On Infinitely Adaptive Structures

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A class of crystalline substances is recognized in which changes of chemical composition are accompanied neither by forming a step-wise succession of phases nor by forming nonstoicheiometric or solid solution phases with disordered, defect structures. Instead, every composition orders into a superlattice and the diffraction patterns invariably show only a single set of superstructure lines which is, however, different at every composition. The true superlattice multiplicity is that of a large unit cell, built up by the ordered repetition of a set of sub-units, which differ in compositions but are structurally closely related and readily interconvertible with a minimum of adjustment of atomic positions. Infinitesimal changes of total composition can then be accommodated in a fully ordered structure by a change in the relative numbers of these sub-units and a consequential change in total multiplicity. The consequences of this adaptive ordering are discussed in relation to phases derived from *L*-Ta_2O_5 and the crystallographic shear structures, and it is shown that the observed complexities in the chemistry of a wider range of solid-state systems can be interpreted consistently on the same basis.

RECENT work on apparently nonstoicheiometric systems obliges us to recognize the existence of a group of crystalline materials which may be designated *infinitely adaptive structures*.

For any perfectly ordered crystal, the unit of translational symmetry completely specifies the composition. In most chemical systems, the equilibrium diagram shows only a limited number of such stoicheiometrically determinate structures (' line phases ') and at intermediate compositions pairs of such line phases coexist in two-component systems. The line phases usually have fairly small unit cells and relatively simple atomic ratios of their components; even where the structural principles generate a sequence of homologous structures, intermediate mixed-valence and ternary phases, their number is discrete and transition from one to the next proceeds through a biphasic composition range. This is essentially true even if the members of such a series intergrow coherently; electron microscopy of (*e.g.*) the crystallographic shear structures indicates that, in the equilibrium state, crystals tend to segregate their component parts into domains of uniform structure. A second recognized situation is that in which a crystalline species incorporates defects (point defects or, more generally, defect complexes) which change the populations of atoms on lattice sites. If these are randomized, so that long-range correlation is lost, the only remaining translational symmetry is statistically that of the parent structure, but the composition is no longer uniquely determined. The phase is then nonstoicheiometric, its thermodynamic behaviour is bivariant and the number of defect centres (and hence the composition) varies continuously with the chemical potential of the components. The range of accessible compositions is restricted and such nonstoicheiometric phases are again related through biphasic equilibria with adjacent phases in the phase succession. This is inherently a high-temperature situation: subject to operational limitations imposed by solid-state diffusion processes, composition ranges contract at low temperatures.* Low-temperature equilibrium corresponds to line phases of unique composition and, commonly, simple formulae.

A third category must now be recognized, defined by two crystal chemical criteria: (i) Within certain composition limits, *every possible composition can attain a unique, fully ordered structure*, without defects arising from solid solution effects and with no biphasic coexistence ranges between successive structures. This is the primary, categorizing criterion.

(ii) For most, but not all, the infinitely adaptive structures (see later) *there may be a multiplicity of discrete, related, fully ordered structures for any one composition*

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* Creation of defect centres in nonstoicheiometric phases makes a positive, and usually large, contribution to the free energy of solution; such phases usually depart strongly from regular solid solution behaviour. Disproportionation and narrowing of the phase range are then already likely at elevated temperatures. In substitutional solid solutions, replacement of one ion by another of similar radius and charge may be almost athermic. The free energy of solution is then dominated by the configurational entropy and the principal driving force for disproportionation is the Third Law requirement that $S_{\text{conf.}} \rightarrow 0$ as $T \rightarrow 0$. It would set in only at low absolute temperatures and is experimentally unattainable. The ' high-temperature ' regime must be understood in a relative sense.

and, for certain compositions, the number of possible structures is potentially infinite.

It will be recognized that the polytypes of such materials as silicon carbide, zinc sulphide, and cadmium iodide provide known examples of this multiplicity of structures for a given composition. In these, the basic sub-units are identical in composition, being two- or three-layered slabs of close-packed structure which can be superimposed in either a cubic or a hexagonal stacking sequence. The very long repeat distances (up to 700 Å) along the unique axis of the structure arise from the periodic repetition of changes between cubic and hexagonal stacking. Frank, Amelinckx, and others have regarded the high multiplicities as non-thermodynamic, and a consequence of the growth of crystals around a screw dislocation with a very large Burgers vector. Occasional stacking faults are thereby propagated as recurrent, periodic features. It is generally agreed, however, that the smaller polytype units, such as the $6H$ and $6R$ polytypes of SiC, are thermodynamic and represent genuine medium-range periodicities. It is possible to regard polytypism as a particular case of the phenomenon under discussion.

Although these postulates cut across the usual canons of crystal chemistry, any assembly of atoms, no matter how irrational its composition, could, in principle, attain a regularly ordered arrangement with a sufficiently large unit cell. The hypothesis that this possibility is, at least approximately, realized, systematizes the behaviour of a number of known systems, ranging from ionic structures (oxides) to intermetallic phases. These include the phases related to low-temperature Ta_2O_5, crystallographic shear phases derived from the ReO_3, rutile and α-PbO_2 types, the lanthanide oxofluorides, the giant cell layer ferrites, $Bi_{1-x}Te$, probably the ' nonstoicheiometric ' transition-metal chalcogenides derived from the NiAs type, and the ' microphases ' of the $CeCd_x$ system.

Common to all of these is experimental evidence of superstructure ordering and monophasic character, irrespective of composition. Their diffraction patterns contain two sets of reflections: (*a*) strong reflections arising from a parent-structure sub-cell, independent of composition; except for possible small, regular shrinkage or expansion as the mean charge state of the atoms alters, this remains constant in dimensions. (*b*) Weaker superstructure lines, which may indicate irrational or very high superlattice multiplicities, which change continuously and progressively with the composition of the crystal and which invariably denote that there is a single mode of superlattice ordering. At no composition are two sets of superlattice lines found; there is no evidence that two structures can coexist.

