REVIEW LECTURE

TOPOGRAPHY AND TOPOLOGY IN SOLID-STATE CHEMISTRY

By J. M. THOMAS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth

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[Plates 6–11]

A survey of recent activity and current trends in solid-state chemistry reveals that several novel and seemingly unrelated physicochemical phenomena, together with some bio-organic, mineralogical and metallurgical attributes of the solid-state, can now be interconnected.

Four main topics are discussed. First, so far as the behavioural patterns of organic solids are concerned, topochemical control is often crucial, and it transpires that the reactivity of many types of unsaturated molecules is governed more by the precise molecular orientation and stacking sequences within the crystal structure than by the intrinsic electronic properties of the molecule itself. This fact has led to the synthesis, by the strategem of 'crystal engineering' (Schmidt 1971), of stereochemically-pure, organic products and also of single-crystal, extended-chain polymers both of which are difficult if not impossible to prepare by conventional (solution) techniques. It has also led to absolute asymmetric syntheses, under abiotic conditions, from optically inactive materials, by inducing solid-state or surface reactions in chiral crystals. The selectivity and high yields of gas reactions with organic solids, and the facile conversion of polymer crystals from their folded-chain to extended-chain forms are other manifestations of topochemical control in organic solid-state chemistry. Structural defects, too, can play a dominant rôle, and they account for the not infrequent production of topochemically 'forbidden' molecules in photo-induced reactions. The existence of stress-induced and photo-induced phase transformations and of structure-mimicry (in which guest species assume the molecular structure of the host) are further recent discoveries in this general area.

Second, topochemical control, which needs to be distinguished from topotaxy, is often important in the reactions of inorganic solids, particularly in intercalation (or its reverse) in which charged or neutral guest species are accommodated between the individual sheets of layered compounds, thereby resulting in expansion of the interlayer separation distances and, generally, some modification of the stacking sequence. Exceptionally selective organic reactions may be carried out in the interlamellar spaces of silicate minerals, and crystal engineering, in the sense that reactant molecules are locked in well defined orientations conducive for subsequent reaction within inorganic matrixes, again becomes a feasible proposition.

The third topic of discussion is stacking sequences and stacking faults, which serve as the nexus between the chemistry of layered solids and the structural principles of inorganic solids in general. The relations between the structural characteristics of a range of inorganic solids, and plausible mechanisms of interconversion based on martensitic transformation, follows logically; and changes of coordination number (in going from NaCl- to CsCl-type structures for example) may be rationalized in terms of continuous topological variation. Stacking faults are intimately connected both with partial dislocations and antiphase boundaries, and these, in turn, figure as important concepts in the understanding of the ultramicrostructure of grossly non-stoicheiometric solids, which is the main theme for the fourth topic discussed here.

The chemical consequences of linear and planar faults are surveyed, there being a summarizing account of their rôle in the reactivity of solids, and a fuller one of single, double and pivoting crystallographic shear planes. Relations between shear and block structures are adumbrated; and the merit of introducing the notion of cylindrical fault boundaries, so as *inter alia* to relate ReO_3-type to tungsten bronze structures, is outlined. The considerable analogical value of dislocation theory in interpreting the ultramicrostructural characteristics of non-metallic solids, especially as revealed by electron microscopy, is emphasized throughout.

1. Introduction

If, five years ago, one had been asked to comment on the impact of topological concepts upon chemical thought, most chemists would, I imagine, have drawn attention to at least two specific examples. The first would have taken us back to the nineteenth-century mathematical crystallographers Fedorov and Barlow – or even earlier to Euler – who, by laying down the principles for the closest packing of polyhedra and spheres paved the way for the subsequent understanding of the architecture of perfect crystals, be they metals, oxides, silicates, clathrates or even foam-like networks. The second could well have been the idea of topological isomers, first suggested by Willstätter (1912), and now very much in the limelight ever since Wasserman, in 1960, focused fresh attention on the interlocked rings of hydrocarbons nowadays known as catenanes.

Both these aspects of topological chemistry continue to elicit much interest as may be judged from the discussions of Wells (1973) – who has dealt with the geometry of repeating patterns in which numbers of octahedra meet at a point – or Kitaigorodsky (1973) – who has applied the principle of close-packing to molecular (particularly organic) crystals – and the recognition of the importance of twisted or knotted molecules, as well as Möbius-strip species, in a wide variety of contexts both in organic and in biological chemistry (Heilbronner 1964; Walovsky 1970; Shen 1973; Wang 1973). Moreover, in the past five years progress has been rapid in the general application of topological and cognate graph-theoretical concepts to chemical bonding, thermodynamics, adsorption, and in the representation of various chemical systems such as Berry pseudo-rotation (Rouvray 1971, 1973; Smolenski 1964; Hosoya 1971; Dunitz & Prelog 1968; Gielen & Depassi-Delit 1969; Jotham 1973). But important as these developments unquestionably are, we shall, in this review, be concerned with rather different kinds of topological concepts.

First (§2) we deal with the notion of *topochemistry and topochemical control*, terms which were originally introduced in 1918. We shall see that, with the aid of these concepts (Kohlschütter 1918, 1920; Hertel 1931), and particularly as a result of their resuscitation and brilliant exploitation by Schmidt and co-workers within the past decade (Schmidt 1967, 1971; Cohen & Green 1973), major advances have been achieved in organic solid-state chemistry, in polymer science and in certain biologically significant areas of chemistry such as absolute asymmetric synthesis under abiotic conditions. We shall also discuss 'crystal engineering', through the agency of which it is now possible to 'design' molecular crystals in which reactive centres on neighbouring molecules are within a certain, fruitful distance apart, a situation hitherto realized under 'ordinary' conditions chiefly through a favoured dispensation of Providence. Defects, in the form of structural imperfections (Thomas 1969, 1970*a*, *b*), are often of crucial importance in topochemical reactions and also in the separation or interconversion of phases within organic solids. These topics will, therefore, also be considered in §2.

In discussing topochemical reactions within inorganic solids (§3), separation of the product into a distinct phase is a more frequent occurrence than in their organic counterparts. It is, therefore, necessary to concern ourselves with the notion of *topotaxy and topotactic reactions*, terms which are sometimes taken (erroneously) to be synonymous with topochemical phenomena. We shall, with the aid of specific examples, distinguish between topotactic and topochemical reactions. It will be seen that intercalation, which refers to the insertion of species between the individual sheets of layered materials, or its reverse – where constitutionally intercalated molecules are removed – serve as particularly appropriate means for emphasizing the distinction between topochemistry and topotaxy in inorganic crystals. Layered solids are also convenient to introduce the idea of stacking sequences, stacking faults and partial dislocations which, in turn, are valuable concepts for interrelating the structural characteristics of and possibly the mechanism of change amongst a range of inorganic solids hitherto regarded as unrelated. These topics constitute §4.

In §5 we turn to the rôle of linear and planar faults in influencing the solid-state chemical properties of simple inorganic materials. Particular prominence will be given to the microstructural aspects of binary and ternary transition metal oxide systems, in which various combinations of stacking faults and so-called crystallographic-shear planes, together with rotation faults (which give rise to cylindrical antiphase boundaries) are now known to be present. It will emerge that high-resolution electron microscopy has revealed exhilarating new perspectives, and afforded remarkable insights of the beauty, ordered complexity and arcane mysteries of the ultramicrostructural characteristics of the grossly non-stoicheiometric metal oxides.

Finally (§6) topochemical factors in heterogeneous, gas-solid reactions, with special reference to organic single-crystals, will be briefly reviewed. Such reactions promise to be of unusual value in synthetic organic chemistry and in wider contexts.

2. TOPOCHEMICAL CONTROL IN ORGANIC SOLIDS

It is has been recognized for almost a century that a number of organic materials will, when irradiated with ultraviolet light, readily undergo chemical changes in their crystalline forms but remain unreactive both in solution and in the molten state. The classic example is *trans*-cinnamic acid, which Liebermann studied in 1889: it dimerizes in the solid (see later) but merely isomerizes in solution. In some cases an organic monomer will photodimerize both in the solid-state and in solution, but the products are stereochemically distinct (see scheme 1 which refers to the photo-induced dimerization of acenaphthylene carboxylic acid studied by Desvergne (1973) and Bouas-Laurent *et al.* (1972)).

These facts demonstrate the specialized nature of chemical reactivity in the organic solid-state, and were, historically, the kind of information that led Kohlschütter (1918) to enunciate his topochemical principle: the *properties and nature of the products* of a solid-state reaction are in large measure *determined by the fact that reaction occurs within or on the surface of the solid.* Without tracing the argument chronologically, it is essential, in order to appreciate what is meant by topochemical control, to recognize three special attributes† that organic molecular crystals possess.

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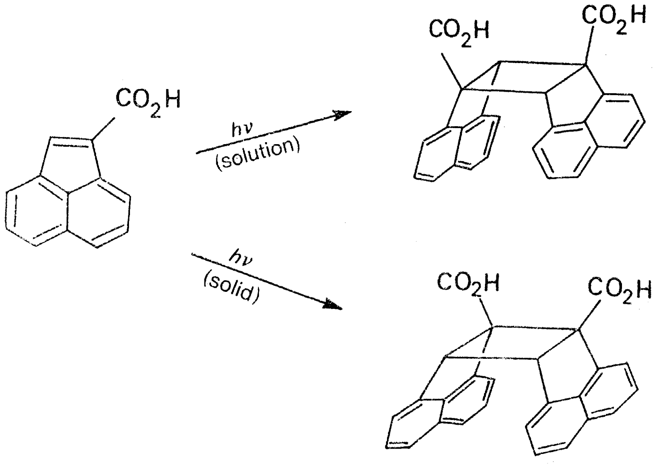
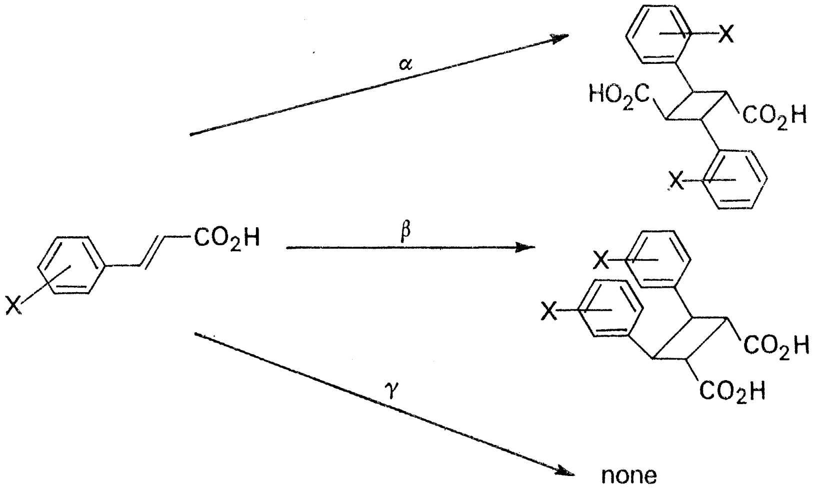
† These attributes have come to light chiefly through the application to X-ray crystallography to organic solids.

(i) All the molecules that occupy the lattice sites in a given organic crystal, of a defined space-group, occur in only a small number of conformations – in many crystals there is but one. This is true even of very flexible, complex molecules which, in non-crystalline states, generally exhibit a multiplicity of conformations (Paul & Curtin 1973; Cohen & Green 1973).

(ii) The geometries and, in particular, space-symmetries relating neighbouring molecules, and the possible types of intermolecular approaches and contacts, are strictly limited and well defined in the crystal, in marked contrast to the situation that prevails in fluid media.



SCHEME 1

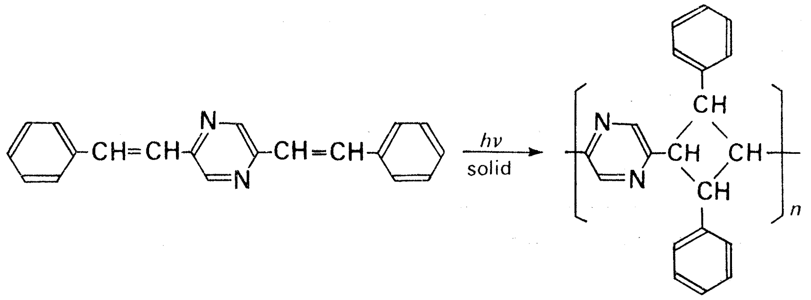


SCHEME 2

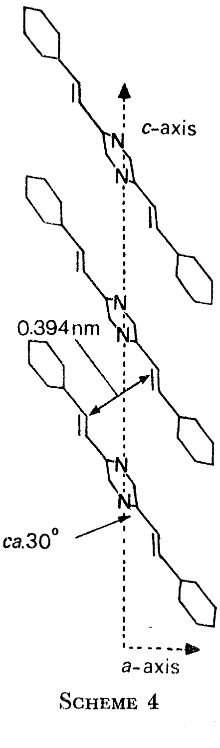
(iii) Many organic molecules display a rich range of polymorphic types (Jones 1974; Jones, Thomas & Williams, in preparation) among which the conformations and space-symmetries which relate neighbouring reactant molecules may vary: the conformations less frequently than the space-symmetries.

