

Structural Evolution of Extended Defects in Nonstoichiometric Solids

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A defect theory for a better fundamental understanding of the structural evolution of extended defects in nonstoichiometric solids is presented. Some novel concepts relating to defects in nonstoichiometric oxides and their role have been proposed in terms of equilibrium concentrations and supersaturations of point defects, the latter being accommodated into extended shear planes, and into other broader types of planar boundaries all serving to accommodate nonstoichiometry. Our model of supersaturation underpins the mechanism of nucleation of dislocation loops in the formation of crystallographic shear planes suggested in the model of Professor Anderson, and fundamental concepts of diffusion controlled solid state chemical reactions in general. *In situ* electron microscopy (EM) in controlled gas environments, atomic resolution EM, and correlated chemical experiments on reactivity have been utilized to understand the physics and chemistry of defect structures. © 1993 Academic Press, Inc.

Professor J. S. Anderson wrote in one of his many classic papers "the constitution of phases of variable composition, namely, nonstoichiometric compounds and hetero-type solid solutions cannot be understood solely in terms of point defects." He then stressed the significance of extended defects such as defect clusters, planar defects including crystallographic shear planes (*CS* planes), chemical twins, topologically com-

patible intergrowths, and superlattice ordering of point defects leading to a structural element of a new crystalline order. He was one of the pioneers of the high resolution electron microscopy (HREM) technique in elucidating the crystallography and compositional variation of defects in real space and developed some far-reaching concepts to explain their formation. Foremost among these are the concept of infinitely adaptive structures where compounds adapt structures to suit the prevailing stoichiometry, and a dislocation model for *CS* planes in ReO_3 and Nb_2O_5 type structures (1–3), and discussed elsewhere (4, 5).

At the present stage of knowledge, we can further develop and modify some of his concepts to understand the origin of these defects, and this is the subject of the present article. To do this, relevant work on defect dynamics using dynamical (*in situ*) electron microscopy technique under *controlled* conditions, developed for the first time at Oxford to study gas–oxide reactions directly at high gas pressures and temperatures (6,

* I was greatly privileged to work with Professor J. S. Anderson as his post-doc. In offering me the job he said that the fact that I was Professor Archie Howie (Head, Cavendish Laboratory)'s student was a good enough qualification! I will never forget the incident when I went up to Oxford to meet him for the first time. He was not in his office, and someone suggested I look into his lab. When I went there I saw a gentleman in a lab overcoat cleaning a furnace and I promptly asked him where I could find the professor. "You are speaking to him!" came the reply! Through him I was honored to meet and work with many eminent scientists including Professor Sir John Thomas, Professor C. N. R. Rao, and many from Australia, the United States, and Japan. I am deeply indebted to him. We kept in touch over the years and he encouraged the work I have described in the following paragraphs.

7), and work of others, have been utilized. Some novel concepts relating to defects in nonstoichiometric oxides and their role have been proposed. It is hoped that this approach should, at least in part, help explain some of the questions he had raised, and fill in some of the missing gaps. It is shown that the concepts highlighted here for shear structures in terms of the accommodation of superconcentration of point defects *underpin* fundamental aspects of solid state reactions and nonstoichiometry.

In classical solid state science and crystallography, the principle of complete order supports the theory of the crystalline state. In practice, however, some compounds can exhibit deviations from stoichiometry, within a certain range, without any "apparent change" in the overall crystal structure. This nonstoichiometry presents a basic problem which has been recognized and is being studied in many laboratories, using HREM at the atomic resolution as the principal technique to reveal the variety of defects that exist locally (e.g., 1-5, 8). However, unless the fundamental structural principles are understood, thermodynamic and other crystal properties (such as chemical reactions and transport properties) and the significance of defect structures in nonstoichiometric solids cannot be explored. This can only be done under carefully controlled dynamic experiments. First, we go back to the basic principles:

1. Point Defects and Extended Defects

From statistical thermodynamics it is understood that crystals are subject to point defect disorder and the structural imperfection is limited to one structural site. However, the equilibrium concentrations of point defects are low. Point defects and interactions between them have provided a basic understanding of the properties of materials such as halides, or semiconductors, where the concentration of point defects can be directly related to the stoichiometric deviation. However, these concepts could not

satisfactorily be invoked for grossly nonstoichiometric solids, i.e., with a large concentration of point defects (~1-10% defective lattice sites). For these solids extended defects occur leading to a substantial modification of the local crystal structure. Interactions between them can lead to homologous series of compounds (1, 2). Extended planar defects specified above (CS, chemical twins, intergrowths) involve nonconservative sites and are nonstoichiometric boundaries where the coordination polyhedra are altered so as to eliminate or create lattice sites. Some of these defect structures and their roles are examined below. Freshly prepared powder samples have been used in general without further sample preparation.

In HREM, which is often used to study lattice defects, it is assumed in the simplest approach that the defect displacement (i.e., shear or Burgers) vector \mathbf{b} lies in the plane of the crystal. This may not be sufficient to obtain the complete geometry of the defect in the three dimensions (i.e., the displacement component normal to the plane), and calculations modeling different shear plane configurations may be necessary. Using two-beam diffraction contrast from defects in several reflections (9) can be advantageous to define the complete defect geometry in complex systems.

2. The Role of Supersaturation of Point Defects in Generating Shear Structures, Leading to Fundamental Concepts in the Formation of Extended CS Defects

One of the most important planar defects accommodating nonstoichiometry in solids is a CS plane (by switching from corner to edge, or face-sharing octahedra) derived from simple ReO_3 or rutile based oxides. An extensive literature on CS planes exists. Interactions between them can lead to reduced intermediate phases (Magneli phases) (1, 5). CS planes are important in understanding transport processes in nonstoichiometric crystals. They are formally (and

empirically) regarded as effecting the elimination of a complete sheet of point defect sites (anion vacancies, or in some cases cation interstitials) lying on a particular crystal plane by simultaneous shear and collapse of the lattice on that plane. The anion coordination number is increased to accommodate the reduced anion/cation ratio. Point defects are consumed in their production, and in the propagation of line defects that form their boundaries (2).