Underlying these systems is a common structural principle. A large unit cell is built up from the ordered repetition of a set of basic sub-units, derived from the small cell of the parent structure by systematic changes in site occupancy, by crystallographic shear or by stacking sequence. If these sub-units constitute a set with multiplicities $m_1, m_2, \ldots m_i$ of the parent structure, corresponding to compositions $x_1, x_2, \ldots x_i$, the ultimate unit of translational symmetry is built up from $a_1, a_2, \ldots a_i$ of these sub-units. It then has a superlattice multiplicity m^* defined by relation (1) and a composition

$$m^* = a_1m_1 + a_2x_2 + \ldots a_ix_i \qquad (1)$$

defined by relation (2). Provided m^* may be large

$$x^* = a_1x_1 + a_2x_2 + \ldots a_ix_i \qquad (2)$$

enough, any atomic ratio can be accommodated by such an ordering pattern. From the known systems, it appears that the possibilities are simplified by the condition that no more than two consecutive coefficients $a_1, a_2, \ldots a_i$ can differ from zero. This would imply that a given basic sub-unit represents a stable configuration only over a restricted range of chemical potentials; a coexistence condition is satisfied within the structure rather than between structurally distinct phases. The total composition range spanned by the infinitely adaptive structure then breaks up into a series of contiguous ranges, based on consecutive pairs of the homologous set of sub-units: $x_1 \leqslant x^*_{12} \leqslant x_2$, $x_2 \leqslant x^*_{23} \leqslant x_3, \ldots$ *etc.*

Attainment of long-range order according to this complex pattern requires: (*a*) that either the cation or the anion sub-lattice, but not both, should be involved in co-operative shifts of position from the sites of the parent structure, (*b*) that this sub-lattice should have a sufficiently high mobility, and (*c*) that the atoms of the other sub-lattice should undergo only small consequential adjustments of position from the sites of the parent structure. It is less easy to define the maximum size of unit cell to which a physical meaning can be attached, *i.e.* the highest significant value of m^*. This question has not, as yet, received any formal analysis. Intuitively, it would seem that some limit must be set by the intrinsic statistical thermodynamics of point-defect equilibria and the stage at which the low native concentration of positionally uncorrelated vacancies or interstitials impairs a complex ordering pattern. Such a hypothetical limit of distinguishability of structures would be temperature-dependent. Operationally, the attainment of very large unit cells may be restricted by the freezing in of self diffusion processes at low temperatures. A limit of distinguishability may probably be reached with unit cells containing $\not> 10^4$—10^5 atoms and detection of coexisting structures with differing, very high m^* values, whether stable or metastable, would then be at or beyond the bounds of practicable experimentation. It might be expected that structures with ordering patterns of such complexity must show order–disorder transitions or hypotectic phase reactions at high temperatures. Evidence on this is lacking, but in certain systems, at least (the L-Ta_2O_5 phases and both ReO_3-type and rutile CS phases) complex ordering seems to be attained at, and stable at, very high temperatures.[1]

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[1] R. S. Roth and J. L. Waring, *J. Res. Nat. Bur. Stand.*, 1966, **70**, *A*, 281.

These considerations underly the first defining criterion for infinitely adaptive structures. The second arises from the possibility of an additional variable in the structure, *e.g.* the incidence of ' distortion planes ' in L-Ta_2O_5 structures, each eliminating one oxygen-atom site per unit cell, or the variable width of the slab of parent structure between successive crystallographic shear planes in CS structures. In that case, every possible value of the net multiplicity m^* generates its own homologous series of compositions. These series overlap, so that a given composition may be compatible with composition points derived from several different m^* values. Certain compositions, such as the ratio O/M 2·50000 in the L-Ta_2O_5 phases, may be common to every possibly value of m^*, and could in principle be represented by an infinity of structures.

Two types of system have been investigated thoroughly enough to establish that the principles outlined are valid and necessary. These, the L-Ta_2O_5 structures and the crystallographic shear structures, will therefore be considered in some detail. Extension of the concepts to interpret other families of compounds will then be more briefly treated.

Structures Derived from L-Ta_2O_5.—Both modifications of Ta_2O_5 present great difficulties for X-ray methods of structure determination and characterization, and the discrepancies between data from different workers are almost certainly due to subtle variations in their materials. For L-Ta_2O_5 and its derivatives, equilibrium studies by Roth, and Parker,[2] and structure analyses by Stephenson and Roth,[3] have clarified the problem; their work will be accepted in this paper. The basic structure is related to that of U_3O_8, for which Stephenson and Roth accept Andreasen's structure:[4] † an orthorhombic-pseudohexagonal unit cell built up from edge-sharing pentagonal bipyramids and distorted octahedra [Figure 1(a)]. This is so modified as to generate a variable superstructure, and each composition examined within the so-called nonstoicheiometric range Ta_2O_5 to $11Ta_2O_5$,-$4WO_3$ was found to have a unique superstructure, with no evidence for coexistence of superstructures in adequately annealed samples. Detailed structure determinations at selected compositions revealed the structural principle and enable the (often high) multiplicities m^* to be assigned. Superstructures arise through the possibilities of folding chains of edge-linked pentagons, so as to generate basic sub-units extended along the b axis, with $b_{SL} = \frac{1}{2}m \, . \, b(U_3O_8)$, where $m = 5, 8, 11 \ldots (3n + 2)$ [Figure 1(b)—(d)]. This homologous series of sub-units has compositions: $M_{10}O_{26}$, $M_{16}O_{42}$, $M_{22}O_{58} \ldots M_{2m}O_{(16m-2)/3}$. In accordance with what has been stated in the foregoing, an infinite series of structures can then be made by ordered stacking of these sub-units along the b direction, in varied proportions, to give true repeating units which could be symbolized as $(5)_a(8)_b$, $(8)_b(11)_c$, *etc.*, with net superlattice multiplicities $m^* = 5a + 8b$ or $8b + 11c$, *etc.* in the successive sections of the composition range. The composition may be represented quite generally as in (3) or relation (4) so that, as the ratio b/a is varied, the

$$M_{2m^*}O_{[16m^* - 2(a+b)]/3} \quad (3)$$

$$O/M = 8/3 - (a + b)/3m^* \quad (4)$$

composition of the crystal can vary continuously between the compositions of its component sub-units (Figure 2).

