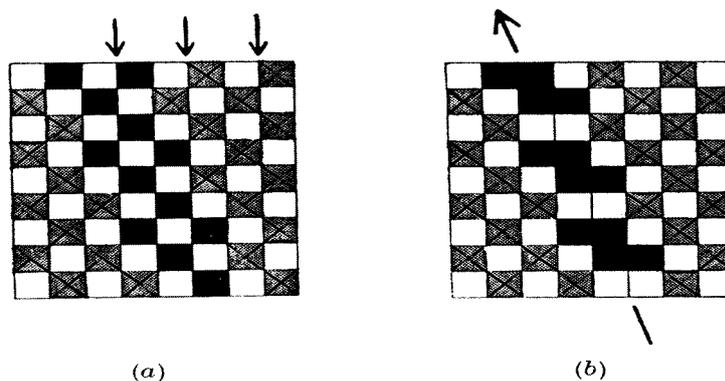


FIGURE 4

(a) The structure of  $\text{WO}_3$  (idealized) in projection, the squares representing octahedra. The black squares are those which adopt a new configuration if blocks of the structure are moved by a hypothetical force applied in the direction of the arrows.

(b) The direction of the discontinuity or shear is indicated by the arrow. The black octahedra now share edges with each other, and corners with unchanged blocks of the normal  $\text{WO}_3$  structure. This type of shear is common to all members of the homologous series  $(\text{MoW})_n\text{O}_{3n-1}$ .

The existence of these series is not in itself remarkable. The members are quite stable and can be crystallized; they form structures which are perfectly rational, and the only difficulty which is presented is that of the valency of the metal ions. But in many diverse chemical systems it is now becoming clear that compounds with mixed or fractional valencies may contain free electrons which are raised in energy level to the conduction band. With their high mobility they give the solid to which they are bound many of the properties of a metal. These oxides are no exception.

What is remarkable about them, from the structural point of view, is that the discontinuities are regular; perhaps the chosen experimental conditions of annealing and of heat treatment favoured the development of these particular phases. But it is possible to devise other structures of a similar kind.

Consider a finite number of regular blocks (let us say seven) separated by a discontinuity designated by the stroke /; the structure can now be represented as -7/7/7/7-. Other kinds of sequence -4/10/4/10- or -5/9/5/9-, etc., can be visualized and, in these, blocks of two (or more) different widths alternate with one another. These represent new phases, each of which would have the same chemical formula and density as one another

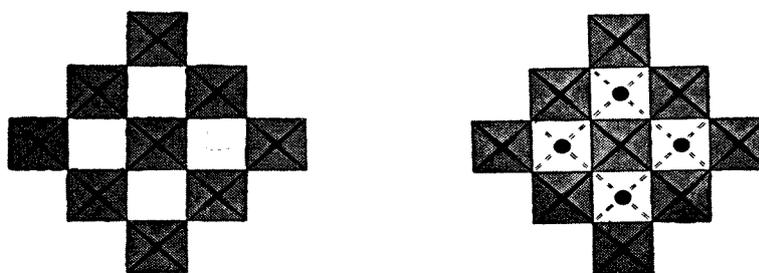


FIGURE 5. - The relationship between the structures of  $\text{WO}_3$  (left) and of the perovskite type (right). The squares are octahedra viewed down a corner, the small black circles additional metal ions which change the formula from  $\text{BX}_3$  to  $\text{ABX}_3$ .

and the original, differing only in the length of one axis and in one angle of the unit cell. Again, perhaps, two (or more) widths of block -6/6/8/6/8/8- would form in no ordered way; or segregate in disordered block "clusters" of one or more kinds -6/6/6/8/8/8/8/8/6/6-. This could well be identified as a two-phase region even although there is every reason to suppose it could exist in one single crystal.

As in the chromium sulphides, these speculations serve to introduce order-disorder which, as a variable, is seldom studied systematically in solid-state chemistry.

The series of titanium oxides ceases with the member  $Ti_{10}O_{19}$ ; there is some evidence that higher homologues do exist (Andersson *et al.*, 1957), but equilibrium conditions are not readily achieved in the region  $TiO_{1.9}$ - $TiO_2$ . If discontinuities of structure similar to those found in  $Ti_5O_9$  do occur, they are probably disordered. But they should at the same time give diffuse X-ray reflexions and these are often difficult to observe. The limiting case is represented by a single shear; this may well be related to the dislocation twin of the solid-state physicist.

Homologous series could well be expected in many of the simple types of lattice - the NaCl-type, wurtzite, and so on. Cerium (Bevan, 1955) and praseodymium oxides (Ferguson *et al.*, 1954) of complex formulae are known, and whilst the structures are based upon the fluorite lattice, it is uncertain whether they contain shears of a new type or ordered omissions of oxygen atoms. Preliminary work (Wadsley, MS. 1958) has demonstrated shear structures formed by mixed oxides of titanium and niobium, a model based upon a comparison of  $V_2O_5$  and  $V_6O_{13}$  having previously been proposed (Wadsley, 1957c). The  $(W, Mo)_nO_{3n-1}$  system, already mentioned, is perhaps the easiest of all to demonstrate, but it is based upon a lattice type which is rare. However, the structure is closely related to that of perovskite ( $ABO_3$  type) for which there are numerous examples (Fig. 5). Recent work has shown that  $SrTiO_3$  has the perovskite structure which persists over a range of composition to  $SrTiO_{2.5}$  (Kestigian *et al.*, 1957). Could a ternary series  $Sr_{n-1}Ti_nO_{3n-1}$ , closely related in every way, be formed? So far there is no evidence either for or against it, as annealing experiments have not as yet been made.