These attributes enable us to understand why the reactivity (especially when it is photo-induced) of an organic molecule locked in the solid-state is dependent more upon the particular polymorphic form of the crystal than the intrinsic reactivity of the molecule. (Before the advent of X-ray structural determinations, this point was not appreciated; and it is pedagogically illuminating to examine the confusion that arose in discussions on the photodimerization of *trans*-cinnamic acid (see, for example, Bernstein & Quimby 1943) in the light of present knowledge.)

The critical importance of molecular packing, rather than molecular conformation in this instance is well illustrated (Cohen & Green 1973) by the variation in photoreactivity of *o*-ethoxy-*trans*-cinnamic acid (scheme 2).



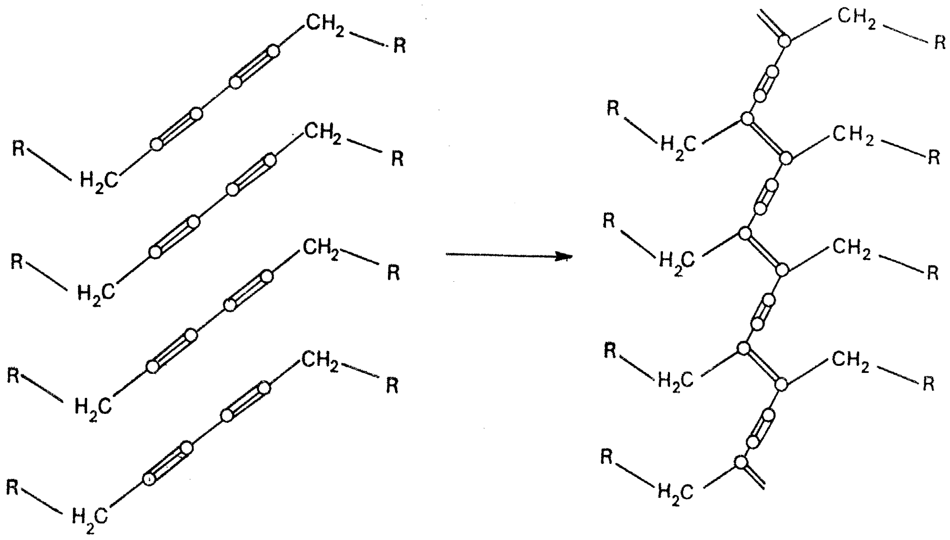
Scheme 3



Scheme 4

The α-type polymorph, which crystallizes from acetone and in which there is centro-symmetric or head-to-tail relation between closely spaced neighbouring monomer molecules, yields the truxillic acid dimer, which is centro-symmetric. The β-type polymorph, which crystallizes from benzene and in which there is mirror-symmetric or head-to-head relation between the closely-spaced neighbouring molecules, yields the truxinic acid dimer which again has the cyclobutane skeleton but which is now mirror-symmetric. And the γ-form, which crystallizes from aqueous ethanol and in which neighbouring molecules are not favourably disposed, both with respect to separation distance and space-symmetry, is light-stable.

Topochemical control of this kind was accidentally harnessed by Koelsch & Gumprecht in 1958 in their remarkable discovery of the low-temperature (*ca.* –60 °C) photopolymerization of solution-grown crystals of 2,5-distyrylpyrazine (DSP) (scheme 3). (Vapour-grown crystals do not polymerize.) The production of linear PDSP and related polymers by means of a sequence of (2+2) photocycloadditions from a diolefinic monomer in the solid-state has been elegantly clarified by Hasegawa and co-workers (see, for example, Iguchi, Nakanishi & Hasegawa 1968; Hasegawa, Suzuki, Nakanishi & Nakanishi 1973). It is clear that within the particular orthorhombic crystals which can be smoothly converted to crystalline, linear polymers, the monomer molecules are so disposed (scheme 4) as to form a plane-to-plane parallel stack (shifted by approximately half a molecule as in the α-type packing of *trans*-cinnamic acids) along the *c*-axis. Within these stacks the olefinic bonds have a separation of only 0.394 nm. The next shortest 'reaction' distance, 0.542 nm, involves molecules in different stacks related by *b*-glide. It is significant that the molecular weight of crystalline PDSP formed in the solid-state surpasses that of solution-grown polymer, which is in any case amorphous, by factors of up to a hundred.



Scheme 5

Wegner and co-workers (Wegner, Munoz-Escalona & Fischer 1970; Wegner 1970, 1972) who skilfully designed† their substituted diacetylene monomers (scheme 5), were able, by deliberately harnessing the principle of topochemical control, to synthesize, both thermally and photochemically, highly stereoregular extended-chain polymers which are impossible to prepare by alternative means. The idea is to produce crystals in which the monomers, each with their two potentially reactive centres, are so oriented that they can rotate in place, by means of a process which Wegner, following Hirschfeld & Schmidt (1964), termed 'molecular shear', to link up with their neighbours without any linear displacement of the molecular centres. It is as if the centre of gravity of the rigid rodlike molecule acts as a fulcrum, as would also be the

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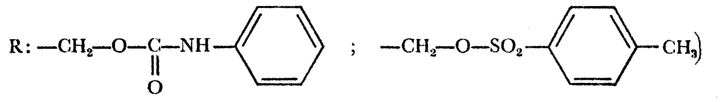
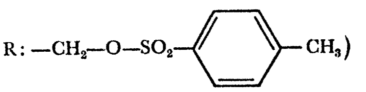
† There had been many previous discussions centred on designing monomer arrangements within solid matrices conducive for subsequent polymerization (see, for example, Letort (1933), who considered the low-temperature polymerization of acetaldehyde; Brown & White (1960), who dealt with radiation-induced polymerization of monomers entrapped in urea-canal complexes; Morawetz (1963, 1966), Hirschfeld & Schmidt (1964) and Cohen & Schmidt (1964) who discussed trioxane, β-propiolactone and diketene polymerization in the solid).

case for the formally analogous situation with DSP (compare schemes 4 and 5). Wegner *et al.* (1973) have carefully selected their substituents R (for example



so as to ensure that adequate net attraction exists between these substituents in adjacent molecules, thereby bringing the reactive centres in neighbouring monomers close enough together to lead, following appropriate photo- or thermal stimulation, to unimpaired polymerization. Massive samples of single-crystal stereoregular polymers are generated in this way. As with PDSP the polydiacetylenes are isomorphous with the monomer. The topochemical polymerization of the diacetylenes and triacetylenes (Kiji, Kaiser, Schultz & Wegner 1973) with conjugated triple bonds is an example of polymerization in solid solution: polymer chains grow as isolated macromolecules within the monomer lattice, and quantitative conversion can sometimes be achieved without phase separation. Colourless crystals of the diacetylene monomer (with, for example



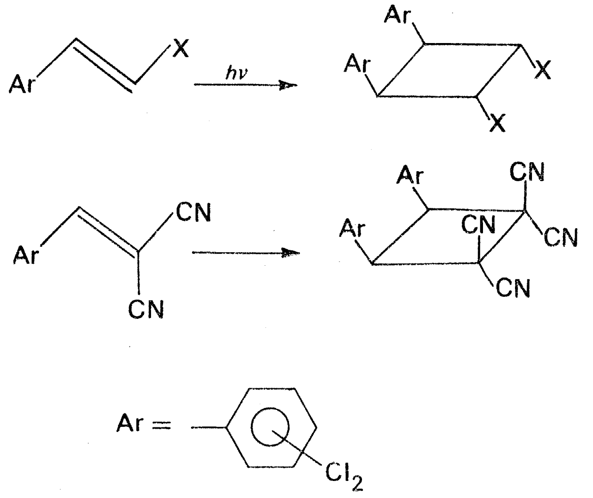
yield single-crystal polymer samples which display marked dichroism: when the plane of polarization of the incident light is perpendicular to the direction of the polymer chain the crystals are transparent, and when parallel they are bright red.

(*a*) *Crystal engineering*

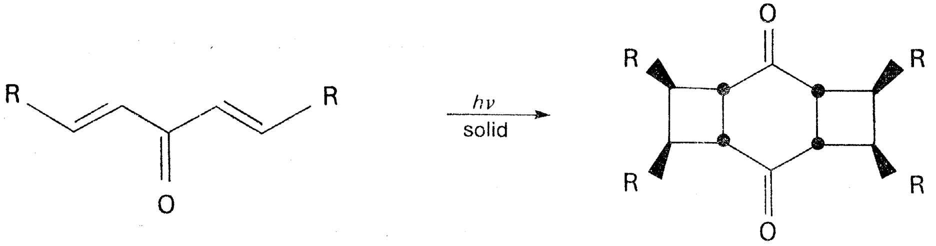
With the exception of the successful efforts of Wegner and Hasegawa and their co-workers to influence the extent of intermolecular contacts in a monomer matrix, no generally applicable method was until recently available to control the nature of the molecular packing that prevailed in a given crystal. To be able to engineer a crystal structure with a particular reaction product in mind is obviously a desirable goal. Fortunately, Schmidt & Green (1971*a*, *b*) have discovered that the simple expedient of halogen, and especially of dichloro, substitution in aromatic and related molecules tends to produce crystalline, modifications which have a shortest unit-cell axis of *ca.* 0.4 nm, signifying a close-packed, highly overlapped, parallel molecular stacking. This widely applicable generalization, which relies on the existence of an incompletely understood attractive interaction between non-bonded halogen atoms – see Epiotis (1973) for further discussions of the $p\pi$ and $p\sigma$ type attractive interactions between lone-pairs in non-bonded atoms – has been successfully utilized by Schmidt & Green (1971*a*, *b*) to 'engineer' the crystallization of structures with 0.40 ± 0.02 nm overlapped-distances for compounds differing widely in their molecular mass, size, functionality, symmetry, polarity and melting point. Indeed many types of carbon skeletons thus manipulated had not previously been found to exhibit this close, overlapped crystal-packing. With such knowledge it soon became possible to synthesize, in a predictable and highly efficient manner, a large number and variety of cyclobutane derivatives possessing mirror symmetry (scheme 6).

A striking exploitation of the existence of 'halogen bonds' in the context of crystal engineering is contained in the first rational construction of the tricyclic diketone ring system shown in scheme 7 ($R = 3,4\text{-}C_6H_3Cl_2$). Green & Schmidt (1970) prepared this decane derivative, where eight carbon atoms have been stereospecifically joined for the expenditure of a single photon, by means of a topochemically controlled solid-state photodimerization in a crystal which had been previously engineered. B. S. Green (private communication) is now extending such controlled syntheses to trienones, which are potentially capable of yielding 4:6:8 fused-ring systems of the required stereochemistry via 8-centre dimerization followed by thermal Cope rearrangements. (Scheme 8 with R = C_6H_5, R^1 = 2,4- or 2,6-$C_6H_3Cl_2$.)

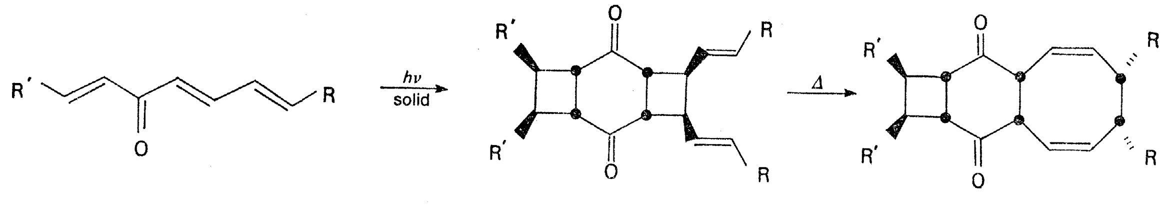
X = Ph, CO_2H, CO_2Me, COCl, CN, CO_2Ph, COMe, 2-thienyl.