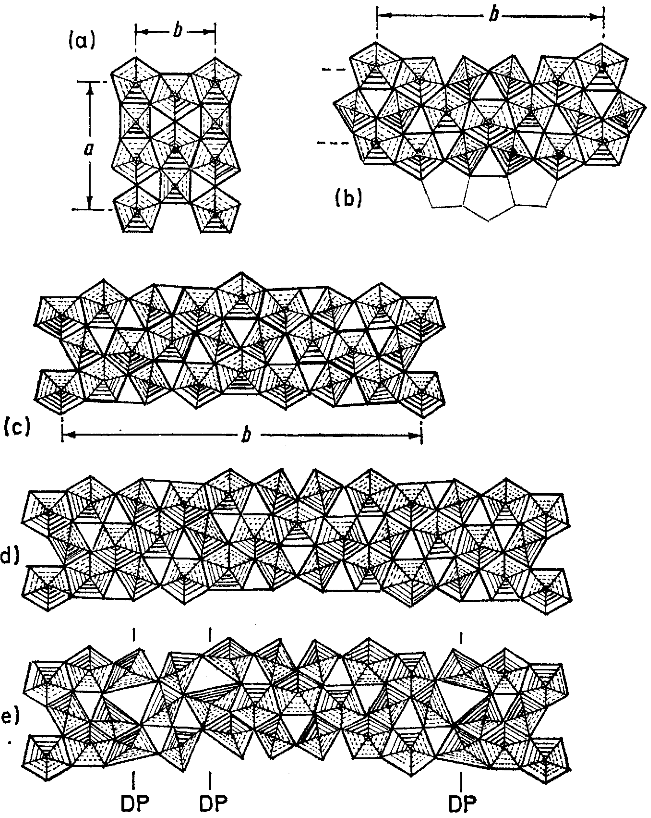

FIGURE 1 Structural principle of the L-Ta_2O_5 structure: (a) U_3O_8, (b) $m = 5$ unit, $M_{10}O_{26}$, showing folding of the chain of pentagonal bipyramids, (c) $m = 8$ unit, $M_{16}O_{42}$, (d) $m = 11$ unit, $M_{22}O_{58}$, and (e) $m = 11$ structure of Ta_2O_5, $Ta_{22}O_{55}$ with three distortion planes (DP) per unit cell

These compositions relate to the ideal or filled structures; the compositions and multiplicities identified in the system correspond to oxygen-deficient unit cells. In the real structures, oxygen-deficiency is accommodated by rearranging co-ordination polyhedra along recurrent planes parallel to (010), each eliminating one anion site per unit cell; discrete compositions arise from the operation of p such distortion planes per true unit cell [Figure 1(e)]. Since either one or two oxygen sites can be thus eliminated at each three-fold group of edge-linked pentagonal bipyramids, the number and

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† The alternative structure of Loopstra,[5] built up entirely from pentagonal bipyramids, is equally compatible with the interpretation. Differences arise only from rather small shifts in oxygen-atom positions.

[2] R. S. Roth, J. L. Waring, and H. S. Parker, *J. Solid-State Chem.*, 1970, **2**, 445.

[3] N. C. Stephenson and R. S. Roth, *Acta Cryst.*, 1971, **B27**, pp. 1010, 1018, 1031, 1037.

[4] A. S. Andreasen, *Acta Cryst.*, 1958, **11**, 612.

[5] B. O. Loopstra, *Acta Cryst.*, 1964, **17**, 651.

nature of the basic sub-units determines the maximum number of distortion planes which can be introduced, $p_{\text{max.}}$. Each idealized structure of multiplicity m^* thereby generates a finite number of oxygen-poorer structures with the composition: $M_{2m^*}O_{\{[16m^*-2(a+b)]/3\}-p}$ where $0 \leqslant p \leqslant p_{\text{max.}}$. Observed structures and compositions fit a consistent pattern if the distortion planes are assigned a mean spacing of $(m^*/p) \,.\, b_0$ (where b_0 is the sub-cell dimension). Then $k = p/m^*$ can be taken as a (scaled) reciprocal lattice vector, measuring the wavenumber of a site-eliminating distortion wave imposed on the ideal structure. Each value of m^* thus gives rise to a discrete set of composition points in a $\boldsymbol{k}$-vector *vs.* composition plot. Figure 3 shows such a diagram for the m^* values recorded in the Ta_2O_5–WO_3 system. It must be emphasized that these lines of constant m^* are arbitrarily chosen to show only the lower identified multiplicities $(m^* \not> 60)$; in principle there is a continuum. Thus, whilst each value of m^* provides a discrete set of compositions, any change in composition, however small, can be accommodated by passage to a near-lying point in the continuum by a change in m^* and $\boldsymbol{k}$.

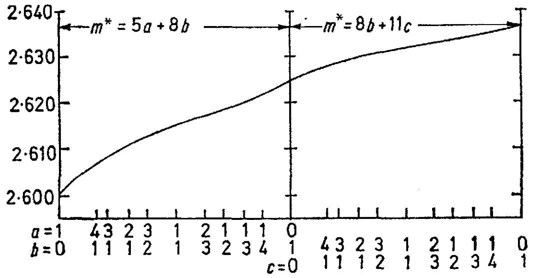

FIGURE 2 Composition *vs.* ratio of sub-units in the composition ranges $(5)a(8)b$, $(8)b(11)c$; plotted as arbitrary functions $f(b/a)$ [$= 2(\tan^{-1} b/a)/\pi$ to open up the ratio scale]. Location of structures with $m^* = 5, 28, 23, 18, 31, 13, 34, 21, 29, 37, 8$; $8, 43, 35, 27, 46, 19, 49, 30, 41, 52, 11$, marked on abscissa

It will be seen that the compositions examined all fall on a regular tie line, marking a stability maximum at the annealing temperature. For L-Ta_2O_5 itself, annealed at 1350 °C, Stephenson and Roth found $m^* = 11$ [*i.e.* the structure symbol $(11)_1$], but it appears from electron diffraction and electron microscopy currently in progress that rather perfect Ta_2O_5 crystals grown at low temperatures have different superstructure multiplicities (m^* 8 and 13). In conjunction with the work of Moser,[6] of Roth and Waring and others, it appears not only that L-Ta_2O_5 illustrates the multiplicity of related structures possible for a constant composition, but also that the relative stability of different structures may depend upon the temperature. Whether the transformations are truly continuous remains to be established. Phases with O/M $2{\cdot}50000 - x$ are formed in the Ta_2O_5–Al_2O_3 system;[7] their structures and multiplicities also fall on a well defined tie line; from consideration of the systematics of both ternary systems it seems likely that the cations are fairly well ordered and systematically distributed between the sub-units of $m = 5$, 8, and 11.