Anderson and Hyde's model (2) advanced the idea of planar aggregation of anion vacancies followed by collapse and shear to give a dislocation ring (i.e., a loop of a partial edge dislocation bounding the collapsed disc of vacancies), thus invoking a dislocation mechanism for crystallographic shear. It may be noted that the most stable collapsed form is a planar dislocation loop which is energetically preferred as described by Frank (10). If the shear vector is normal to the ring, an edge dislocation would result (as in non-conservative CS), and if the ring were parallel to the vector, a screw dislocation. Mixed defects with edge and screw components are also possible, and partial dislocations are energetically favorable (11). It was further suggested in the model that the elastic strain at the ring was a sink for anion vacancies so that the CS plane expanded by consuming vacancies wandering in the lattice. Two important factors result from this model: (a) the elastic strain sets up a chemical potential gradient for vacancies facilitating their drift to the dislocation ring, and (b) this growth proceeds by climb of the partial edge dislocations in planes normal, and parallel, to the glide plane. Since this pioneering work, it was presumed by catalyst workers that the rearranged closer linkage between the cation polyhedra at the CS plane in oxides to be active centers in catalysis, assuming of course, that these defects occurred at catalyst operating temperatures (12, 13); the role of the extended CS defects in oxygen diffusion is one of the most basic issues in heterogeneous catalysis and we will return to this point later.

However, the fundamental question of

why the vacancies collapse into discs was not addressed in the classic Anderson-Hyde model. To resolve this issue, we ask: what causes the CS planes to nucleate and grow? Although CS is an elegant structural phenomenon accommodating nonstoichiometry, it has challenged the basic model for point defect, or ionic diffusion in solids. Clearly, crucial experiments to reconcile these issues would be to study defect structures, including CS planes, occurring under appropriate reaction conditions directly by dynamic EM (6, 7). Consequently, we put forward a plausible mechanism for the production of CS planes in terms of point defect supersaturation. We further discuss the thermodynamic implications and formulate some novel concepts about the extended defects, and try to resolve the paradox concerning diffusion.

The thermodynamic behaviour of solids is determined by the free energy changes in response to changes in their chemical composition. In apparently stoichiometric oxides Schottky or Frenkel defects can exist. In the oxygen-deficient ReO_3 -related oxides considered here, e.g., model catalytic oxides such as MoO_3 , V_2O_5 , or WO_3 , oxygen deficit occurs due to the loss of structural oxygen, O^{2-} (e.g., in catalysis or in other high temperature reactions), and doubly charged anion vacancies predominate (13). The oxygen deficit can be accommodated by isolated vacancies, or by collapsed discs of vacancies by crystallographic shear.

Let us consider MoO_3 (orthorhombic, $a = 3.96 \text{ \AA}$, $b = 13.85 \text{ \AA}$, $c = 3.69 \text{ \AA}$), for example; the formulations described here are valid for all the ReO_3 -related and other shear structures. Detailed experimental and theoretical studies of gas-solid reactions have been carried out at various temperatures in reducing environments (e.g., H_2 , CO, or propylene) (6, 7). They have shown that at $\leq 380^\circ\text{C}$, pure shear (where the shear vector $\frac{1}{2}\langle 101 \rangle$ is parallel to the shear plane) leads to the nucleation of two sets of partial screw dislocations at the surface, bounding stacking faults in (101) planes (Figs. 1a and