SCHEME 6



SCHEME 7



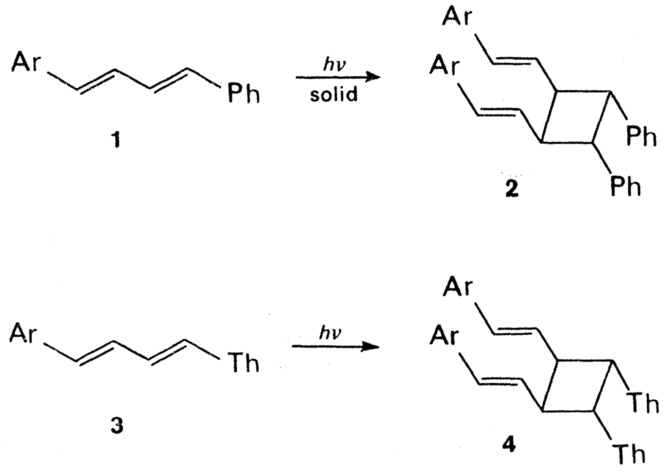
SCHEME 8

Dichlorosubstitution has also been used to good advantage as an anchoring device to aline molecules in two-component mixed crystals for the directed synthesis of so-called mixed (or hetero) photodimers, a key process in the production by Elgavi, Green & Schmidt (1973) of an optically active molecule from optically inactive starting material. This is described in the next section. It is clear, however, that on the basis of the extensive semi-empirical information already available (Kitaigorodsky 1961, 1973) regarding atom–atom potentials abundant scope exists for further crystal-engineering operations besides that based on the halogen bond.

(*b*) *Asymmetric synthesis*

The possibility of accomplishing asymmetric synthesis by performing solid-state reactions on molecules which are optically inactive in solution but which form chiral single crystals opens up new perspectives in organic chemistry and is of considerable interest in discussions concerned with the prebiological origin of optical activity (Wald 1957; Orgel 1972).

Once it was realized by M. Lahav, B. S. Green & G. M. J. Schmidt (private communication 1969) that the formation of unequal amounts of enantiomens might result from the irradiation of a two-component (solid-solution) chiral crystal, the operation of crystal engineering, through appropriate halogen substitution, could then be utilized to proper advantage. Elgavi *et al.* (1973) took 1-(2,6-dichlorophenyl)-4-phenyl-*trans*, *trans*-buta-1,3-diene (**1** of scheme 9) which crystallizes in the space group $P2_12_12_1$ with stacks of closely-spaced (*ca.* 0.4 nm) and strongly overlapped neighbouring molecules. Irradiation of **1** in the solid state yields a single photoproduct, the mirror-symmetric **2**. The analogue of **1**,1-(2,6-dichloro-phenyl)-4-thienyl-*trans*, *trans*-1,3-butadiene (**3**), is isomorphous with **1**, has the same space group, and upon irradiation also affords the topochemically expected photodimer (**4**). When crystals containing **1** and **3** in solid-solutions are irradiated, the formation of dimers **2** and **4** may be suppressed by using a small (*ca.* 15 %) amount of the thiophene compound **3**, which absorbs at slightly longer wavelengths than does the phenyl compound **1** and irradiating through appropriate cut-off filters so that, ideally, only **3** absorbs light. (The dilution of **3** minimizes the number of **3**...**3** contacts, making it difficult for **4** to be formed, while lack of excitation of **1** prevents formation of **2**.)

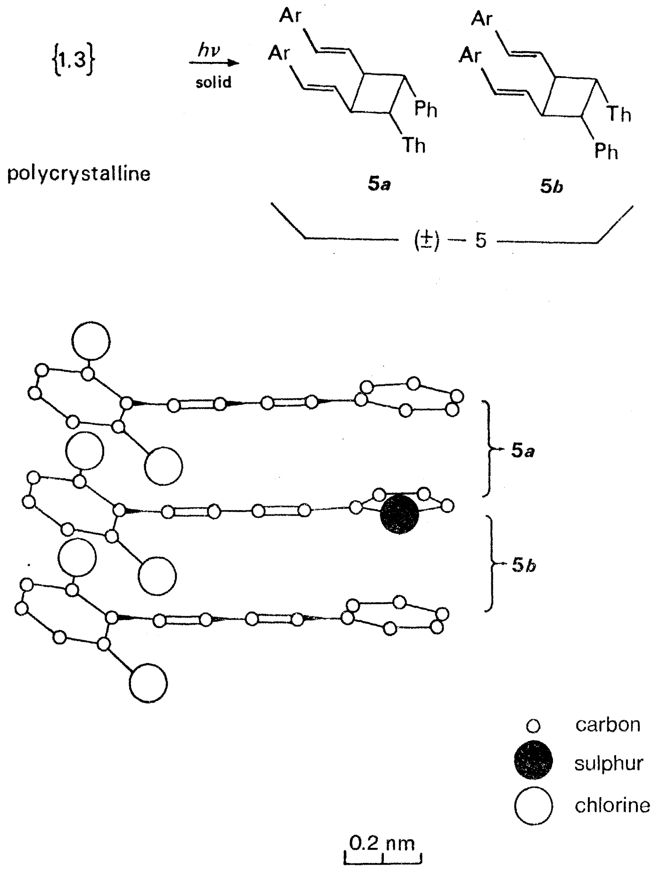


Scheme 9

Now if photo-excited molecules of **3** contained in stacks of **1** display differences in reactivity of their 'upper' and 'lower' faces during reaction to give **5**a and **5**b (scheme 10), respectively, unequal amounts of these heterophotodimens will form and the product will, therefore, exhibit optical activity.[†] This is demonstrated to be the case, and the mixed dimer **5** was consistently found to be active, some crystals affording dextrorotatory and some laevorotatory material. $[\alpha]_D$ ± *ca.* 1°. (Transformation of optically active **5** to less-symmetrical molecules resulted in a several-fold enlargement of specific rotation.)

[†] The ground-state perturbation of translational symmetry produced by inclusion of guest molecules **3** is believed to be negligible.

Once the absolute configuration is determined of both a given single, mixed crystal (i.e. whether stacks of molecules are twisted as shown in scheme 10 or as in its mirror image) and of the dominant cyclobutane photoproduct (**5**a for **5**b) from that crystal, it will be possible uniquely to describe the excited-state geometry responsible for cyclodimerization and, in particular, determine which face of the diaryl butadiene is the more reactive. Such information will provide insight into the reaction coordinate as ground-state molecules, initially separated by 0.4 nm, move to a final bonding distance of *ca.* 0.15 nm. It is of great interest to report that B. S. Green (private communication 1974) has shown that when bromine vapour is added to single crystals of **3**, optically active di- and tetra-bromo products are formed. When the absolute configuration of the enantiomer that dominates under these conditions is known, it will provide a striking comparison of the relative enantiotopic reactivity of molecule **3** having an exactly defined pre-reaction geometry, both as an excited-state species (in the photochemical reaction) and as a ground-state species (in the gas-solid reaction).



Scheme 10

The feasibility of executing photodimerizations which lead to optically active heterophotodimiers encourage thought of the possibility of synthesizing chiral polymers by using, for example, a sequence of (2 + 2) photocyclo additions, such as in the work of Hasegawa mentioned earlier. The systems studied so far by Nakanishi, Ueno, Hasegawa & Sasada (1972) all yield polymers with cyclobutane units containing centres of symmetry and are thus optically inactive. Similarly the topochemically-controlled cyclobutane polymers formed from $1,1^1$-trimethylenebisthymine (see, for example, Frank & Paul 1973; Leonard, McCredie, Logue & Cundall 1973) yield single crystal of achiral polymers which consist at the molecular level of exactly the same number of polymer chains of opposite chirality. There is, however, considerable scope for manoeuvre here and it ought soon to be possible topochemically to synthesize optically active biopolymers (M. Lahav 1973, private communication).

(*c*) *Role of structural defects*

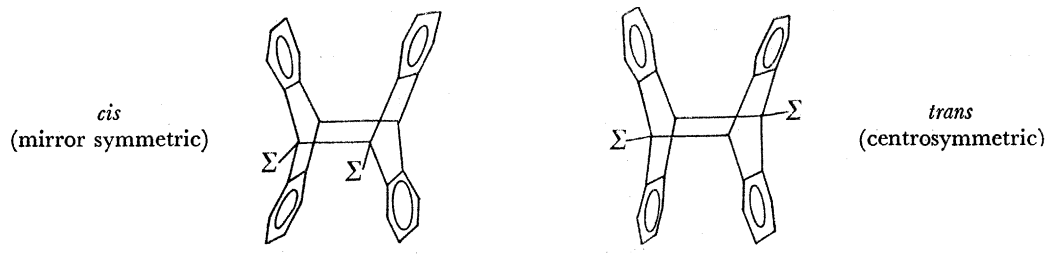
The impression conveyed in our discussion so far is that the perfect, idealized crystal structure is paramount in dictating the nature and pathway of chemical change in a solid-state reaction. It is implied that, provided the intermolecular distances and space symmetries comply with the kind of topochemical requirements that we have already described, the appropriate, predictable reaction will take place. While this is frequently true it is not universal, and there are important exceptions which we shall now consider.

In the topochemically controlled photopolymerizations which involve the production of crystalline polymers in solid-solution within the monomer matrices no phase-separation occurs, and it is understandable (Thomas, Evans & Williams 1972) that such processes should be far less sensitive - but not totally so (see, for example, Schermann, Thomas, Wegner & Williams, in preparation) – to structural imperfections than many other types of solid-state polymerizations (Bamford & Eastmond 1969, 1972; Chapiro 1972; Adler 1971) in which phase-separation and crystallization either succeeds or occurs concurrently with the process of polymerization. And in the topochemically controlled photodimerizations of the various derivatives of *trans*-cinnamic acid, excitation-energy transfer appears to be inefficient (Cohen *et al.* 1973), so that photoreaction takes place at or very close to the site of photon absorption. Consequently, molecules situated at such structural imperfections as are present in the structure (Thomas & Williams 1971, 1972) exert an insignificant influence, since their concentration is negligible in comparison with those in ordered arrays. In crystals of anthracene and many of its derivatives the situation is very different, and energy transfer is often quite extensive (Cohen 1972). As a result, an exciton can migrate through appreciable distances within the solid, and in so doing serve as a probe for various types of structural imperfections which, in turn, function as exciton traps (Cohen, Ludmer, Thomas & Williams 1971; Goode *et al.* 1974). The local order or topology of the molecules at these defects is therefore crucial since it now dictates, again in a topochemical sense, the nature of the chemical change.

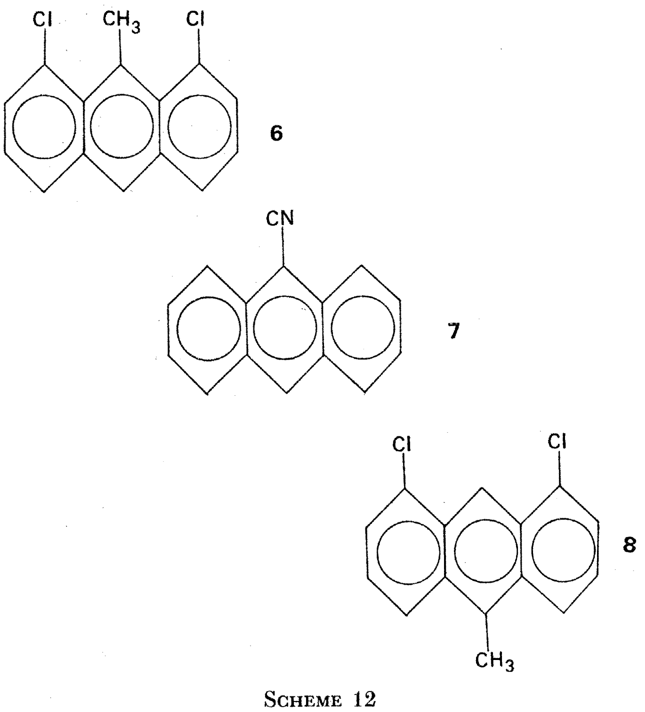
(i) *Anomalous photodimerization of anthracene and some of its derivatives*

It is a considerable challenge to explain in terms of the topology of structural imperfections how it comes to be that some monomers which, according to their idealized crystal structure, should not photodimerize yet do, while others which, again according to their crystal structure should yield one type of dimer product ('*cis*' for example, scheme 11) yield an unexpected ('*trans*'). Anthracene and 1,8-dichloro-9-methyl anthracene, **6**, belong to the first category, whereas 9-cyano anthracene, **7**, and 1,8-dichloro-10-methyl anthracene, **8**, belong to the second.

To tackle this question, it is necessary to develop some means of examining, at the molecular level, the local microstructure of the defective regions of the crystal. Unfortunately, the most powerful direct technique, transmission electron microscopy, which has afforded valuable information (principally from diffraction-contrast techniques, see Hirsch *et al.* (1965)) on the microstructure of metallic and many inorganic solids, is not readily applicable to organic crystals owing, chiefly, to the extreme sensitivity of these types of materials to electron-beam damage. Consequently, indirect and rather less discriminating, but nevertheless informative, approaches have been made through, for example, X-ray topography (Lang 1970; Minkoff, Thomas, Williams & Evans, in preparation) and especially through optical microscopic examination of the surface topography of deformed, cleaved and etched surfaces of many organic crystals (Thomas 1969; Thomas & Williams 1971, 1972).