From the thermodynamic standpoint, the behaviour of such a system must be represented in four-dimensional (free energy–composition–temperature–configuration) space, and the distortion-wave vector $\boldsymbol{k}$ can conveniently be taken as the configurational co-ordinate. Figure 3 may then be regarded as a projection on the $\boldsymbol{k}$-X plane. In the isothermal $(G,X)_T$ projections there is a quasi-continuum of infinitesimally spaced line-phases, but the macroscopic properties of the system suggest that the envelope of their free-energy minima approximates to the free-energy curve of an orthodox two-component system. Differences in lattice energy between alternative structures must be so subtle that the free energy at constant composition can vary but little with the particular structure adopted. Nevertheless, a particular structure is observed to be preferentially stable and it must be inferred that there will be a shallow free-energy minimum at a particular spacing between distortion planes in any $(G,\boldsymbol{k})_{T,X}$ section and at a particular composition in a $(G,X)_T$ plot along a section of constant m^*.

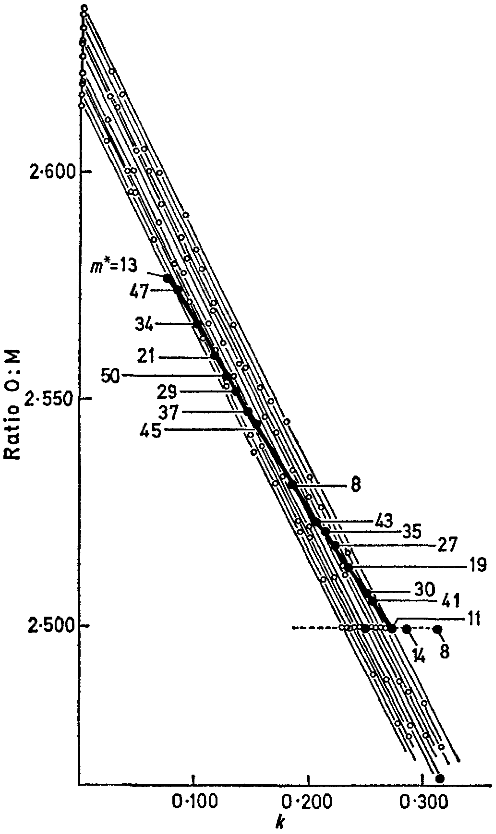

FIGURE 3 Composition *vs.* mean reciprocal distortion plane spacing for some selected, observed values of m^*. Heavy line joins some compositions and structures identified in the Ta_2O_5–WO_3 system

L-Ta_2O_5 and its derivatives provided the first evidence that infinitely adaptive structures must be postulated. It is highly likely that the obscure phase relations and supposed nonstoicheiometry of U_3O_8 and of ternary

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[6] R. Moser, *Schweiz. min. petrograph. Mitt.*, 1965, **45**, 35.

[7] N. C. Stephenson and R. S. Roth, *Acta Cryst.*, 1971, **B27**, 1025.

oxides derived from U_3O_8 and α-UO_3 can be interpreted in exactly the same way, as also can the pseudo-hexagonal ternary oxides, close in composition to Nb_2O_5, formed from high-temperature melts.[8] It could be held, however, that the difficult crystallographic problems presented by these materials introduce structural uncertainties sufficient to make the conclusions doubtful. It is therefore important that a second group of materials, now well investigated, fits into and requires the same generalizations.

Infinitely Adaptive Structures in Crystallographic Shear Phases.—It is now firmly established that, in each of the crystal structure types exhibiting crystallographic shear (the rutile, ReO_3-type, MoO_3, and α-PbO_2 structures), the CS planes can adopt more than one orientation. The possible orientations all lie within a single zone and a common displacement vector is operative throughout; the energetically preferred orientation depends upon the anion–cation ratio of the crystal. Thus, in slightly oxygen-deficient rutile, isolated CS planes and the CS planes of the upper homologous series Ti_nO_{2n-1} ($16 \leqslant n \leqslant 36$) lie on $\{132\}$;[9] in the original Magneli series ($4 \leqslant n \leqslant 9$) they lie on $\{121\}$.[10] The transition between these, in the composition range $TiO_{1\cdot 889}$ to $TiO_{1\cdot 937}$ was elucidated through work on the related Cr_2O_3–TiO_2 system:[11] the CS planes were unambiguously proved to pivot around in an absolutely continuous manner, traversing every intermediate orientation in the $[1\bar{1}1]$ zone. No matter how irrational the indices of the CS plane, the resultant structures in the $(Cr_{2x}Ti_{1-2x})_nO_{2n-1}$ series proved to be rather well ordered,[12] as shown by direct lattice imaging electron microscopy. For obscure reasons, ordering appears to be less facile in the pure binary oxides. Similar considerations hold for other structural types, *e.g.* for WO_{3-x} and related materials.[13]