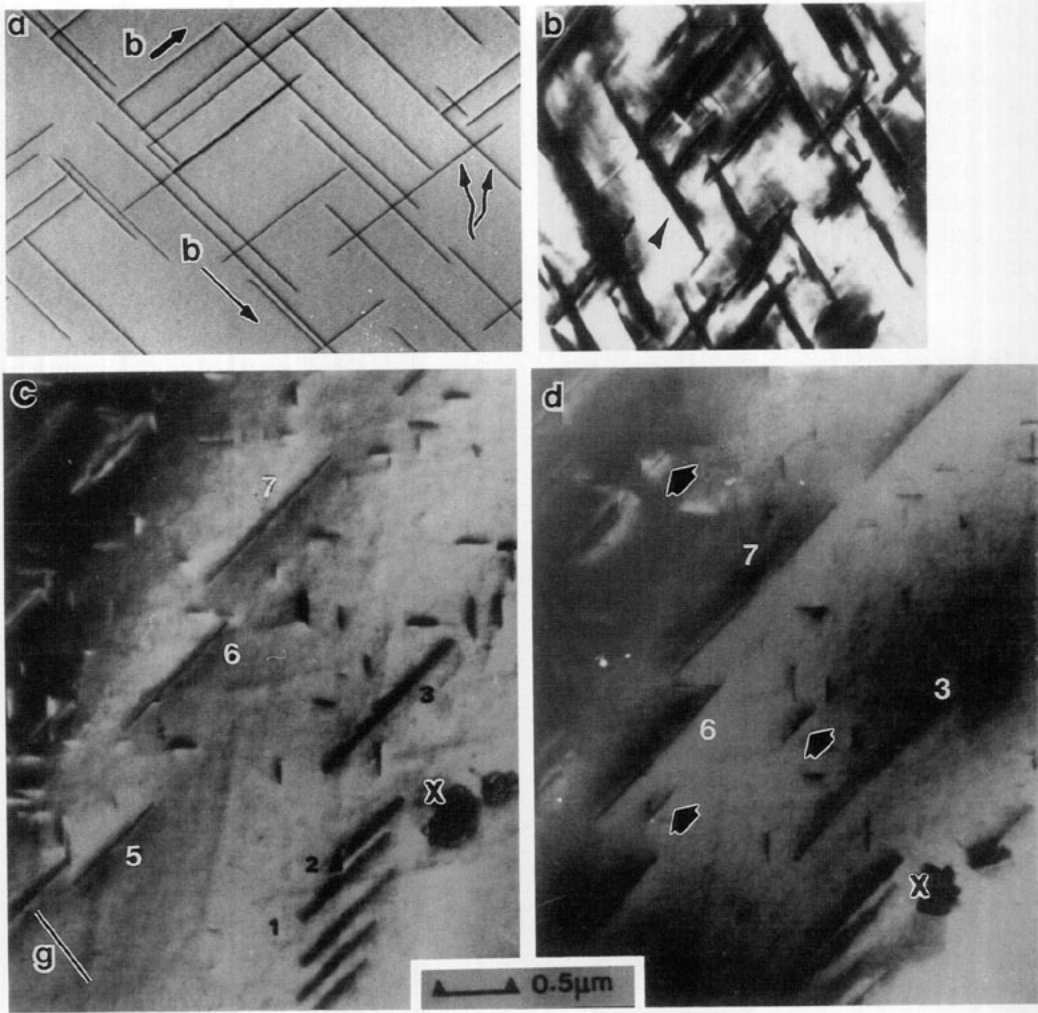


FIG. 1. (a) Two sets (shown by, e.g., curly arrows) of misfit partial screw dislocations in reduction of (010) MoO_3 . They accommodate misfit between the reduced surface layer and the underlying matrix at low temperatures ($\sim 100^\circ\text{C}$). (b) Micro-domains observed up to $\sim 380^\circ\text{C}$. Point defect (anion vacancy) interactions can lead to vacancy ordering in the domains. These are formed by the same shear vector, $\frac{1}{2}\langle 101 \rangle$ in $\{304\}$ planes, and may be visualized as martensites or chemical twins. (c) Crystallographic shear planes at operating temperatures ($\sim 400^\circ\text{C}$). (d) Dynamic growth of the defects during reaction (e.g., 6, 7) at $\sim 460^\circ\text{C}$. New CS loops are also formed (arrowed). (The same area, around marker x). $g = 200$ reflection; CS defects are along $[001]$.

2a), or to martensitic type transformations with the same vector but in $\{304\}$ planes leading to microdomains (Fig. 1b). In the latter case, superlattice ordering of the empty sites can take place following point defect interactions, and vacancy diffusion is essential. The screw dislocations accommodate the misfit between the reduced sur-

face layer and the crystal matrix, and minimize the overall free energy at their interface. The product of the shear is of unchanged composition (i.e., an antiphase boundary (APB)). These defects may be nucleated as surface shear loops expanding by a lattice strain driven glide on $\{101\}$ planes (Fig. 2b, 14).