The shear or discontinuity mechanism will undoubtedly be recognized in future studies as a common one. Experiments could be devised, as they have been, to find evidence for it in different structural types. In the most favourable circumstances a closely related homologous series is found, but the experimental conditions, unless carefully chosen, may lead only to the observation of a solid solution which, again, must be regarded as a special case.

### Phase Rule

What has been discussed in this lecture may perhaps be described as speculations based upon experimental observations, and with questions posed by techniques and theories drawn from diverse disciplines. The classical approach to problems of this kind is based ultimately upon the Phase Rule which, in turn, is concerned with the relationship between phases in equilibrium with one another. But in these solid systems order-disorder phenomena are common, or could be expected to occur. The degree of order is a function of temperature and can be a continuous variable. The attainment of equilibrium at a particular temperature is a rate-controlled process which, in practice, may

never be achieved. Ubbelohde (1957), in a review of thermal transformations in solids, discusses these and other matters in terms of a modified equation

$$F = C + 2 + \sum \pi - P$$

where  $\sum \pi$  are additional "degrees of freedom", the other symbols having their usual meaning.

Indeed, at the present level of understanding a *phase* itself cannot be rigorously defined (Brindley *et al.*, 1958).

### Chemical Bonds

Little emphasis has so far been placed in this lecture upon the role of the chemical bond in solid inorganic substances. To the structural crystallographer, bonds exist between an atom and its nearest neighbours, and in practice this works out quite well. The nature of a bond, tetrahedral, octahedral or the like, is well established, but its character leaves room for speculation as the bond "lengths" and the "angles" between them are seldom ideal and rarely equal to one another. There is much current work, in chemical theory on the one hand and in coordination chemistry on the other, which has as its object the elucidation of the character of a chemical bond, and the help of the crystallographer is sought when anomalies arise or when precision is required. But the crystallographer has his own particular problem which, for want of a better term, can be called a structure-determining property of an ion, or perhaps a second-order bond effect.

In inorganic chemistry there are certain well-known groups of elements which, from the viewpoint of crystal chemistry, have identical characteristics - ionic radius, number of stable valency states and types of primary bond. Yet the compounds formed by the elements of any one group are not always alike, as one might well expect. As an example, the chemistry of zirconium and hafnium is virtually identical. Yet the crystal structures of the sulphides differ. ZrS has the NaCl structure, and the unit cell contains equal numbers of vacancies of both Zr and S. It has an extended homogeneity range to Zr<sub>2</sub>S<sub>3</sub> which still is based upon the same structure. HfS, on the other hand, has a complex unknown structure, probably related to CrS. Hf<sub>2</sub>S<sub>3</sub> is hexagonal and is related to Cr<sub>2</sub>S<sub>3</sub>, not to Zr<sub>2</sub>S<sub>3</sub>. Both ZrS<sub>2</sub> and HfS<sub>2</sub> have the same structures of the CdI<sub>2</sub> type (McTaggart and Wadsley, 1958).

Examples could be quoted for other pairs of elements, but it is not the function of this lecture to review the literature. In this particular case, both Hf and Zr form an octahedral grouping with the sulphur atoms. The structures they form are based upon the different arrangements of the octahedra, a second-order effect resulting in a cubic packing for the lower sulphides of Zr, a hexagonal for Hf. One could relate this behaviour in a qualitative way with some variable: the ionization potential; to an empirical measure of the effective shielding of the core of an atom by the electrons remaining after the bonding electrons are removed (Ahrens, 1954); or to the polarizability of the ion. But these variables cannot predict those compounds likely to differ in structure, nor why the effect is limited to certain specific compounds.

Trace amounts of foreign ions may also in this way influence the structure of solids. Ti<sub>3</sub>O<sub>5</sub> has one type of structure when it is very pure (Åsbrink and Magnéli, 1957). The substitution of iron for titanium even at the limit represented by the formula Ti<sub>2.9</sub>Fe<sub>0.1</sub>O<sub>3</sub>

involves a complete reorganization to another, the pseudobrookite arrangement (Zhdanov and Rusakov, 1954). In both the metal atom is in octahedral coordination.

However well based the conception of a new solid might be, and however well the choice of composition is made, the chemist is faced with the possibility of failure because these unknown or unforeseen matters cannot be assessed. It is still a matter of experimental trial and error, and therefore a subject for systematic research.

### Conclusions

In the terms of his bequest, the late Professor Liversidge suggested that this particular lecture would "stimulate the lecturer and the public to acquire new knowledge by research". This I have attempted to do by showing that as more is learned about the way in which solids are built, fresh avenues for study and for thought are revealed.

This branch of inorganic chemistry had its origins in mineralogy, and still continues to draw upon minerals as the raw material for study, as themselves or as chemical models. Whilst a complete phase study from this point of view is impractical, in an individual mineral the element of time as a degree of freedom can be eliminated.

At present, inorganic compounds, many of which are suggested by the chemical constitution of mineral analogues, are the subject for intensive research work in diverse fields of solid-state physics in which the objectives are the complex interrelationships between composition, structure and properties. The current need for high temperature technological materials is also an urgent matter in which solid-state chemistry plays a vital role. These and other needs have already led to a great deal of research which will undoubtedly expand in many ways. But, as is often the case, much of that which is basic to the subject has been by-passed or overlooked. May I say how highly I value the opportunity to discuss some of these matters with you, through the wisdom and generosity of a very remarkable man.

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### Scientific Publications of A.D. Wadsley

The following list of scientific publications by A.D. Wadsley was very kindly supplied by Professor Bruce Hyde who has written a detailed biographical memoir - "Wadsley's Science"- that has yet to be published.

1. Cole, W.F., Wadsley, A.D. and Walkley, A. "An X-ray diffraction study of manganese dioxide", *Trans. Electrochem. Soc.*, 1947, **92**, 133-154.
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