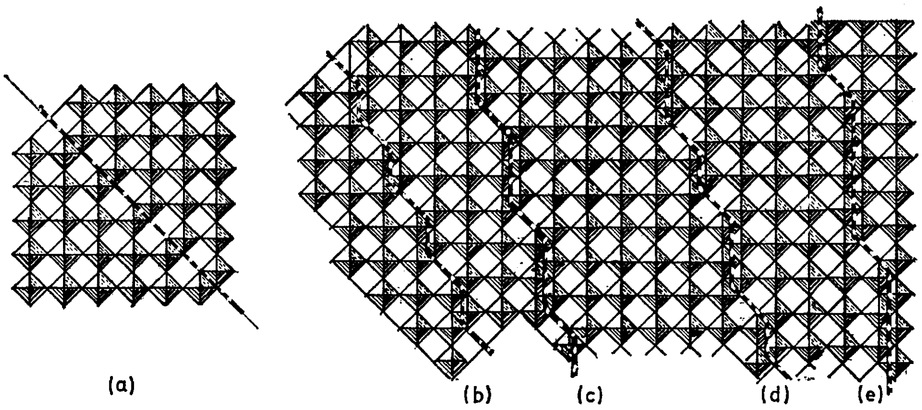

FIGURE 4 Crystallographic shear in the ReO_3 structure. (a) Antiphase boundary (APB) on $\{110\}$; site-eliminating shear on: (b) $\{210\}$, (c) $\{310\}$, (d) $\{520\}$, and (e) $\{510\}$. Dotted lines show succession of site-eliminating segments parallel to $\{100\}$ and APB segments parallel to $\{110\}$

This pivotting of CS planes provides another mechanism for accommodating continuous changes in composition without introduction of disorder or defects at any stage. For simplicity in representation, it may be examined in terms of the ReO_3 structure, for which Figure 4 represents the CS operation $a/2\,\langle 1\bar{1}0\rangle/(hk0)$, for some low- and high-index planes of the [001] zone. Whatever the CS plane orientation, the trace of the CS plane is divided into segments of two kinds: (100) oriented segments, along which anion sites are eliminated; (110) oriented segments, across which the slabs of ReO_3 structure are in anti-phase relationship. Any arbitrary orientation $(hk0)$ can be built up by alternation of $(h-k)$ segments of the first kind with k of the second; any integral values h, k are possible, in principle, and the transition is continuous. In the rutile-related structures, the antiphase segments are parallel to $\{011\}$, the site-eliminating segments parallel to $\{110\}$. CS planes (hkl) are made up of a (110) steps plus b (011) steps, where $h = a$, $k = a + b$, $l = b$. This situation has been analysed by Hyde[11,14] and the mechanism of pivotting during a change in composition has been briefly treated by Gibb and Anderson.[12]

In the L-Ta_2O_5 structures, the translation vectors defining the basic sub-units were collinear, so that two elements of translational symmetry (a, c) remained unaltered; adaptive superstructure ordering involved a single crystallographic direction: stacking along the b axis. Homologous series arose from an additional, collinear, periodic perturbation. CS structures can be regarded as involving the stacking of slices of antiphase structure with slices of a basic crystallographic shear unit. Since these are defined by non-collinear vectors, two

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[8] E. M. Levin, *J. Res. Nat. Bur. Stand.*, 1966, **70**, *A*, 5, 11; J. L. Waring and R. S. Roth, *ibid.*, 1965, **69**, *A*, 119.

[9] L. A. Bursill, B. G. Hyde, S. Terasaki, and D. Watanabe, *Phil. Mag.*, 1969, **20**, 347.

[10] S. Andersson and A. Magneli, *Naturwiss.*, 1956, **43**, 495; S. Andersson, B. Collen, U. Kuylenstierna, and A. Magneli, *Acta Chem. Scand.*, 1957, **11**, 1641.

[11] L. A. Bursill, B. G. Hyde, and D. K. Philp, *Phil. Mag.*, 1971, **23**, 1501.

[12] R. M. Gibb and J. S. Anderson, *J. Solid-State Chem.*, 1972, **4**, 379.

[13] L. A. Bursill, 'Solid State Chemistry,' Nat. Bur. Stand. Special Publ. 364, 1972, 727.

[14] B. G. Hyde, 'Reactivity of Solids,' eds. J. S. Anderson, M. W. Roberts, and F. S. Stone, Chapman and Hall, London, 1972, p. 23.

translational vectors of the superstructure are determined by the overall orientation of the CS plane; for structures derived from the ReO_3 type, one axis (*c* of the ReO_3 structure) is thereby held constant. The third translation, however, is arbitrary in that it is defined by the width of the slab of parent structure between successive, recurrent CS planes; it is variable in discrete steps. Hence, every CS plane orientation within the continuum of possible orientations can generate a homologous series of structures.

Adaptive ordering requires the regular sequence of antiphase and true CS segments along the CS planes; it is conditioned by minimization of the boundary energy (largely a strain energy) for an effectively plane CS interface. Electron microscopic evidence indicates that it is attainable, even for high-index orientations, within the limits of lattice resolution hitherto applied to the problem, even though kinked and ' dog-legged ' CS planes have been found in the binary TiO_{2-x} system, undoubtedly representing out of equilibrium conditions.[13,15] A second, independent, and less facile mode of ordering is needed to impose a regular recurrence of CS planes along the third direction: variability in CS plane-spacing, and the difficulty of preparing a fully ordered crystal of one member of a given homologous series, must be clearly distinguished from the high degree of adaptive ordering which determines the orientation of the CS planes themselves.

If the CS plane orientation in ReO_3-type structures is written as (h' 10), where $h' = h/k$ and may be irrational, the composition of a structure with recurrent shear on every n^{th} (h' 10) plane becomes: $O:M = 3 - \frac{(h' - 1)}{n}$. Within any one homologous series, this defines a set of discrete compositions, for which the stoicheiometric deficit is proportional to d^*_{CS}, the reciprocal of the normal spacing between CS planes. This is a primitive reciprocal lattice vector. Figure 5 shows the relation between composition and d^*_{CS} for a few CS planes, between {410} and {110}, arbitrarily selected from the continuum of possibilities; only a few of the composition points are shown for each line. Lines of constant *n* define paths by which infinitesimally small changes of composition can be accommodated by pivotting of CS planes, without any change in their number. As long as the CS surface stays planar, the crystal can maintain an ordered, defect-free structure whilst presenting the macroscopic operational characteristics of a classical nonstoicheiometric compound. This situation is now well documented for the rutile-related CS phases. At the extremes of composition ($n >$ or $<$ some critical range), the CS plane may remain constant, and changes of composition are accommodated by changes in *n*; in the intermediate range, relatively narrow for TiO_{2-x}, wide for $Cr_{2y}Ti_{1-2y}O_{2-y}$, CS planes pivot whilst retaining a nearly constant spacing. The same is true for the high-temperature phase $Cr_2Ti_2O_{7\pm x}$, based on the α-PbO_2 structure. It follows, further that points for alternative structures with identical compositions may be found on the x–d^*_{CS} lines for several different CS plane orientations. Thus, for ReO_3-type structures the necessary condition is that: $(h_i - k_i)/n_ik_i$ = constant, where n_i is an integer.