Scheme 11



Scheme 12

Electron microscopy is not, however, totally inappropriate provided certain additional sophisticated devices (see, for example, Williams & Thomas 1972; Jones 1974; Jones, Thomas, Williams & Hobbs (in publication)) are also utilized and model systems carefully selected. Thus, although anthracene itself has rather too short a lifetime (Glaeser 1974; Jones 1974) under low-temperature electron-microscopic conditions, much can be learned by examining instead the behaviour of a very closely related crystal, *p*-terphenyl, which is more beam stable and has the same space-group, $P2_1/a$, as anthracene. The micrographs (figure 1*a*, *b*, plate 6) reveal strong evidence for the existence of dislocations which glide on (001) planes and possess a

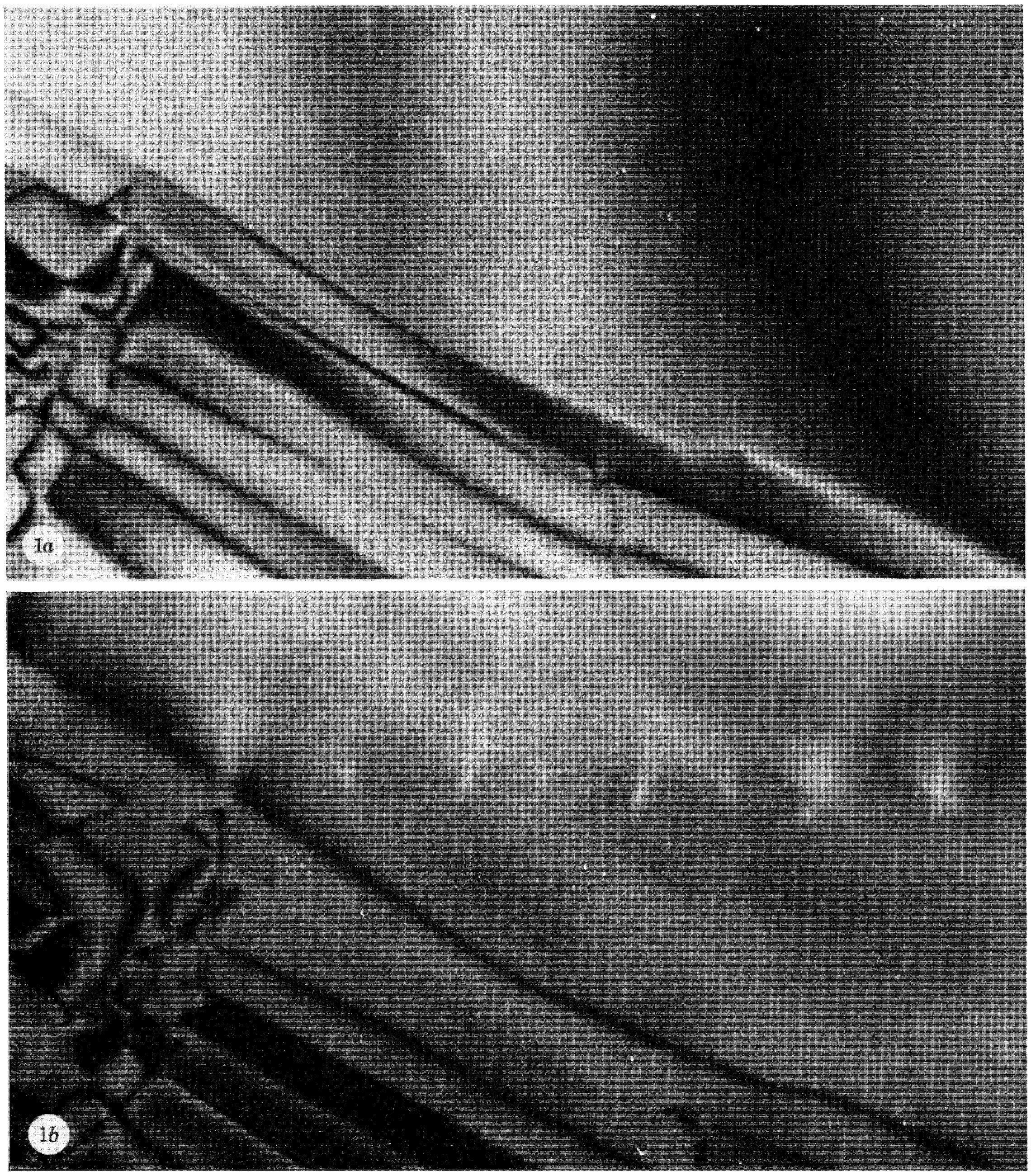


FIGURE 1. Electron micrograph showing dislocations, rendered visible by diffraction contrast, in *p*-terphenyl. One of the dislocations in (*a*) has become invisible under different diffracting conditions (*b*). The Burgers vector of this dislocation, which glides on (001) planes is [12*w*]. (Jones, Thomas, Williams & Hobbs (in the Press).) (Magn. × 12000.)

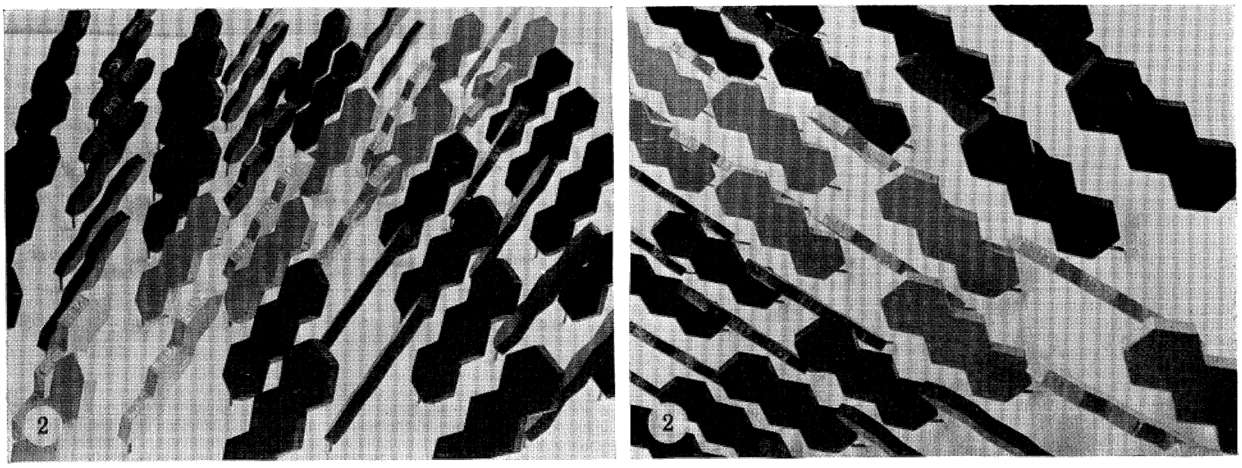


FIGURE 2. Photographs of a scale model of an anthracene crystal containing an extended (001) dislocation of Burgers vector $\frac{1}{2}[120]$. Note the occurrence of dimer pairs along the dislocation core.

FIGURE 4. Optical micrograph of (*ac*) face of 1,8-dichloro-9-methyl anthracene showing preferential nucleation of the *trans* dimer product along [201], $[20\bar{1}]$ and [100], as predicted. (Desvergne, Thomas, Williams & Bouas-Laurent 1974.)

Burgers vector in the direction $[12\omega]$. Edge-dislocations of this identity would certainly bring two molecules into an overlapped 'incipient dimer' configuration along the core of such linear defects. Moreover, a partial dislocation of screw character with Burgers vector $\frac{1}{2}[120]$ would lead to an entire array of pairs of incipient dimers, periodically separated by lattice-dilated regions, along the dislocation core (figure 2, plate 7). We can now understand precisely how dislocations, long known to facilitate photodimerizations (Thomas & Williams 1967, 1969; Rood, Emerson & Milledge 1971), function as favoured sites for the process.

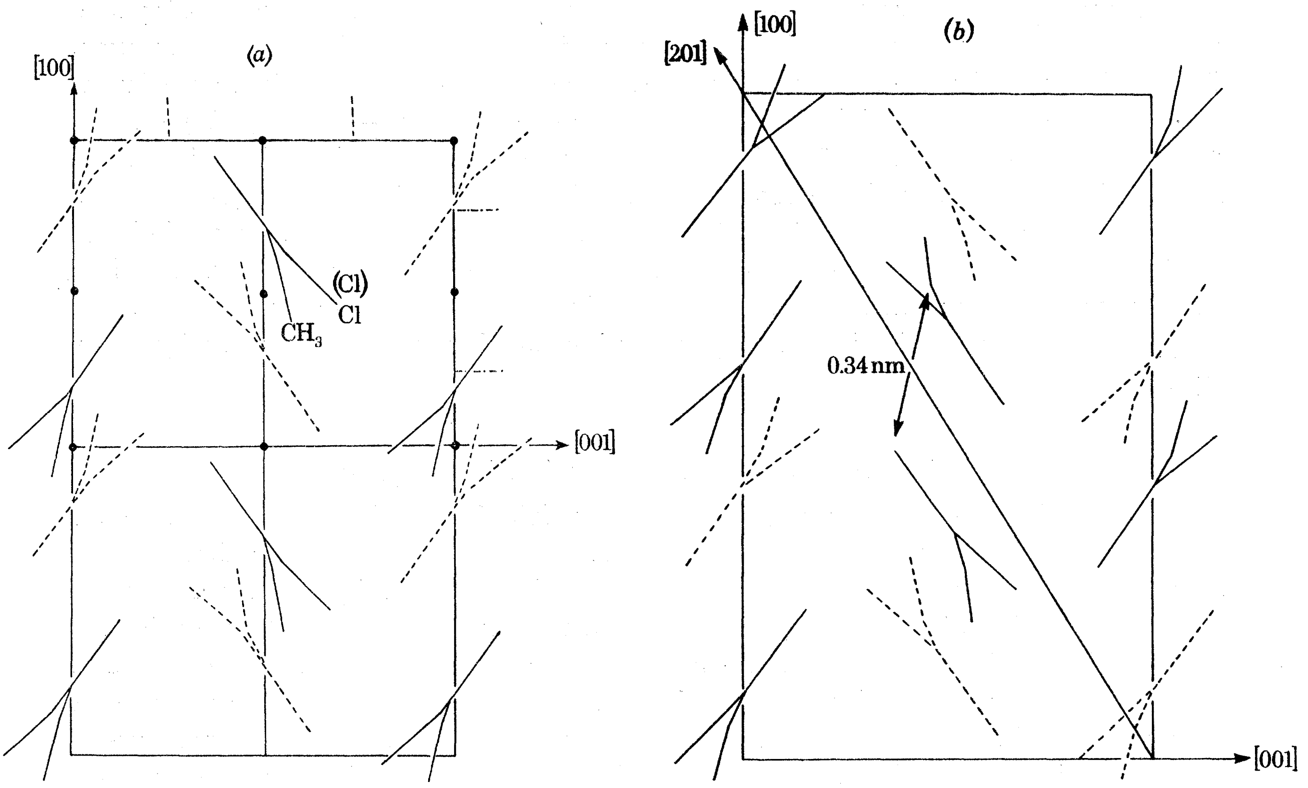


Figure 3. (*a*) Scalar illustration of the (*ac*) projection of the crystal structure of 1,8-dichloro-9-methyl anthracene. (*b*) Illustration of the molecular arrangement brought about as a result of the translation (201) $\frac{1}{2}[010]$. Note that, along the defect, contiguous molecules have 9...10′ and 9′...10 distances of *ca.* 0.34 nm.

It is very likely, as has been discussed fully elsewhere (Cohen *et al.* 1971; Thomas & Williams 1972; Cohen & Green 1973), that the presence of stacking faults – a type of defect considered more fully later (§3) – on (221) planes of crystalline 9-cyanoanthracene can also account for the production of the *trans* (centrosymmetric) photodimer in this solid, rather than the *cis* (mirror-symmetric) one topochemically predicted on the basis of the idealized crystal structure. All the results of energy-transfer measurements reported recently by Cohen and co-workers (Cohen 1972, 1973), and particularly their observation that the quantum efficiency for dimer formation increases with percentage photo-converted in 9-cyanoanthracene support the earlier interpretive formulations of Cohen *et al.* (1971).

So far as 1,8-dichloro-9-methyl anthracene is concerned, it is clear (figures 3*a*, *b*) that either isolated partial dislocations or antiphase boundaries both with translation slip systems (201) $\frac{1}{2}[010]$ or (100) $\frac{1}{2}[010]$ are the agencies responsible for facile photodimerization resulting in the production of the centrosymmetric product (see Desvergne, Thomas, Williams & Bouas-

Laurent (1974) for further details). Such defects bring adjacent molecules situated at the core of the defect into a favourable mutual orientation and separation distance conducive for the production of the *trans* dimer. The optical microscopical study (figure 4, plate 7) of the preferred orientation of dimer nuclei at (*ac*) faces of the monomer lends credence to this interpretation (Desvergne *et al.* 1974).