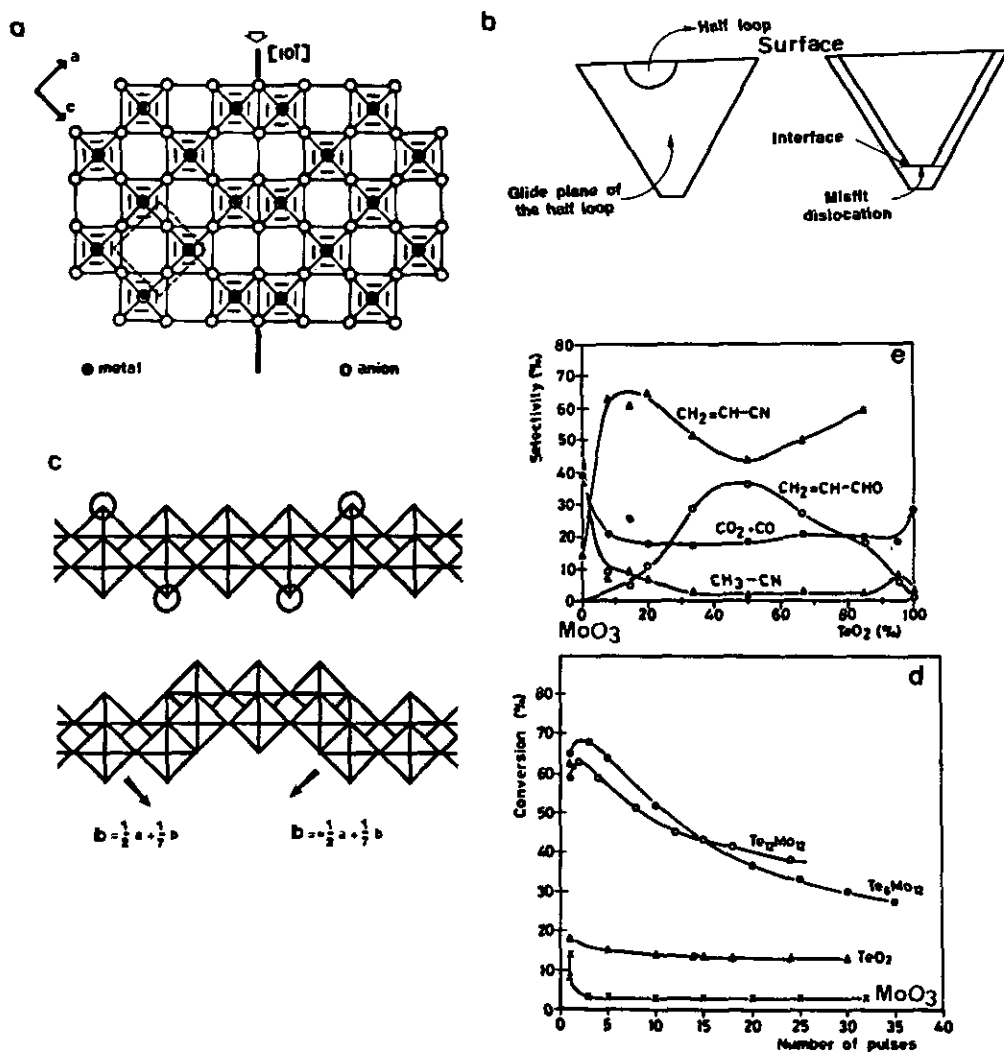


FIG. 2. (a) Model for the stacking fault in the idealized structure, bounded by the misfit dislocations formed by pure shear. The shear vector $\mathbf{b} = \frac{1}{2} \langle 101 \rangle$ is parallel to the shear plane $\{101\}$ (of each set of the dislocation), resulting in unchanged composition. (b) Small shear loop nucleated at the surface (left). The loop expands by lattice strain driven glide to form a misfit dislocation at the reduced surface layer-matrix interface (right). (c) Elimination of anion vacancies by CS. (d) and (e) Catalyst conversion and selectivity in ammoxidation of propylene at $\sim 400^\circ\text{C}$. Trends for selectivity to acrolein for MoO_3 with time are similar. MoO_3 (and TeO_2) exhibits poor selectivity and conversion with increasing CS planes and time. Mixed metal systems, e.g., Te-Mo-O are superior.

At catalyst operating temperatures of $\sim 400^\circ\text{C}$, the surface defects formed are indeed collapsed discs of vacancies on $\{120\}$ planes, bounded by partial edge dislocations with a shear vector $\langle a/2, b/7, 0 \rangle$ (Fig. 2c) leading to a lowering of the free energy of the system (7). The configuration of the CS

is similar to that in (5). The depth of the dislocations (which determines the position of the diffusion front of the vacancies) following nucleation at the surface, is estimated as $\sim 300 \text{ \AA}$ in $\sim 35 \text{ sec}$ by dynamic studies and the defects are $\sim 0.25 \mu\text{m}$ in length. In further reduction, the CS planes

in motion, their growth (e.g., *CS* planes marked 6, 7), and the simultaneous nucleation of new *CS* loops (arrowed) are indicated in Fig. 1c and d.

There have been some important reports in the literature about the concentration of isolated vacancies in the presence of *CS* planes which suggest that there exists an equilibrium concentration of point defects in systems containing a finite number of *CS* planes. It is readily seen that the concentration of isolated vacancies is governed by the difference between the free energy of an isolated vacancy and of the one collapsed in a *CS* fault plane. Thermodynamic parameters for many of the complex oxides are unknown, but estimates can be made. At equilibrium between isolated vacancies and a collapsed disc, the background equilibrium concentration of vacancies (c_0) can be deduced by using a simple relation between the free energy of a vacancy (ΔG_v) and of the one absorbed in a *CS* planar fault,

$$c_0 = \exp\{-(\Delta G_v - \gamma ds/dn)/kT\} \quad (1)$$

where γ is the surface free energy of the fault plane and (ds/dn) is the area per vacancy on the fault plane for the dislocation climbing in a (120) plane (6). This second term is small to a first approximation. k is the Boltzmann constant and T is the temperature in Kelvin. It may be noted that c_0 is independent of external gas pressure. Most importantly, the equilibrium between c_0 and a collapsed *CS* plane is maintained by exchange of vacancies at dislocations which bound the *CS* plane. This equilibrium cannot be maintained except by the nucleation of a dislocation loop and such a process requires *supersaturation* of vacancies. Thus we introduce the concept of supersaturation of point defects in the nonstoichiometric oxides, which is the driving force for the nucleation of *CS* planes.

From thermodynamics, $\Delta G_v = \Delta H_v - T\Delta S$, where ΔH_v and ΔS are the enthalpy and vibrational entropy of formation, respectively, of doubly charged anion vacancies. From empirical relations (15), $\Delta H_v =$

$2(E_{\text{atm}}/y - 167)$ kcal. per mole, where E_{atm} is the energy of atomization of an oxide with the general formula M_xO_y . It is the energy required to dissociate the oxide into gaseous atoms of the components. Further, $E_{\text{atm}} = -\Delta H_f + xL_s + y\Delta D$, where $-\Delta H_f$ is the heat formation of the oxide, L_s is its heat of sublimation at 298 K, and ΔD is the dissociation energy of the oxygen molecule (respectively, ~ 86 , 70, and 120 kcal/mole for MoO_3) (16). (Qualitatively, ΔH_v is the energy needed to remove one mole of oxygen atoms from anion sites in the oxide and (E_{atm}/y) is an average bond strength of the oxide per gram-atom oxygen). Using the above values, we obtain $\Delta H_v \sim 0.4 \text{ eV} \pm 0.1 \text{ eV}$ for MoO_3 , $\sim 1.3 \text{ eV}$ for V_2O_5 , and $\sim 3 \text{ eV}$ for WO_3 (which is quite large, suggesting higher activation energies for vacancy formation in this system). Substituting this value for MoO_3 (assuming γ to be small), $c_0 = (4 \pm 1) \times 10^{-4}$.