Other Adaptive Stacking Systems.—Several apparently nonstoicheiometric systems exhibit adaptive ordering without, simultaneously, introducing a second type of periodic perturbation, which provides for families of homologous compounds derived from every structure. They therefore have a continuum of structures and compositions without a multiplicity of structures for any one composition.

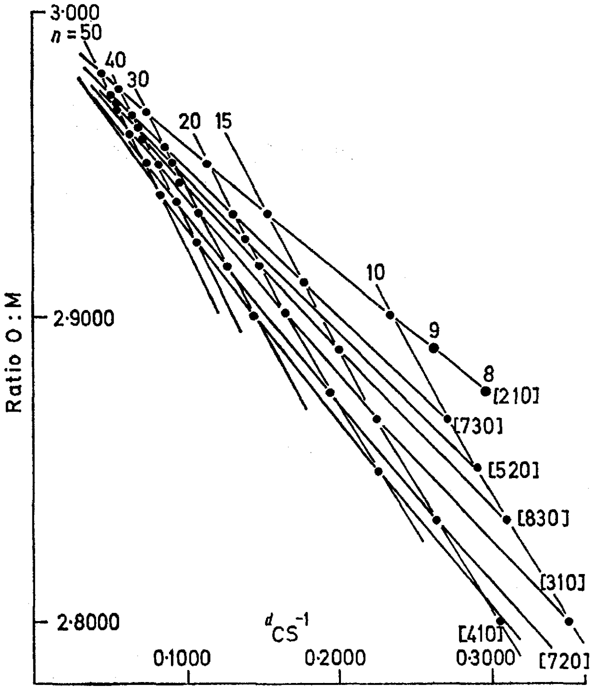

FIGURE 5 Composition *vs.* reciprocal spacing between CS planes for a few low-index CS plane orientations in the [100] zone of the ReO_3 structure. Fine lines form composition points of constant *n* in M_nO_{3n-m}. Location of a few of the well characterized phases (Mo_8O_{23}, Mo_9O_{26}, $W_{20}O_{58}$) are shown

(i) *Hyperstoicheiometric fluorite structures.* Bevan and Mann[16] have shown that, in the ' solid solutions ' formed between the lanthanide fluorides LF_3 (L = lanthanide; most detailed investigation for L = Y) and the fluorite-structure oxofluorides LOF, the apparently nonstoicheiometric phase covering the composition range $LX_{2\cdot130}$ to $LX_{2\cdot220}$ has the characteristic feature of infinite adaptivity. Every composition examined has its own, single superstructure, with no two-phase regions. The superstructure multiplicity m^* does not change monotonically with composition but measures, as before, the net repeat length of a stack $(m_1)_a(m_2)_u$ of identifiable sub-units $m_1, m_2 \ldots$, each of the composition $L_mO_{m-1}F_{m+2}$ ($m = 4, 5 \ldots 8$ identified). In each sub-unit, $(m - 1)$LOF fluorite cells and one fluorite cell with an ' interstitial ' fluorine are superimposed along *b*; to any but high-resolution

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[15] J. G. Allpress, *J. Solid-State Chem.*, 1972, **4**, 173.

[16] D. J. M. Bevan and A. W. Mann, *J. Solid-State Chem.*, 1972, **5**, 410; D. J. M. Bevan, in ref. 13, p. 749.

diffraction methods, the materials appear to be a continuous, variable composition, orthorhombically distorted fluorite phase. Structures identified are listed in the Table. The pseudo-fluorite series $Nb_2O_5,yZrO_2$ $(y = 5—8)$ [17] proves to be isostructural with these oxofluorides, and shows evidence for stacking of sub-units with $7 \leqslant m \leqslant 10$.

m^*	23	7	19	45	6	17	47	57	28	41
Structure	$(8)_2(7)_1$	$(7)_1$	$(7)_1(6)_2$	$(7)_3(6)_4$	$(6)_1$	$(6)_2(5)_1$	$(6)_2(5)_7$	$(6)_2(5)_9$	$(5)_4(4)_2$	$(5)_5(4)_4$
Composition (y in LX_y)	2·130	2·143	2·153	2·155	2·167	2·176	2·191	2·193	2·214	2·220
b/Å	126·7	38·6	104·9	248·2	33·1	94·0	260·0	315·4	155·2	227·4

(ii) $Bi_{1-x}Te$. Brebrick [18] found that, for a range of compositions (at intervals of 1 mol-% Te) between $BiTe_{1·000}$ and $BiTe_{1·225}$, each preparation had its own superstructure. As before, superstructures did not coexist even though compositions were quite irrational; the preparations were monophasic. These materials have a common hexagonal sub-cell, the dimensions of which change only slowly with composition; the superstructure is along the c axis and its multiplicity is not a simple function of composition. The results can be rationalized only in terms of a periodic stacking of slabs of the Bi_2Te_3 structure, of variable thickness, with Bi_2 layers, of the same hexagonal mesh, giving net repeat distances along the c axis up to several hundred Å in length. Although the main features are not in dispute, this system is at present less clearly understood than those dealt with in the foregoing, because the stoicheiometry is affected by some substitutional disorder (probable replacement of Bi by Te at the 1 atom-% level).