More remains to be learned about the rôle of dislocations and stacking-faults in photodimerization and photo-oxidations (Donati, Guarini & Sarti-Fantoni 1972; Gougoutas 1972; Julian 1972; Lonsdale, Nave & Stephens 1966), especially in those systems where there is phase-separation of the product from the monomer matrix within which it is initially in solid solution. Dark-field transmission electron microscopy (see figures 5*a*, *b*, plate 8) promise to be of value here, as in the study of precipitation and the occurrence of Guinier–Preston (G.P.) zones in alloy systems. The assessment of the importance of spinodal decomposition, in which (Cahn 1968) periodic fluctuations in composition occur along the elastically soft crystallographic directions, has hardly begun, and much more needs to be known of structure mimicry,† previously reported in the context of organo-metallic molecules (Sacconi, Ciampolini & Speroni 1965) and now well documented in the realm of organic chemistry by Paul & Curtin (1973) and McCullough, Curtin & Paul (1972) and discussed in wider terms by Kitaigorodsky (1961, 1973).

(*d*) *Convertibility of phases in organic molecular crystals*

The generation of a new phase within another (precipitation, exsolution, formation of G.P. zones, etc.) constitutes one facet of the general phenomenon of phase transformation which, if only because of the greater molecular and conformational complexity and wider range of polymorphs involved, is appreciably more complicated in organic than in inter-metallic, and possibly mineralogical, systems. Whereas it would be premature to enumerate those features which seek to characterize this aspect of the behaviour of organic solids, it is nevertheless instructive to refer to a few novel attributes of organic molecular crystals, since new experimental techniques are available for detailed studies in this area of solid-state chemistry.

First, we note that phase transformations can be stress-induced. It may appear surprising that certain organic crystals should transform into a new structure at any desired temperature simply as a result of the application of a well defined strain. Yet, once it is realized that crystallographic twinning occurs freely (Cahn 1954) under like circumstances, this phenomenon appears natural. (In twinning there is a change of shape but the crystal structures before and after deformation are the same). Frank, Keller & O'Connor (1958) recognized that stress-induced martensitic transformation occurs when the orthorhombic form of polyethylene is converted to the monoclinic analogue upon the application of strain. Frank *et al.* (1958) outlined reasons why such processes should be operative in long-chain compounds, and also commented on the mechanisms relating to nucleation and growth of one phase within the other. Many of their predictions have been substantiated, chiefly by Allan & Bevis (1974). It is particularly interesting to note that a minute crystal of polyethylene (*ca.* 1 μm wide, 10 nm thick), in its folded-chain orthorhombic form may be partly converted on straining to a biphasic material in

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† There is now little doubt that a reaction product which is normally of a different molecular shape from that of the reactant may adopt a new configuration in order to fit into the matrix of the starting material. Work on the Beckmann–Chapman rearrangement of the picryl ether of benzophenone oxime to the corresponding *N*-picrylbenzamide illustrates well the reality of structure mimicry (Paul & Curtin 1973; Cohen 1968).

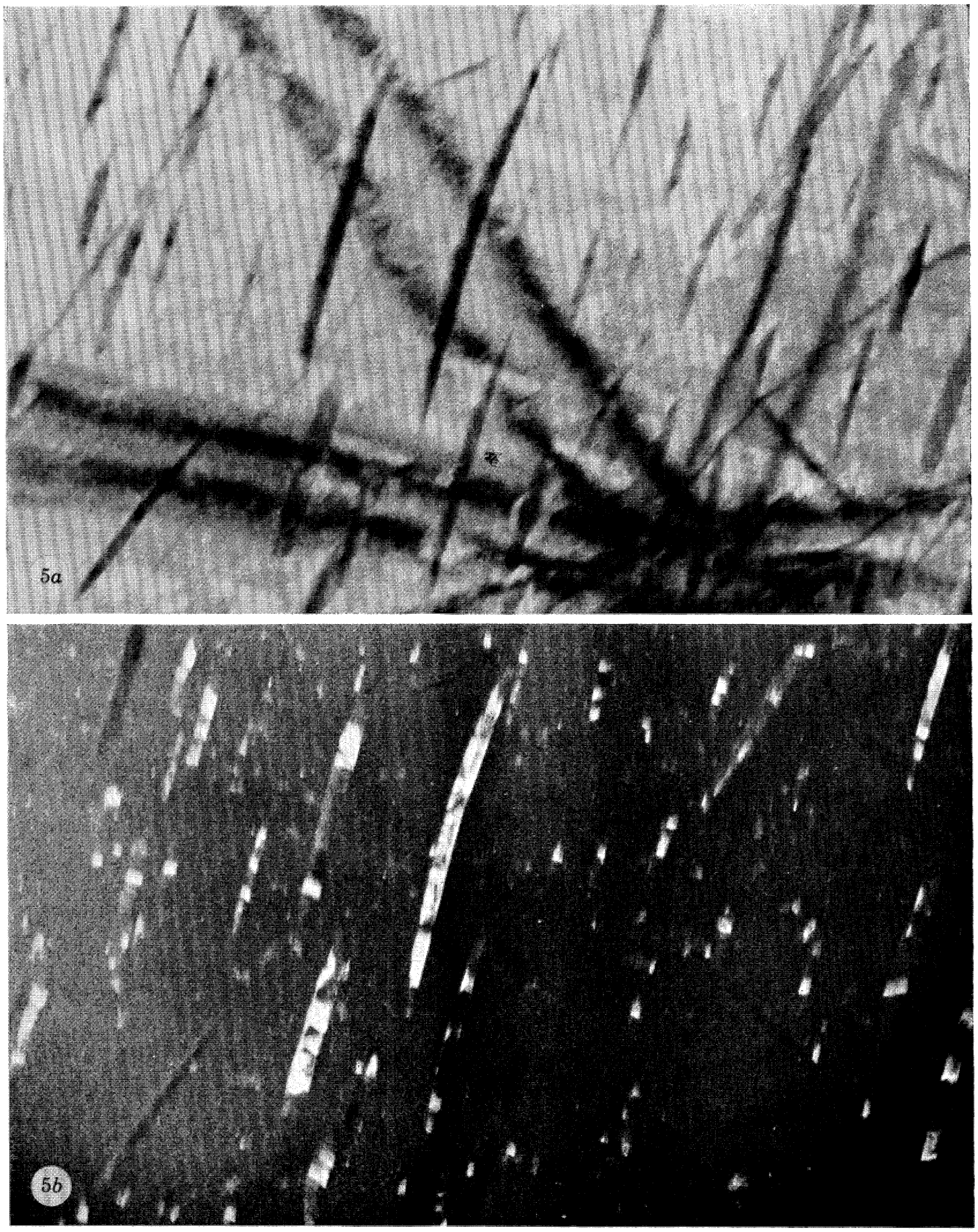
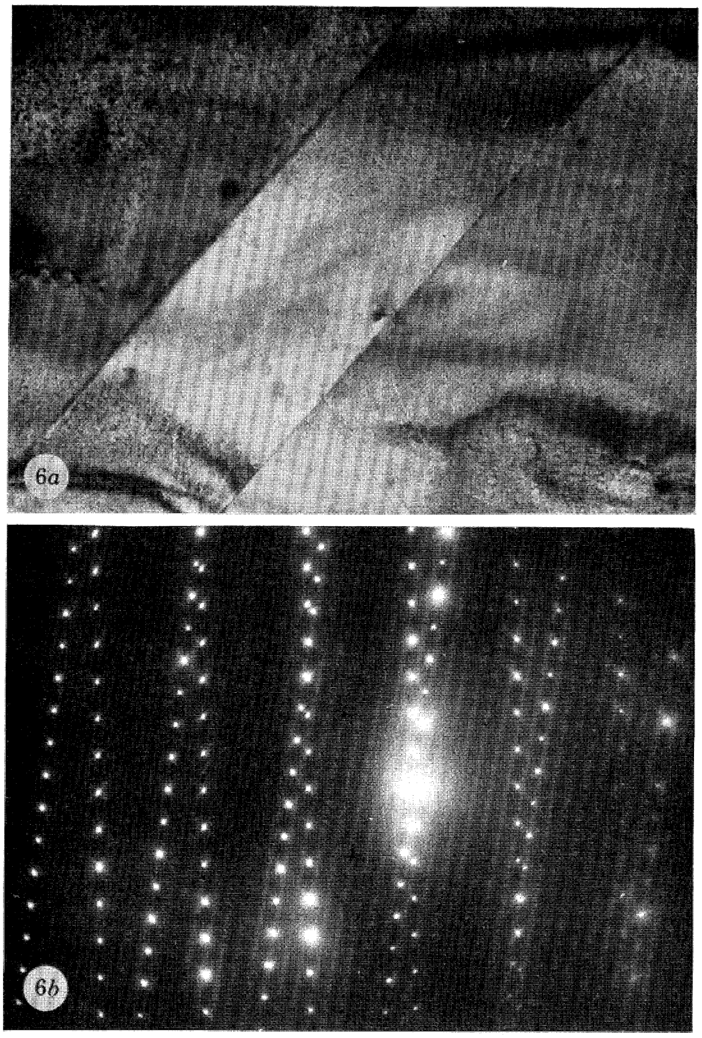


FIGURE 5. Bright field (*a*) and dark field (*b*) of anthracene after it had been photo-oxidized to yield nuclei of anthraquinone. The dark field photograph was taken on the (210) diffracted beam from anthraquinone (Jones 1974.) (Magn. × 10000.)



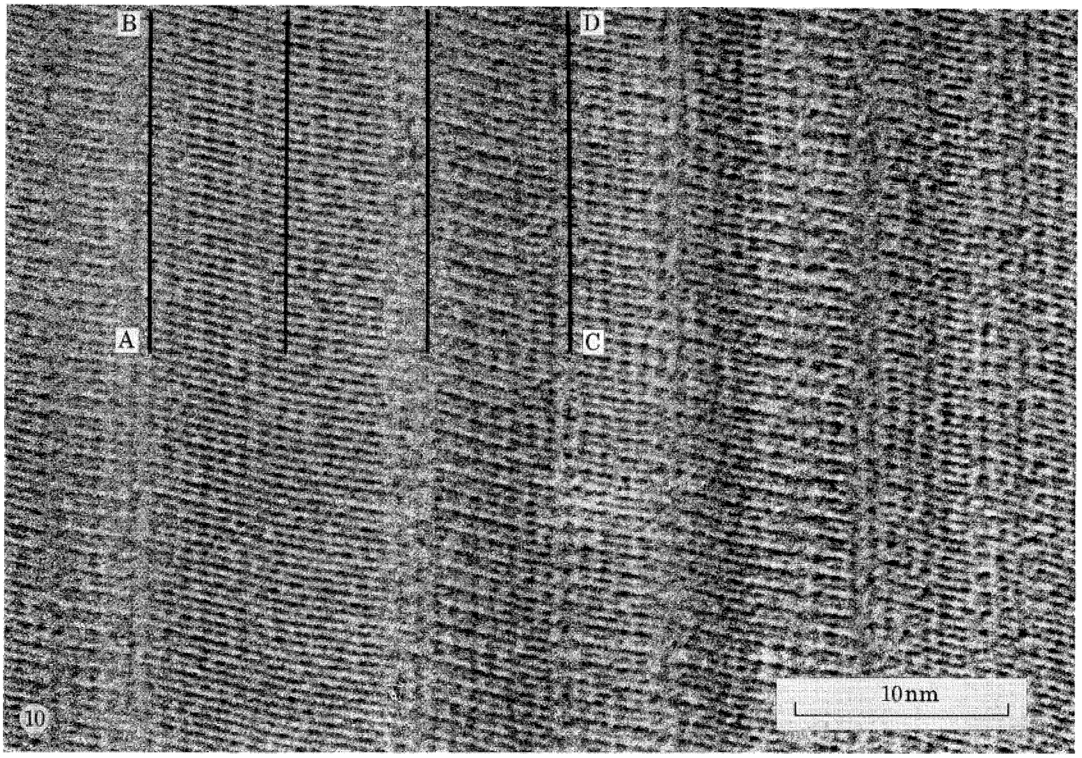


FIGURE 6. (*a*) Bright-field electron micrograph showing coherent boundary between two crystal forms of 1,8-dichloro-10-methyl anthracene. (Magn. × 10000.) (*b*) Corresponding diffraction pattern ((*h*0*l*) reciprocal lattice net) showing that a single crystal → single crystal stress-induced transformation is involved. (Jones, Thomas & Williams 1974.)