The actual concentration of vacancies (c) in the collapsed discs, at a temperature T , due to external (gas) reactions, can be estimated from the density of the defects observed, and the area covered by their depth (i.e., density \times area, (17)), assuming that most vacancies are absorbed by defects into collapsed discs. (c can also be determined by chemical studies; e.g., by measuring the rate constants of the reactions (6)). From dynamic EM studies the density of *CS* planes $\sim 3 \times 10^9/\text{cm}^2$, the nucleation rate (density/time) is then $\sim 8.5 \times 10^7/\text{cm}^2 \text{ s}$, and $c \sim 3 \times 10^{-2}$. This gives the supersaturation (c/c_0) of $\sim 10^2$ at the surface, necessary to nucleate the *CS* planes.

From the discussion in Section 2, it follows that *CS* planes are formed by eliminating vacancies in supersaturation to preserve equilibrium. Supersaturation is defined relative to the background concentration of vacancies in equilibrium with *CS* planes. The driving force for the nucleation of a *CS* planar fault is therefore the difference between the chemical stress due to the supersaturation of vacancies of the faulted crystal and the force required to create the fault. In fur-

ther reduction of the oxide, *only* vacancies in supersaturation are consumed by the advancing CS plane. The chemical potential gradient for the vacancy exchange mechanism in fact results from this supersaturation and is given by $kT \ln(c/c_0)$. Thus some of the principles advanced by Anderson can be reconciled using our model of supersaturation of point defects which is accommodated by the extended defects. The model is consistent with energy considerations involved in the classical nucleation theory of dislocation half loops (11, 17) and with the dynamic growth rates observed for the CS planes (Fig. 1d). Furthermore, by identifying the depth of the dislocations to the diffusion front of the vacancies, the value for activation energy of migration of vacancies (due to the dislocation-point defect interaction in supersaturation) obtained from the dynamic electron microscopy (~ 1 eV, Ref. 6) is consistent with the value of ~ 1 eV from chemical reduction studies reported in the literature (18).

In selective oxidation of hydrocarbons (or of allylic intermediates) and methanol, selectivity begins to decrease with the increase in the concentration of CS planes (above $\sim 380^\circ\text{C}$) (6, 7, 13, 19). Figures 2d and e show examples of conversion and selectivity for MoO_3 , TeO_2 , and some mixed metal Te-Mo oxides, in the ammoxidation of propylene, at $\sim 400^\circ\text{C}$. For MoO_3 trends for selectivity to acrolein are similar to those found for conversion shown in (d). A correlation between the microstructure and reactivity shows that the conversion and selectivity of MoO_3 are not increased as a function of time (pulses) and the concentration of CS planes (which increases with time) (6, 7). Similar observations are made in the oxidation of methanol (19). Prior to the nucleation of CS planes, there is growth of microdomains containing anion vacancies (sources of anion vacancies), and the samples also have an equilibrium concentration of vacancies, as described before. The CS planes are formed by eliminating the point defect supersaturation, and loss in cat-

alyst selectivity is also observed at this stage, establishing a link between the elimination of anion vacancies and the loss in selectivity. Slightly anion-deficient WO_3 with a finite number of CS planes used in some studies (13) also contains a certain concentration of anion vacancies in equilibrium with the CS planes, and the role of these vacancies should be considered in the interpretation of catalytic activity. A further important factor is that in many of the commercially relevant mixed-metal oxides (e.g., oxides of Te-Mo, Bi-Mo, Fe-Mo), dynamic electron microscopy under controlled conditions of gas pressures and temperatures reveals that CS planes are absent at catalyst operating temperatures, and quite different surface energy and environment driven phenomena occur, leading to ordered microdomains which are often active phases (6, 7). The data on the reacting model oxides described above indicate that anion point defects are active centers in the fast diffusion of oxygen, and that CS plane structures which only accommodate the supersaturation of these point defects (eliminating the active sites) are in general secondary or detrimental to catalysis. They are thus consequences of the reactions, rather than the origin of the activity. Thus the model of supersaturation can answer the fundamental point about the role of the extended defects in catalysis, and the paradox regarding point defect or ionic diffusion in solids.

3. Nonstoichiometry in High Temperature Superconducting (HTSC) Ceramic Oxides

Imperfections in HTSC ceramic oxides, which are invariably nonstoichiometric, could be the key to new materials and to new high technology devices. Many of the concepts proposed by Prof. Anderson are also applicable to this class of compounds, which exhibit considerable structural elegance and complexity. For superconductivity Cu ions should be in a mixture of +2 and +3 formal oxidation states. We will consider those oxides in which the charge

carriers responsible for HTSC are mobile holes in conducting CuO_2 planes. The nonstoichiometry plays a major role in controlling carrier concentrations, transition temperatures (T_c), and supercurrents, and the choice of defects is therefore critical (20). The high defect concentrations suggest that the materials are not in equilibrium at room temperature. Atomic imaging EM and electron diffraction have elucidated the complexity of real structures not evident in the 'averaged' structures derived from other diffraction techniques. The intergrowths revealed by HREM have allowed new phases, often with higher T_c 's, to be synthesized.