(iii) *The mixed-layer ferrites.* Approximating to the adaptive structure concept are the mixed-layer compounds in certain multicomponent systems, which generate families of structurally related phases based on the regular recurrence of unit building blocks. The ferrites of the magnetoplumbite series, in particular, thereby build up crystals with the longest repeat distances found for any inorganic crystals.[19]

All of these are based on close-packed oxygen layers, and involve both cubic and hexagonal stacking sequences. As Kohn and Eckart have shown, all the structures can be ultimately analysed into the stacking of three basic sub-units: (i) a two-layer (cubic) spinel block S which may be either cationic (S^{2+}), with the composition Fe_6O_8, or neutral (S^0), with composition $Me_2Fe_4O_8$ ($Fe = Fe^{3+}$ throughout; Me a divalent transition-metal cation); (ii) an inherently anionic, three-layer hexagonal block R, $BaFe_6O_{11}$ (R^{2-}); and (iii) a neutral, four-layer hexagonal block T, $Ba_2Fe_8O_{14}$. These can be combined in a very wide range of combinations, to form rhombohedral or hexagonal crystals (both polymorphs usually represented) with c axes up to 1500 Å in length. The most widely represented series of compounds lies between the end members $BaFe_{12}O_{19}$ (Braun's phase M = combination $R^{2-}S^{2+}$) and $Ba_2Me_2Fe_{12}O_{22}$ (phase Y, $= TS^0$), although other combinations of these units certainly exist (*e.g.* Braun's phase $W = RS_2$, phase $X = R_2S_3$). It is therefore convenient to represent the main series as stacking combinations of the larger, composite building blocks, with the general formula M_aY_b. Of this general series, those identified correspond to the sequences:

$a = 2$ $b = 1, 2, 3 \ldots$ to 13, 15, 18, 21
$a = 4$ $b = 5, 8, 9, 10, 13, 15, 33$
$a = 6$ $b = 14$
$a = 8$ $b = 27$

Figure 6 shows how finely graded are the compositions corresponding to these stacking ratios, as identified by X-ray diffraction methods for individual crystals isolated from flux-growth preparative experiments. Mixtures of numerous members of the series are invariably formed, indicating that small changes in the chemical potentials of the component oxides BaO and MeO produce a change in the stacking pattern. These known structures build up a discontinuous series. However, it is by no means certain that every structure formed has been recognized and characterized. To differentiate between species with closely similar a/b ratios in mixed stacking families is very difficult; assigned multiplicities may rationalize formulae in terms of the sequences with small a values. The compounds, indeed, transcend the practicable limits

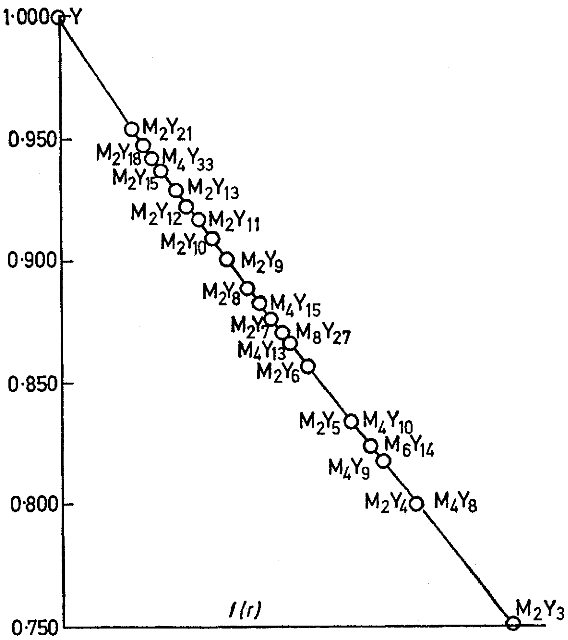

FIGURE 6 Observed compositions in long-axis ferrite compounds. Ordinates: transition metal : Ba; Abscissa: arbitrary functions of stacking ratio M : Y

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[17] R. S. Roth, J. L. Waring, W. S. Brower, and H. S. Parker, in ref. 13, p. 183.

[18] R. F. Brebrick, in ' Chemistry of Extended Defects in Non-metallic Solids,' eds. L. Eyring and M. O'Keeffe, North Holland, Amsterdam, 1970, p. 183.

[19] P. B. Braun, *Phillips Res. Report*, 1957, **12**, 491; J. A. Kohn and D. W. Eckart, *Z. Krist.*, 1964, **119**, 454; 1967, **124**, 69; R. O. Savage and A. Tauber, *Mat. Res. Bull.*, 1967, **2**, 469.

of *X*-ray diffraction methods, and the most complex members (*e.g.* M_8Y_{27} and M_4Y_{33}, with $c = 1455$ and 1577 Å respectively) were characterized by a remarkable direct method: direct counting of the ledge structure of etch pits in the surface of crystals arising from differences between M and Y layers in the rate of etching reactions.[20] Evidence that such crystals are homogeneous and truly periodic in structure is lacking; direct lattice imaging methods offer the only possibility of determining whether a crystal can build up a genuinely regular stacking sequence with such long periodicities and whether other stacking sequences, filling in a yet finer-grained range of compositions, occur either as extended slabs or as isolated lamellae.

Probably Adaptive Structures.—(i) *Nonstoicheiometric transition-metal chalcogenides.* Closely related to the stoicheiometric compounds MX with NiAs structure (M = transition metal, X = S, Se, or Te) are both successions of well defined, ordered phases, M_nX_{n+1}, and (*e.g.* in the Fe–S system) metal-deficient nonstoicheiometric phases. The structural principle common to the first group is well established:[21] the sulphur sub-lattice is perfect and the sheets of metal atoms stacked along the *c* axis, each presenting a hexagonal array of sites, are alternately fully occupied and partially occupied. In the latter, the unoccupied cation sites are fully ordered and constitute a rational fraction of the sites in the sheet, so defining the compositions of a discrete number of possible intermediate phases. Denoting a filled cation sheet as M_0, and the several possible ordered, incompletely filled sheets as M_1, M_2 . . . *etc.* all the ordered phases conform to the stacking pattern $M_0M_iM_0M_i$-M_0M_i . . . In the nonstoicheiometric phases, it is generally considered that cation vacancies are formed in alternate sheets, but that their fraction is continuously variable and that all sites are statistically equivalent.[22] This may be the case: the $Fe_{1-x}S$ phase, stable above 300 °C, may be formed by an order $\rightleftharpoons$ disorder reaction. However, lattice-energy calculations by Bertaut[23] (and unpublished work by Burch) indicate a strong energetic advantage in the ordering of vacant sites, which suggests that within any one incomplete cation-layer the fraction of vacant sites may not be a continuous variable. Mobility in these systems is sufficiently high to permit of establishing more complex long-range order, and it is predictable from the considerations set out in this paper that there may be some temperature range, at least, within which a quasicontinuous succession of structures is built up by mixed stacking of the ordered sub-units in varied proportions: $(M_0M_i)_a(M_0M_j)_b$. Since these materials are sensitive to electron bombardment (unpublished experiments) it may be difficult to determine the true microstructure of the nonstoicheiometric phase by electron diffraction methods.