FIGURE 10. High-resolution (*h*0*l*) lattice-image of zussmanite showing faint traces of (001) planes and, more clearly, the (201) planes traversing them. The variation in direction of the (*h*0*l*) planes in the two polytypes may be discerned. (Jefferson & Thomas, in the Press.)

which two of the four sectors in the flat crystal have taken up the monoclinic structure (Allan & Bevis 1974). We therefore observe that there is direct experimental proof of the so-called 'hybrid crystals' which Ubbelohde (1966) and others (Everett & Norton 1960) have invoked to assist in the interpretation of hysteresis in crystalline phase-transformations.

We also note that there is a well defined orientational relation between the crystallographic axes of the new phase and those of the parent within which the stress-induced phase transformation occurs. This is of considerable interest since exhaustive studies by Mnyukh (1963), Kitaigorodsky (1965, 1973) and co-workers (Kitaigorodsky & Myasnikova 1972; Kitaigorodsky, Mnyukh & Asadov 1965) lead them to conclude that, even when organic solids undergo single-crystal → single-crystal transformations there is no special orientational relation between the daughter and parent phases and that the same laws as govern the growth of a crystal from the melt dictate the growth of the new crystal from the old. It may well be that this is a widely applicable generalization in organic solid-state chemistry. But it is pertinent to report that some monomeric organic solids, such as 1,8-dichloro-10-methyl anthracene studied recently in these Laboratories (Williams 1973; Jones *et al.* in preparation), do display all the symptoms of stress-induced martensitic transformations (figures 6*a*, *b*, plate 9) and orientational relations are, consequently, well defined between the parent and daughter phases. Clearly when stress-induced transformations can be effected – so that it is possible, by judicious application or release of strain at a fixed temperature, rapidly to interconvert across a coherent boundary one phase into another – the generalization of Mnyukh & Kitaigorodsky does not seem to apply.

It is relatively simple to construct a plausible mechanism for stress-induced transformations (Jones *et al.* in preparation), by, for example, invoking Cottrell & Bilby's (1951) ideas on the pole mechanism of deformation twinning. What is at present much more difficult to understand is how relatively minor changes in molecular structure can have such profound consequences so far as the feasibility of interconversion of phases is concerned. Thus, we know (Jones 1974) that 1,8-dichloro-9-methyl anthracene, unlike its closely related 10-methyl isomer (see scheme 12) does not undergo a phase transformation, but merely deformation twinning.

Another remarkable type of conversion is photo-stimulated phase transformation. By using single crystals of acridine-rich, anthracene-acridine solid solutions it was found (Sworakowski, Thomas & Williams, to be published) that a wavelength sensitive phase transformation may be induced by straightforward irradiation of the mixed-crystal surface with visible light of wavelength lower than 418 ± 5 nm. More work is needed to characterize such changes, which are governed by the crystallography of the parent matrix as indicated by the preferred directions of growth of the daughter-crystal. Such optically-responsive changes, which are not likely to be reversible, in contrast to the electrically-responsive changes that can be effected within ambidextrous inorganic crystals (Iwasaki & Sugii 1971; Newnham & Cross 1974), have no counterparts in intermetallic systems. They may be bound up with the question of metastable phases and the abnormal solid-state solubility of one organic material within another (Kitaigorodsky 1973; Sloan 1973).

3. Topochemical and topotactic reactions in inorganic solids

The distinction between topotactic and topochemical reactions is best clarified by bearing in mind that topotaxy (see, for example, Bernal, Dasgupta & Mackay 1959; Lotering 1959; Dent-Glasser, Glasser & Taylor 1962; Brindley 1963; Lonsdale 1969; Ostwald 1969; Günter & Ostwald

1970) is concerned with the three dimensional orientational relations between the crystallography of the product and reactant phases in much the same way as epitaxy and epitactic reactions refer to the two-dimensional orientational relations that exist when a new phase forms on the surface of another. A reaction is said to be topotactic if (i) the lattice of a solid product shows one or a small number of crystallographically equivalent, definite orientations relative to the lattice of the parent crystal; and (ii) the reaction has proceeded throughout the bulk of the reactant. Topochemical reactions, as we have seen, are those in which the properties, including the nature, of the products are governed by the fact that the chemical changes proceed within the solid. It follows that, because of the existence of catenation, topochemical control in organic reactions may often lead naturally to topotaxy – some of the systems discussed by Hasegawa *et al.* (1973) in their study of solid-state polymerizations illustrate this point. In other instances (e.g. the formation of the polyacetylenes) no phase-separation takes place so that, under such circumstances, the concept of topotaxy is supererogatory. It is obvious from the work of Robertson & Ubbelohde (1938) that the phenomenon of topotaxy had been identified in organic solids long before the term itself was coined.†

(*a*) *Topotactic reactions*

Topotactic reactions are legion in inorganic chemistry (see, for example, the reviews of Dent-Glasser *et al.* (1962) and Brindley (1963) who have discussed *inter alia* a wide range of decompositions and recrystallizations especially in mineralogical contexts, and Boldyrev (1973)); and the mere existence of such reactions implies that numerous solid-state chemical processes proceed in an orderly manner at the atomic level. So far as minerals and many binary and ternary oxides (such as spinels), hydroxides and oxyhydroxides are concerned, the topotaxy and orderliness seem to stem from the maintenance of the organization of the oxygen and/or hydroxyl ions within the structure as reaction proceeds. The oxygens are usually the largest ions in the structures in question, and they tend to be in close-packed or nearly close-packed states with the smaller cations in interstitial positions. One, therefore, envisages (Brindley 1963; Katz, Nicol & Roy 1969; Nicol & Roy 1970) long-range diffusional processes involving the cations, with the oxygen ions being little disturbed. The exsolution behaviour of the framework aluminosilicates is interpretable, in part, in these broad terms, but, in addition, as with other systems (Bollmann & Nissen 1968), the energetics of the newly established phase boundaries have also to be considered, irrespective of whether the mechanism of exsolution involves heterogeneous nucleation (involving long-range diffusion) followed by growth or spinodal decomposition (Owen & McConnell 1971; Lorimer & Champness 1973).

One interesting example of topotactic reaction merits attention since it illustrates how, in special circumstances, a crystal structure may be proposed for an intermediate phase based solely on considerations of topotaxy (Günter 1972). The crystal structure of the parent material, molybdenum trioxide dihydrate is well known. There are (figure 7) two types of water molecule present here. The structure is built up from slightly deformed layers of strongly-distorted octahedra [$MoO_5(H_2O)$] sharing corners, parallel to (010). These layers are stacked above one another, with layers or sheets of intercalated water in between. The water molecules within the intercalated sheets participate in hydrogen bond formation involving, on the one hand, hydrogen atoms of water molecules coordinated to Mo atoms to interlayer water molecules, and,

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† The term topokinetic is used by some authors (for example, Sakovich 1963) to describe kinetic processes in solid-state reactions.

on the other, hydrogen atoms of interlayer water molecules to coordinated oxygen ions. Gunter (1972) found that dehydration occurs in two stages:

$$MoO_3.2H_2O\ (D) \rightarrow MoO_3.H_2O\ (M) + H_2O$$

followed by:

$$MoO_3.H_2O\ (M) \rightarrow MoO_3\ (A) + H_2O$$

yielding ultimately the anhydrous form (A), the crystal structure of which is also well known (figure 7). X-ray studies revealed the following topotactic relations:

$$(010)_D//(010)_M; \quad [\bar{1}01]_D//[001]_M; \quad \text{and} \quad [101]_D//[100]_M$$

with the (010) plane remaining essentially unchanged and the interlayer spacing considerably reduced, and:

$$(010)_M//(010)_A; \quad [100]_M//[001]_A; \quad \text{and} \quad [001]_M//[100]_A$$

with the dimensions of the (010) again being only slightly altered. From the close relation in lattice constants, and in orientation, of the monohydrate to both the parent dihydrate and to the final anhydrous product, it is plausible to assume that all three crystal structures are analogous. A reasonable structure for M consists of layers of corner-sharing octahedra $[MoO_5(H_2O)]$, similar to the layers of the dihydrate structure, stacked on top of one another and connected by hydrogen bonds from water molecules coordinated to Mo atoms in one layer to oxygen ions in the next (see figure 7*b*). Oswald, Günter & Dabler (1974) have separately determined the crystal structure of M and they confirm that it matches well that predicted from topotactic arguments.

(*b*) *Topochemical reactions*

Although topochemical reactions tend nowadays to be associated with organic solids, there are a number of inorganic processes which are best thought of, and have traditionally been classified (Kohlschütter 1923; Freundlich 1924) as topochemical. One of these processes is intercalation, which was first widely studied in relation to the two dimensional charge-transfer complexes formed between graphite and a variety of species which may be readily accommodated between the layers (Fredenhagen & Cadenbach 1926; Croft 1960; Rüdorff 1959; Ubbelohde & Lewis 1960). Other noteworthy examples, which are currently of considerable technological and academic interest are the insertion of Lewis bases between the sheets of the transition-metal chalcogenides (Wilson & Yoffe 1969; Gamble *et al.* 1971; Bach & Thomas 1972), and the insertion of both neutral and positively-charged organic species between the layers of the sheet-silicate minerals (Weiss 1958; Brindley 1951; Barrer 1964; Bodenheimer, Heller, Kirson & Yariv 1969; Suito & Yoshida 1971).

In all three instances, no separation of a new phase is involved, but rather a lattice-expansion of the parent matrix which, by virtue of its intrinsic geometric and electronic properties, governs the nature of the entities that may be incorporated between the sheets and also the stoicheiometry of the final complex. A great deal of new information continues to emerge about the properties of these interlamellar complexes, and the recently discovered specificity of reactions that take place within the expanded but still restricted interlayer spaces is of intense academic and commercial interest. Thus the benzidine rearrangement (Tennakoon, Thomas, Tricker & Williams, in the Press) and other important organic reactions, such as the synthesis of peptides from amino acids (Weiss 1969), may quite freely be effected in the interlamellar spaces of expanded sheet silicates. But hardly a start has yet been made to capitalize upon the conformation and packing arrangements taken up by reactive organic molecules intercalated by the various dichalcogenides of the metals of groups IVb, Vb and VIb (Beal 1973).

(i) *Crystal engineering with the intercalation compounds of inorganic solids*

The fact that transition-metal cations known to possess the electronic properties necessary to effect certain specific types of catalysis, can be readily placed, by ion-exchange, into a defined, restricted crystallographic environment in the interlamellar space of montmorillonoid silicates, has prompted a study, in these Laboratories, of the inorganic equivalent of what we have, in organic contexts (§2), labelled crystal engineering. The idea, again, is to bring potentially reactive molecules, under the influence of the chosen metal ion, to within conducive separation distances so as to synthesize stereochemically clean products. Tennakoon (1974) has found that the olefinic double-bond in a relatively large organic molecule is preferentially activated when that molecule is intercalated by copper-exchanged montmorillonite. As a result, it is easy to prepare, by heating to low temperatures (*ca.* 400 K), dimer molecules which would not be formed under comparable conditions by thermally activating the 'free' molecule. Indene and *trans* stilbene, for example, have been shown to yield clean dimer products when their intercalates with metal-exchanged montmorillonite are mildly heated. Two other reactions which are readily and cleanly effected using the organic reactant in its intercalated form on the appropriately ion-exchanged montmorillonite (Tennakoon, Thomas, Tricker & Graham 1974) are shown in scheme 13, p. 275. The 4,4′ diamino *trans*-stilbene, which is probably so well 'locked' in the expanded montmorillonite that it does not thermally isomerize to the *cis* form (as it would in the free state), yields aniline as the sole gaseous product (Tennakoon, Thomas & Tricker, in the press) upon mild heating of the interlamellar complex. Clearly the significance of such conversions both in respect to biomimetic synthesis (Breslow 1972) and to supported heterogeneous catalysis is considerable.