In the complex Bi-Sr-Ca-Cu-O system (21) with idealized formulation $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1$ to 4), HREM has revealed strong deviations (modulations) from the averaged structure (Fig. 3a). Samples normally prepared in air, or oxygen exhibit superstructure modulations (22), shown in the structure image in Fig. 3b, for the $n = 2$ 2212 phase, in (010). They are incommensurate with the basic structure, with a modulation periodicity $\sim 4.7 \times a$ -cell. X-ray microanalysis has shown strontium vacancies ($\sim 16\%$) in the samples. It may be noted that the nonstoichiometry contributes to superconductivity by doping holes in the CuO_2 sheets, as the 'defect-free' stoichiometric 2212 is nonsuperconducting. The periodicity of the modulation is sensitive to the annealing environments: it is commensurate (Fig. 3c and d) in samples annealed in nitrogen (for 36 hr, with a $T_c \sim 90$ K), and also in samples prepared entirely in nitrogen (nonsuperconducting), but is incommensurate in oxygen (with a T_c of ~ 70 K). The results in N_2 demonstrate that the modulations are intrinsic to the materials, i.e., not due to oxygen interstitials as reported in the literature (23). They may arise from a lattice mismatch between the BiO and the perovskite layers, as also indicated in the single crystal X-ray diffraction study (24). The data suggest that an optimum superconducting structure is formed in samples (containing cation vacancies and an anion stoichiometry near ~ 8) annealed in N_2 . In the oxygenated samples anion interstitials between the adjacent BiO layers result in an incommensurate periodicity and in the overoxidation of the CuO_2 sheets, resulting in a reduced T_c . Coherent, nonstoichiometric intergrowths belonging to other phases in the homologous series are also often present. Specialized synthesis or lead substitution is necessary to stabilize the high T_c phases.

3.1. Intergrowths and "Shear" Structures in HTSC

3.1. Intergrowths and "Shear" Structures in HTSC

The concept of topologically compatible intergrowths is of considerable significance in nonstoichiometric solids. Coherence can be achieved by point defect ordering, or by a polyhedral shear process leading to models for defect mechanisms. We have some evidence that topologically compatible intergrowth stacking faults are nucleated as shear loops of partial dislocations which can expand by glide, or climb, depending on the nature of the dislocations bounding the faults (25, 20). As described in the preceding sections, dislocations may be nucleated by pure shear to accommodate the lattice strain, e.g., during phase transformations, or by collapsed discs by CS by eliminating point defect supersaturations.

The idea of "shear structures" with edge sharing CuO_6 octahedra accommodating oxygen deficiency in high T_c oxides was first suggested using detailed diffraction contrast EM experiments in the complex $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system (25).

Homologous series of oxides intermediate between LaCuO_3 and La_2CuO_4 (26) can, in principle, be derived by the insertion of CuO layer(s) by shear (25, 27). Intercalation of CuO intergrowths by shear in the Y-Ba-Cu-O system has also been described (27).

The atomic image (Fig. 4a) elucidates stacking fault defects (arrowed) in the $n = 2$ phase in the Bi-system, leading to different compositions in the upper and lower part of the defects. However, the sums of the