(ii) *Microphases in the* $CeCd_x$ *intermetallic system.* Using a highly precise tensimetric technique for the determination of cadmium equilibrium pressures, Elliott and Lemons[24] found that, at 639 °C, the Ce_2Cd_9 phase appeared to span the composition range from $CeCd_{4\cdot6932}$ to $CeCd_{4\cdot3440}$, in bivariant equilibrium. Closer examination of the relation between cadmium activity and mole fraction of cadmium, for small excursions from equilibrium, showed discontinuities which could be interpreted only as arising from transformations between an extremely large number of thermodynamically distinguishable species. Thus, there was evidence for at least 25 such 'microphases' between 0·813886 and 0·813217 mole fraction cadmium, corresponding to distinguishability of structures differing in composition by one cadmium atom in 8000.

These results cannot readily be explained away, and appear to furnish evidence for a close succession of structures, accommodating very small changes in stoicheiometry by an adjustment of some pattern of long-range order. The structural principle whereby deviations from simple stoicheiometry are assimilated is not known; diffraction evidence extends only to the detection of small changes in superstructure reflections.[25] It was inferred that the tensimetric results revealed a succession of univariant equilibria whereas, as indicated earlier, a completely adaptive system should simulate a single bivariant equilibrium. Two comments can be made upon this disagreement with prediction. First, the differences in composition between successive observed structures appear to be comparable in magnitude to the minimum degree of point-defect disorder which must be expected at the temperature of experiment. As previously indicated, this factor must set a limit to the attainable degree of long-range correlation in any structure; it is not so clear how this would affect the thermodynamic properties at the operational level. Secondly, the act of measuring an equilibrium activity itself perturbs that equilibrium. In most contexts this is irrelevant; in a system of extremely closely spaced structures and compositions, however, the transient enrichment or depletion of the surface may produce a disproportionately large local fluctuation of composition. In terms of the free-energy surfaces, the measured chemical potential is then determined not by the true tangent at a particular composition point but by the chord between close, but not strictly adjacent, composition points. The experimental evidence for a large number of distinguishable species in this intermetallic system seems well established, but neither the structural nor the thermodynamic characteristics are fully explained.

In the best understood systems, considered earlier, the complexity of ordering has been reduced to a one-

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[20] J. A. Kohn, D. W. Eckart, and C. F. Cook, jun., *Mat. Res. Bull.*, 1967, **2**, 55.

[21] Y. P. Jeannin, in 'Problems of Nonstoicheiometry,' ed. A. Rabenau, North Holland, Amsterdam, 1970, p. 108; J. S. Anderson, *ibid.*, p. 14.

[22] G. G. Libowitz, in ref. 14, p. 107; G. Hägg and I. Sucksdorff, *Z. phys. Chem.*, 1933, **22**, *B*, 444.

[23] E. F. Bertaut, *Acta Cryst.*, 1953, **6**, 557.

[24] G. R. B. Elliott and J. F. Lemons, *J. Phys. Chem.*, 1960, **64**, 137; A.C.S. Adv. in Chem. Ser. 39, 1964, pp. 144, 153.

[25] R. B. Roof, jun., and G. R. B. Elliott, *Inorg. Chem.*, 1965, **4**, 691.

dimensional problem: the stacking of closely related lamellae in a regularly recurrent pattern with, possibly, a very long translational repeat distance. It may well be held that this implies the operation of extremely long-range interactions, but since numerous structures are now known with cell dimensions exceeding 100 Å, this problem is inescapable. The feature common to all these systems is that the sequence of sub-units can be described in terms of perturbations imposed on some parent structure. These perturbations are of two kinds: (*a*) fluctuations of composition (changes of site population in one sub-lattice), and (*b*) fluctuations or consequential adjustments of structure, *e.g.* a crystallographic shear displacement, a stacking fault or occupation of a set of interstitial sites. In this form, the problem of long periodicities may be better treated through the Fourier representation of the periodic, translational properties of a crystal lattice, in reciprocal space.[26] For a perfect crystal of the parent structure, the corresponding Fourier components are at the nodes of the reciprocal lattice. Any fluctuation in the position and the occupation of lattice sites generates a new set of terms in the Fourier representation, each involving a displacement coefficient, a pair correlation coefficient that takes account of the change in composition, and a wave-vector $\boldsymbol{k}$ ($\boldsymbol{k} <$ primitive wave-vector of the reciprocal lattice). The perturbation as a whole is then represented as the superposition of a set of fluctuation waves,[27] each characterized by a periodicity, in direct space, of $\boldsymbol{k}^{-1}$. The conditions under which adaptive ordering should occur is then determined by which of three possible configurations minimizes the free energy: (i) randomized fluctuations, represented by a diffuse, continuous distribution of $\boldsymbol{k}$-values throughout (or along certain directions in) the first Brillouin zone, and corresponding to the formation of a nonstoicheiometric crystal, (ii) a single wave-vector, defining regularly recurrent fluctuations and a superlattice, which leads to adaptive ordering, or (iii) a very strong and highly localized fluctuation which generates an interface and a new structure; this corresponds to unmixing and the classical coexistence of phases. Into this energetic balance sheet there enter not only the usual coulombic and other interactions, but also terms related to the vibrational energy, *i.e.* the phonon spectrum of the crystal, arising from small displacements of atomic positions and distortions of co-ordination polyhedra. These vibrational energy terms not only mediate the adjustment of structure to produce regularly recurrent fluctuations, but may be decisive in determining the stable configuration.

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[26] J. D. C. McConnell, *Phil. Mag.*, 1965, **11**, 1289; *Min. Mag.*, 1971, **38**, 1.

[27] M. A. Krivoglaz, ' Theory of *X*-Ray and Thermal Neutron Scattering by Real Crystals,' Plenum, New York, 1969.