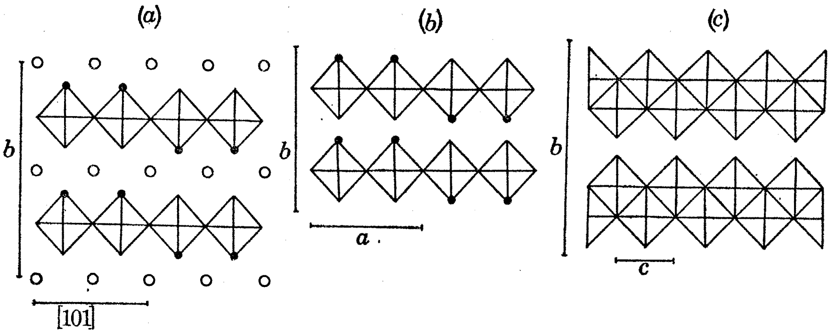
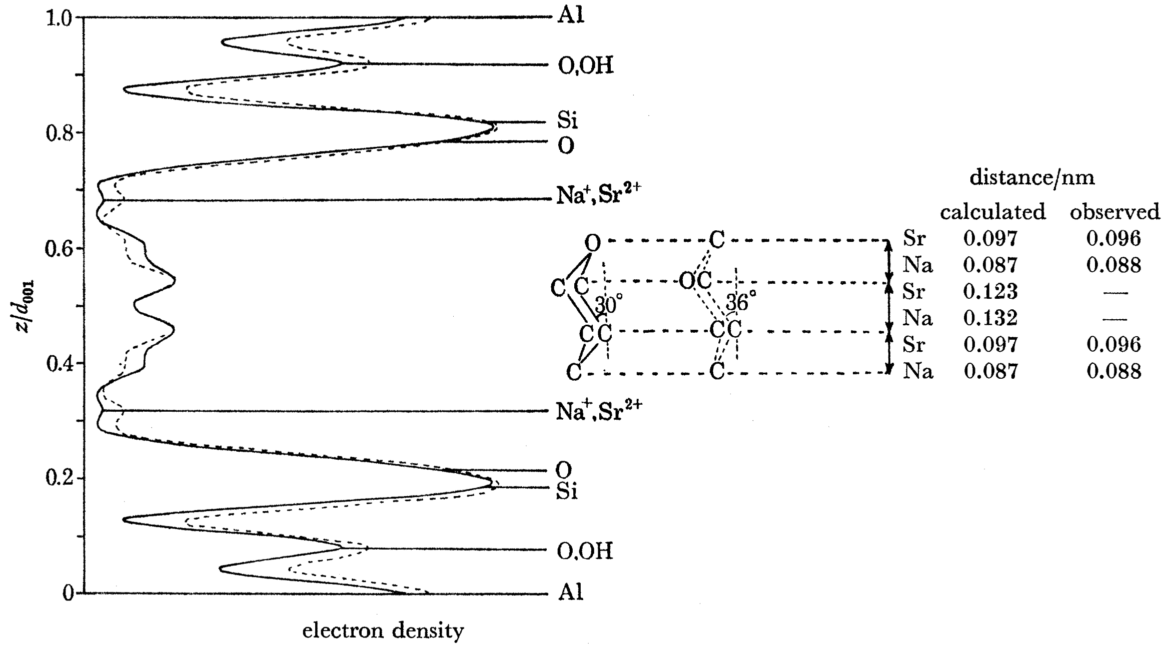


FIGURE 7. Comparison of the schematic structures involved in the topotactic dehydration of $MoO_3.2H_2O$: ●, coordinated H_2O; ○, interlayer H_2O. (*a*) ($\bar{1}01$) projection of $MoO_3.2H_2O$, the octahedra being $[MoO_5(H_2O)]$; (*b*) (001) projection of $MoO_3.H_2O$ (proposed), the octahedra being $[MoO_5(H_2O)]$; and (*c*) (100) projection of MoO_3, the octahedra being $[MoO_6]$. (See text.) (After Günter 1972.)

A prerequisite for future advances in exploiting the solid-state chemistry of the intercalates generally is the establishment of reliable crystal structure data, which, for a variety of reasons are not as easy to accumulate for the more reactive interlamellar compounds of the sheet silicates and the transition-metal chalcogenides as they are for the rather more stable graphite complexes (Ubbelohde, Parry & Nixon 1965). Only when the detailed three dimensional structures of the interlamellar complexes before and after reaction are assembled will major progress be achieved and the aura of magic presently associated with the specificity of the conversions finally exorcised.

Two relevant examples of recent structural investigations are, however, worthy of comment. First, the intercalates of montmorillonites and kaolinites have been examined by J. M. Adams and D. A. Jefferson in these Laboratories. Adams (1974, in the Press) has measured the electron-density distribution perpendicular to the basal planes in Na^+- and Sr^{2+}-exchanged montmorillonites, which had subsequently taken up either tetrahydropyrane or dioxane between the layers. The results (figure 8) show that subtle changes in the orientation of the guest molecules may result from minor changes, such as the replacement of Na^+ ions by Sr^{2+} as the exchangeable interlayer cations. Note that a change in the nature of the cation results in a change both in the orientation of the rather rigid organic molecule and in the nature of the atom within the latter which is nearest to the alumino-silicate sheet. Specimens of swellable silicate minerals are usually too small to permit straightforward analysis of *hk* reflexions, so that details of changes in the lateral disposition of the individual sheets following intercalation cannot, in general, be assessed. Often, however, examination of the modifications of the unit-cell dimensions brought about by intercalation (e.g. alteration of the β-angle for a layer-structure such as dickite which is monoclinic before and after incorporation of formamide – D. A. Jefferson (1974, private communication)) is enough to demonstrate that the individual sheets are indeed laterally displaced following uptake of the organic molecule.



	distance/nm	
	calculated	observed
Sr	0.097	0.096
Na	0.087	0.088
Sr	0.123	—
Na	0.132	—
Sr	0.097	0.096
Na	0.087	0.088

FIGURE 8. Electron density distribution of Na^+-exchanged (—) and Sr^{2+}-exchanged (– – – –) montmorillonite with intercalated tetrahydropyrane. (Adams 1974.)

The second example of structural investigation is taken from the work of Parry, Scruby & Williams (1974), who recently conducted an X-ray study of the intercalation of TaS_2 single crystals with pyridine. It emerged that, as well as *c*-axis expansion following the uptake of approximately half a molecule of pyridine per formula unit of hexagonal TaS_2, there are also changes in the stacking arrangement of the transition-metal chalcogenide itself. These are summarized in figure 9, and may be symbolized:

$$\mathrm{AcA\ BcB} \rightarrow \mathrm{AcA|AbA},$$

where the capital letters refer to the position of the chalcogen and the small letters refer to the metal atoms. The vertical stroke denotes a layer of pyridine sandwiched between two juxtaposed $\mathrm{TaS_2}$ layers.

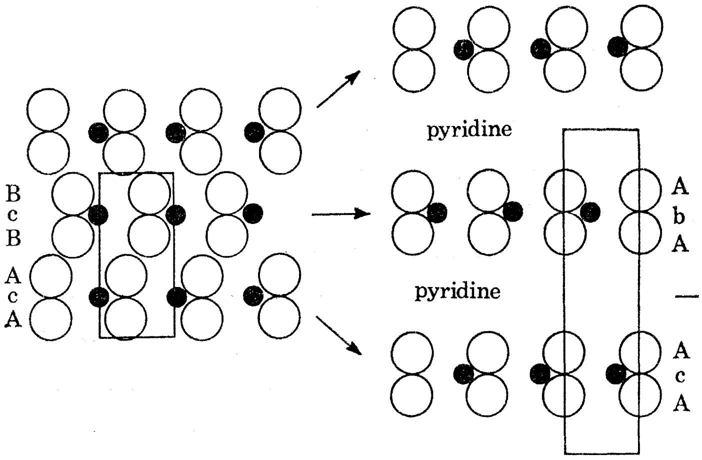


FIGURE 9. The expansion of the layer separation when $\mathrm{TaS_2}$ is intercalated with pyridine is accompanied by a stacking change. The $(11\bar{2}0)$ sections are schematized. (After Parry *et al.* 1974.)

4. Stacking sequences, stacking faults and partial dislocations

The fact that the usual stacking sequence of the individual sheets of layered solids may be systematically modified as a result of intercalation serves as a means of focusing attention on the value of the stacking sequence as a concept for unifying the various inter-relations between numerous apparently unrelated structures.

Ever since the days of Barlow (1883) – and even earlier, possibly (see, for example, Harriott *ca.* 1585; Kepler 1611) – it has been known that the two main ways of achieving the closest packing of spheres result in hexagonal and face-centred cubic structures. It has also long been recognized that since successive planes may be stacked in two alternative positions, there is the possibility that one structure will show occasional stacking faults, in which there are infractions to the stacking rules. This idea has been utilized by Hendricks & Teller (1942) for the sheet silicates, by Edwards & Lipson (1942) and Wilson (1942) for cobalt, and by Jagodzinsky & Laves (1949), who introduced the concept of 'eindimensionale Fehlordnung', for other layered minerals such as graphite and zinc sulphide. Probably the most convenient method of describing stacking sequences was that introduced by Frank (1951), who also showed how a twinned crystal could be regarded as a mirror-related stacking (i.e. $\ldots\Delta\Delta\Delta\Delta\ldots \rightarrow \ldots\nabla\nabla\nabla\nabla\ldots$) of the parent.

If the stacking fault does not extend right across the crystal, there is a boundary in the stacking plane between the regions of perfect and faulted stacking. This boundary constitutes a partial dislocation. We may, therefore, appreciate that the stacking sequences of all solids may be modified by the passages of the necessary number of glissile partial dislocations throughout the layers.

When cobalt, for example, undergoes its phase transition from h.c.p. (low-temperature stable form) to f.c.c. (high-temperature stable) at 517 °C, the stacking fault ribbons constituting h.c.p.

lamellae bounded by partial dislocations can be seen by low-resolution electron microscopy (Votova 1961; Bollmann 1961) visibly to contract into undissociated (unit-strength or perfect) dislocations. In graphite, low-resolution electron microscopy reveals that the hexagonal structure contains numerous stacking fault ribbons bounded by partial dislocations. The ribbons themselves are effectively the rhombohedral form of graphite and they occur at various levels in the parent crystal. In other layered solids (zussmanite, for example, see below) the stacking faults, as seen by high-resolution electron microscopy extend right across the layer.

These facts demonstrate clearly how our knowledge of the microstructure of solids has been transformed by electron microscopy. We note that whereas the space-averaging and time-averaging procedure of X-ray diffraction led early investigators to propose a structure for cobalt at room temperature in which, on average, one whole layer every eleven was 'wrongly' stacked, electron microscopy shows that what, in reality, occurs, is that slivers (or ribbons) of the f.c.c. form are randomly dispersed, at various levels in the *c*-direction, within the h.c.p. matrix. We note, too, that the width of the stacking fault ribbon is inversely related to the magnitude of the stacking-fault energy; so that, in essence, no sharp distinction exists between linear defects (dislocations) and planar ones (stacking faults). (When the stacking-fault energy is large the ribbon contracts to a narrow line.) Moreover, it follows that, for structural-chemical purposes, a stacking-fault boundary may be regarded as a so-called anti-phase boundary (a.p.b.). We can now see that, if the a.p.bs, or whole-plane stacking faults, were ordered they could represent a distinct new structure. The transformation of f.c.c. ⇔ h.c.p. in metals, and hexagonal ⇔ rhombohedral in minerals simply involve recurrent ordering of a.p.bs, a state of affairs which could be attained by systematic dislocation movements such as those postulated in the pole mechanism (Cottrell & Bilby 1951), recognized for almost a quarter of a century as being a feasible means of effecting deformation twinning and martensitic transformation.

It would patently profit the structural inorganic chemist if, in his attempt to classify and correlate seemingly disparate crystal structures, he were to invoke some of these ideas, which have already proved so illuminating in metallurgical contexts. Magnéli (1950) had obviously appreciated some of the advantages of this approach. Very recently (Grey, Reid & Allpress 1973) a.p.bs have been elegantly invoked to correlate the basic identities of the familiar rutile and α-PbO_2 structures. Many binary metal chalcogenides are known to interconvert between these structural types under various conditions of temperature and pressure. Moreover, specific changes in the anion stacking sequences, from ...ABCABC... to ...AAA..., form the basis of the recent discussions of Hyde & Bursill (1972) and Hyde (1972) in which they talk of continuous topological variation to describe, *inter alia*, the well known (see, for example, Megaw 1973) martensitic transformation of a NaCl-type structure (6:6 coordination) to a CsCl-type (8:8). Continuous topological variation with its consequential change in stacking sequence may also be used to interrelate rutile, baddeleyite, α-PbO_2 and fluorite.

Polytypism, too, can be rationalized in terms of recurrent stacking sequences. And it is particularly interesting to note that, with the advent of lattice-imaging techniques in high-resolution electron microscopy (Allpress 1972; Allpress & Sanders 1973; Iijima 1973; Anderson & Tilley 1974) direct evidence for particular (e.g. single-layer triclinic or three-layer rhombohedral) sequences which extend across the entire crystal can now (Jefferson & Thomas, accepted for publication) be obtained. Figure 10 shows the ($h0l$) lattice image of zussmanite with faint traces of (001) planes, and, more clearly, the (201) planes traversing them. In the region bounded by the traces of the (001) lattice fringes AB and CD, the ($h0l$) fringes can be interpreted as (200) planes of a single layer ($1T_2$) structure extending over seven layers, followed by ($20\bar{1}$) planes of a $3R_1$ structure extending over seven layers, then by (200) $1T_2$ planes for another eight layers. The projection of the lattice on to the ($1\bar{3}0$) planes of the $3R_1$ hexagonal cell in figure 11 shows the corresponding structural arrangement.