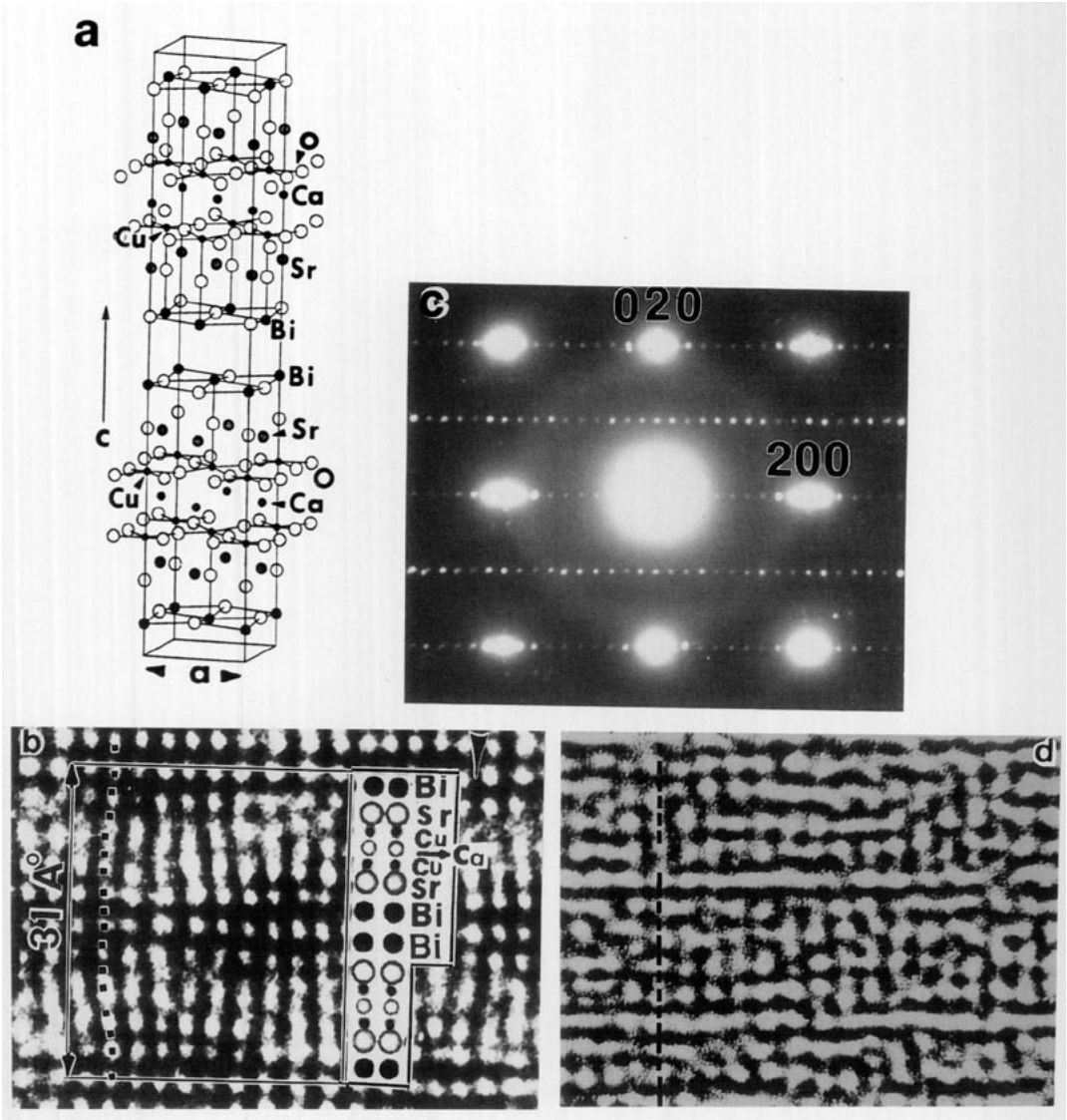


FIG. 3. (a) Average structure of 2212-Bi₂Sr₂CaCu₂O₈: the Bi-O layers and the perovskite layers are shown. The unit cell is orthorhombic ($a = 5.39$, $b = 5.41$, $c = 30.8$ Å and contains two BiO, two CuO₂, two SrO, and one Ca layer. (b) Atomic image showing the modulated structure (wavy lattice). The modulated supercell and the atomic arrangement are indicated. (c) Commensurate modulation (periodicity of 5) found in the samples annealed, or prepared in N₂ indicating that modulations are intrinsic. Note that the modulation amplitude decreases compared to that in O₂ (indicated by the dotted line).

magnitudes of the lamellae in the upper and of the lower portions are equal (shown in the schematic in (b)). The closure-failure of the Burgers vector component parallel to the c -axis, enclosing the partial dislocations, is near zero. Such images indicate that in-

tergrowths of different widths are formed, or adjusted, to accommodate the prevailing stoichiometry via a dislocation mechanism. Observations suggest that in HTSC, perovskite intergrowth layers are readily formed. It is possible that the planar fourfold coordi-

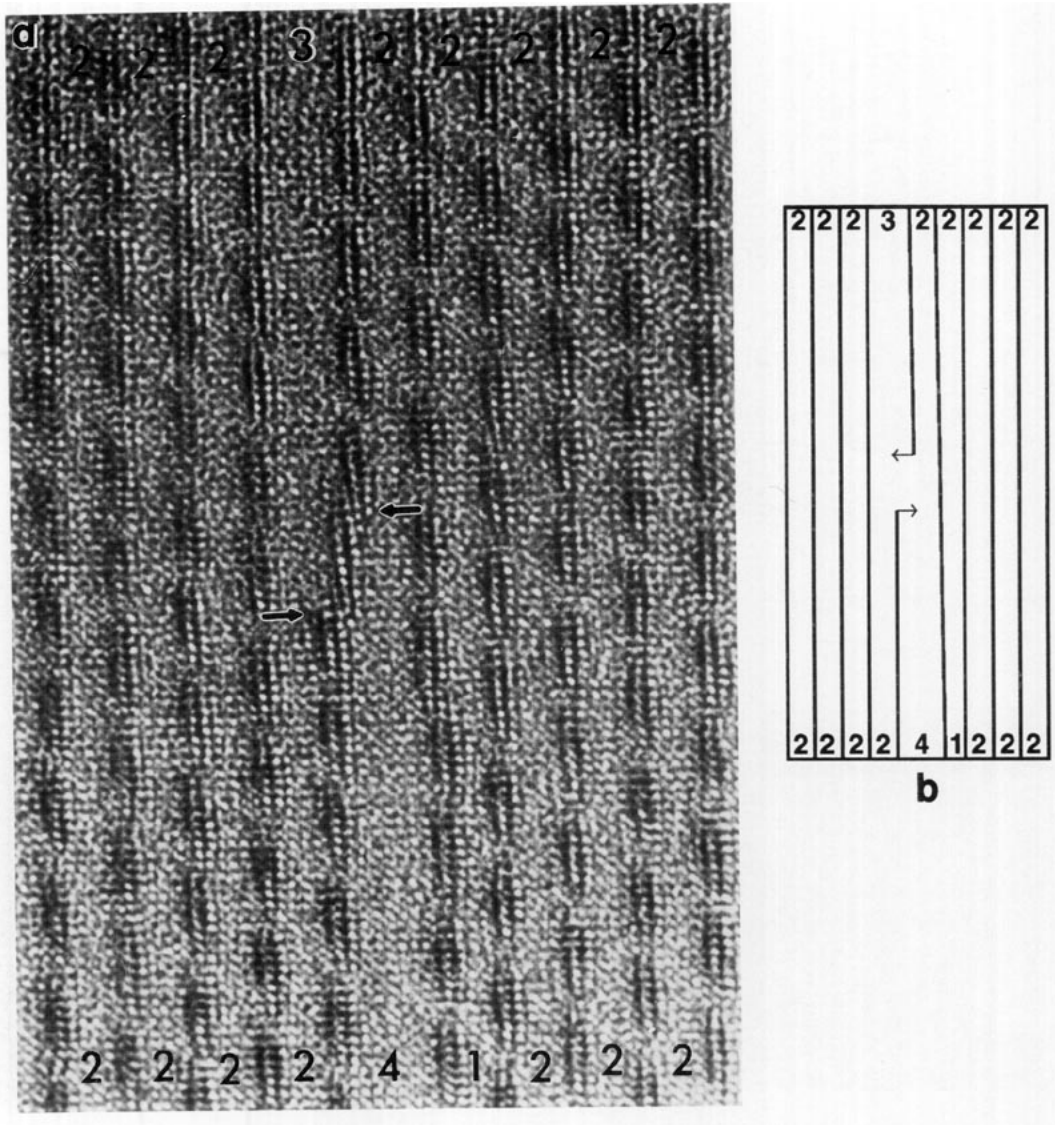


FIG. 4. (a) HREM of a defect intergrowth in 2212, with intergrowths of $\frac{1}{2}$ c -spacings: of $n = 4$ ($c/2 \sim 21 \text{ \AA}$), $n = 3$ ($c/2 \sim 18 \text{ \AA}$), $n = 1$ ($c/2 \sim 12 \text{ \AA}$). The layers marked 2 have $c/2 \sim 15 \text{ \AA}$. The sum of the c -lattice parameters above and below the defects (arrowed) is equal and the long range strain field due to the defects cancel. (b) A schematic of the layers in (a). (c) High resolution image of the mixed polytype of 1223/2223 in Tl-Ba-Ca-Cu-O. (d) and (e) are structures of the two phases.

nation of copper is energetically preferred. Furthermore, by controlling synthesis it is possible to generate new structures of two (or more) intergrowth phases occurring in a semiperiodic fashion, with interesting properties. This is revealed uniquely by HREM

in the example in Fig. 4c: the intermediate structure is a mixture of the single $\text{TlBa}_2\text{Cu}_3\text{O}_9$ (1223) and the double $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223) phases. The structures of the phases are indicated in Fig. 3c and d, respectively. Although the symmetry of the two

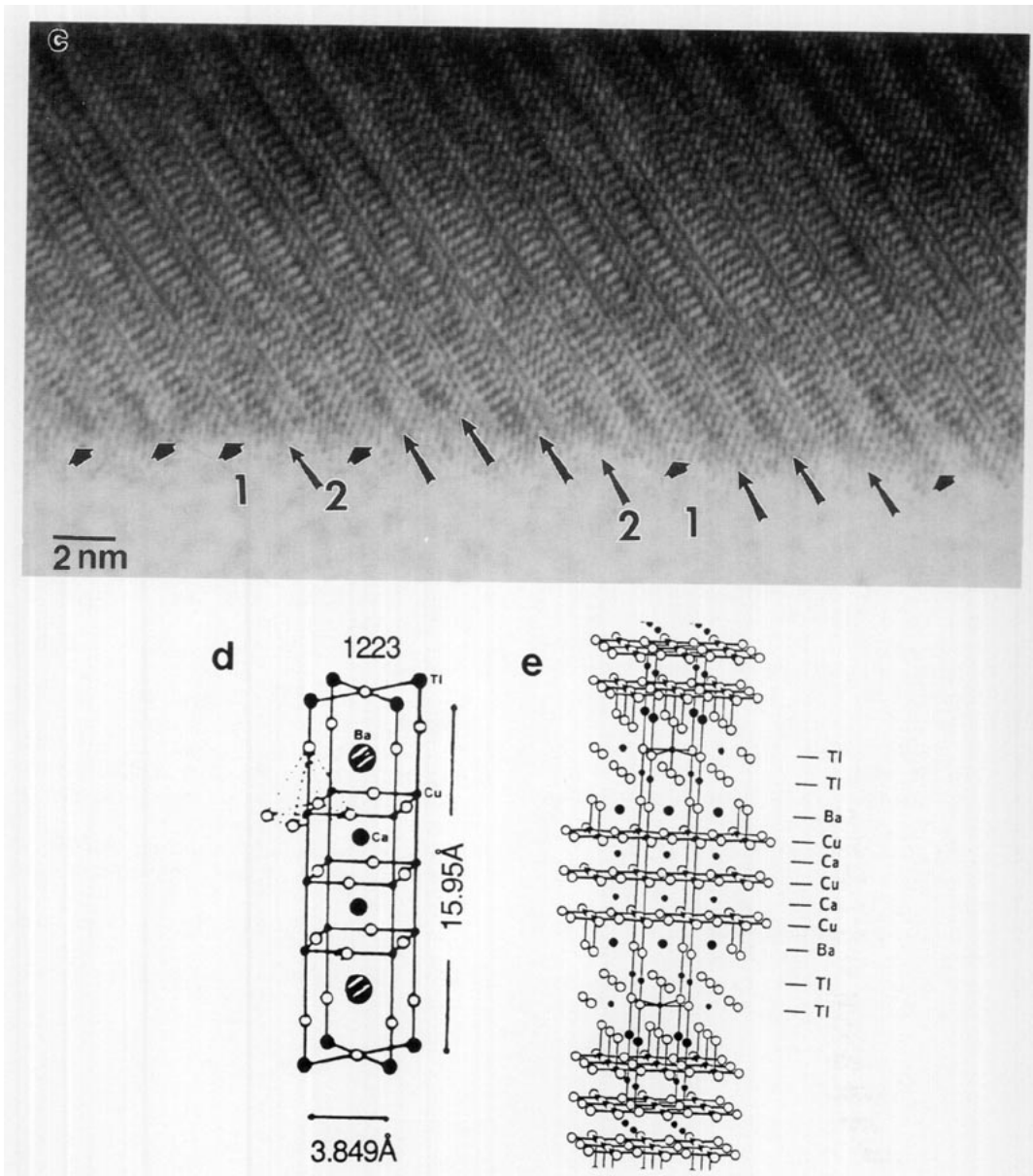


FIG. 4—Continued

phases is different ($P4/mmm$ for 1223, and $I4/mmm$ for the 2223), the mixed polytype phase is body centered.

We thus return to the first sentence: we propose that the constitution of nonstoichiometric solids can be understood in terms of equilibrium concentrations and supersatu-

rations of point defects, the latter being accommodated into extended *CS* defects, and into other broad types of planar boundaries all serving to accommodate point defects. Our model of supersaturation underpins the mechanism of nucleation of dislocation loops in Professor Anderson's model,

and fundamental concepts of diffusion-controlled solid state oxide reactions in general.

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