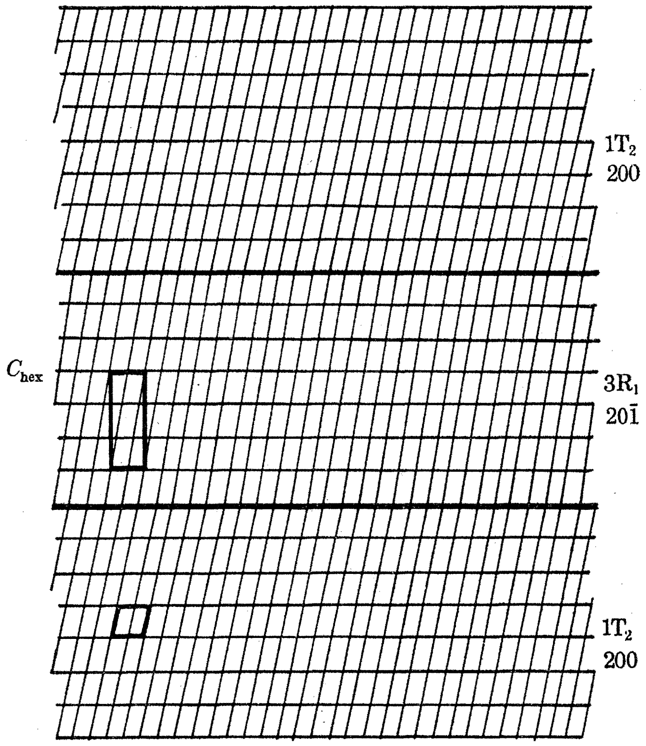


FIGURE 11. Projection of the lattice of zussmanite on to the ($1\bar{3}0$) plane corresponding to the region between the (001) planes AB and CD in figure 10. The hexagonal and triclinic unit meshes are outlined.

5. CHEMICAL CONSEQUENCES OF LINEAR AND PLANAR DEFECTS

It is now widely recognized that the undissociated linear defect (dislocation) when present either in isolation or in various alinements which constitute planar, small-angle boundaries, exerts a profound influence on the chemical properties of a range of inorganic and organic solids. Only a few synoptic examples need be recalled here: some others have been alluded to earlier in §2 (*c*) and (*d*). Reactivities of solids are especially sensitive to dislocations, and many detailed accounts are available which present the precise kinetic details of: the gasification of minerals such as graphite (Thomas 1965; Roscoe & Thomas 1967; Thomas *et al.* 1972) and molybdenite (Bahl, Evans & Thomas 1968; Evans, Bahl & Thomas 1968); the thermal decomposition of inorganic salts and their hydrates (Thomas & Renshaw 1967; Jacobs 1969; Jacobs, Herley & Levy 1971, Clarke & Thomas 1969*b*; Boldyrev 1973); dissolution in aqueous media (Thomas *et al.* 1971; Williams *et al.* 1971); and a host of solid-state reactions of metallurgical (Hirsch 1972) and optical (Haasen 1969; Hobbs 1973) interest. A typical optical micrograph which strikingly demonstrates how emergent dislocations function as preferred sites for thermal decomposition is shown in figure 12, plate 10, which depicts the decomposition nuclei (of calcium oxide) formed at the sites of emergence, alined along [110] on a {100} face of calcite

(Thomas & Renshaw 1967). The role of isolated and alined dislocations in governing the electronic (see, for example, Hannay 1960; Sworakowski 1973; Aris *et al.* 1973; Owen *et al.* 1974) and excitonic (Thomas & Williams 1969; Williams & Thomas 1973; Sworakowski, Thomas, Williams & Williams 1974; Goode *et al.* 1974) behaviour of semi-conducting and semi-insulating solids has also been well documented.

To date, however, apart from the few examples quoted in the preceding section, no systematic attempt has been made to utilize the language of dislocation theory in classifying and interrelating the structural chemistry of inorganic solids. It has been a step in the right direction to recognize the essential unity of linear and planar faults, and the re-introduction of the a.p.b. as a conceptual feature, with the realization that a.p.bs may be created or eliminated by the appropriate flow of glissile partial dislocations, has paved the way for the further assimilation of dislocation theory into chemical thought. This assimilation has already been, and is likely to continue to be, catalysed by the application of high-resolution transmission electron microscopy to the study of the ultramicrostructure of solids of chemical interest. Apart from confirming the existence of dislocations and sub-grain boundaries electron microscopy has also confirmed the reality of planar faults of the type first predicted and fully described by Wadsley (1964) and nowadays known as crystallographic shear (c.s.) planes. These planar faults, along with various admixtures (see below) of a.p.bs, play a crucial role in the understanding of the ultramicrostructural characteristics of a range of metal oxides and mixed oxides. C.s. planes are, however, very similar to the so-called imperfect prismatic (or partial) dislocation loop, first discussed by Frank (1951) in the context of general dislocation theory.

(*a*) *Crystallographic shear – single, double and pivoting*

For a considerable period it proved extremely difficult to understand the structural and architectural principles of the Magnéli phases (1950) which, for the oxides of the metals W, Mo, and Re, could be represented by formulae such as M_nO_{3n-1} or M_nO_{3n-2}, with n integral and variable, thereby generating 'homologous' series for these grossly, almost perversely, non-stoicheiometric solids. Other transition metals, in lower oxidation states, such as Ti, V (Anderson & Hyde 1967; Anderson 1972; Anderson & Tilley 1974) and Cr (Alario Franco, Thomas & Shannon 1974) also form grossly non-stoicheiometric, Magnéli oxide phases representable by M_nO_{2n-1}, M_nO_{2n-2}, M_nO_{2n-3}, ... In the mixed oxides too (e.g. in the W–Nb–O system) gross non-stoicheiometry is possible, and the materials are ostensibly quite stable from the extremes of low- to high-oxygen deficiency.

In his seminal article which sought to explain the occurrence of Magnéli phases, Wadsley proposed (1964) that diminution of the oxygen/metal ratio could be accommodated by localized variations in the manner by which coordination octahedra share atoms. Such variations were assumed to be confined to specific low-index 'planes', and their geometry could be described as a removal of an oxygen 'layer' from the stoicheiometric crystal followed by a fusion of the two half-crystals with a displacement (shear) which has a component parallel to the missing layer. A schematic representation of the creation of a c.s. plane, as envisaged by Wadsley, is shown in figure 13. Even though the O/M ratio decreases, the coordination number is preserved when octahedra change from either their usual corner-sharing (as in the ReO_3-type structure) to the new edge-sharing, or the usual edge-sharing (as in the rutile-type structure) to the new face-sharing mode in the non-stoicheiometric solid.

(i) ReO_3-*based shear structures*

Non-stoicheiometric tungsten oxides belonging to the Magnéli series W_nO_{3n-1} have been demonstrated by high-resolution electron microscopy (Sunberg & Tilley 1974) to arise from quasi-ordered arrays of (120) c.s. planes the separation distance between the c.s. planes governing precisely the value of n. (Homologous series for oxides with the general formula M_nO_{3n-m} derived from the ReO_3- structural type is formed by omission of every nth ($hk0$) sheet of oxygen sites, where m depends upon the c.s. plane orientation ($hk0$). The normal spacing, $d_{c.s.}$ between c.s. plane is related to n by: $d_{c.s.} = d_{(hk0)}(n-c)$ where c the fractional collapse.) It is clear, therefore, that the homologous series, with n varying may be represented by a set of composition points on an essentially linear plot of composition against the reciprocal superlattice distance, ($d^*_{c.s.} = 1/d_{c.s.}$), which is readily measured from the electron diffraction pattern recorded down the appropriate zone-axis (see Anderson & Tilley 1974). Tungsten oxide Magnéli phases belonging to the series W_nO_{3n-2} are now known to be based on (130) c.s. planes, and again the precise composition (value of n) is governed by the inter-c.s. spacing. Clearly both the W_nO_{3n-1} and W_nO_{3n-2} families of Magnéli phases may be regarded as being topologically coherent biphasic material. Moreover, there are very good reasons for believing (Sunberg & Tilley 1974, see figure 14, plate 10) that coherent intergrowths of (120)- and (130)-based c.s. phases coexist within a given non-stoicheiometric tungsten oxide of a particular overall composition. The lower part of figure 14, plate 10, reveals 'well ordered' $W_{19}O_{55}$ which belongs to the W_nO_{3n-2} family, as expected from the operative (130) c.s. planes. There is a short segment of a (120) c.s. plane clearly visible in this micrograph, as well as some unordered groups of WO_6 octahedra. (Note that the high-resolution electron micrograph offers convincing evidence for the recurrent gaps and clusters of six (for 130) and four (for 120) edge-shared octahedra along the c.s. planes. The individual octahedra are not resolved.)

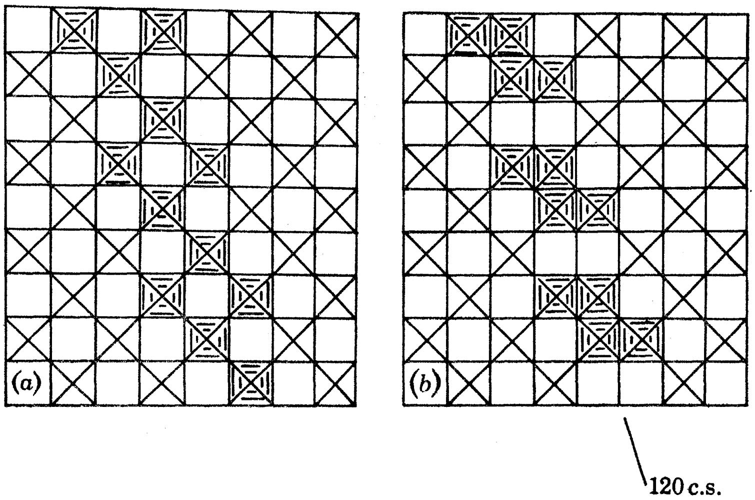
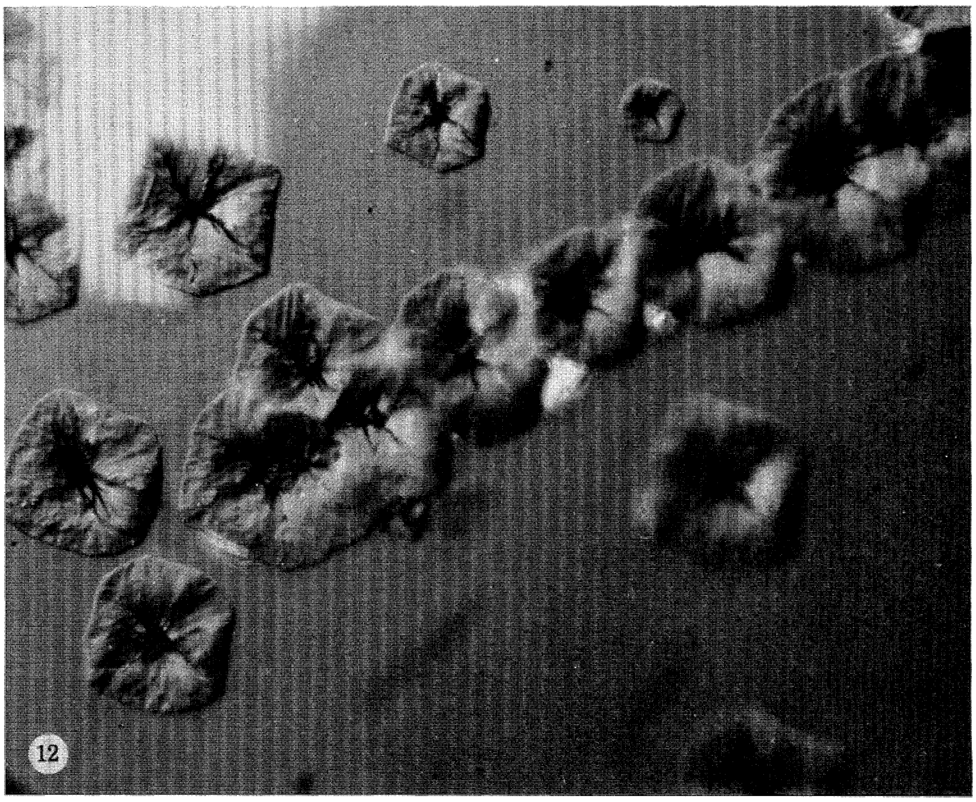


FIGURE 13. Schematic illustration of the way in which the usual corner-sharing octahedra in a ReO_3-type structure are rearranged, to yield groups of edge-sharing octahedra separated by oxygen gaps, at a (120) c.s. plane.

(ii) *Rutile-based shear structures*

In the titanium oxides belonging to the family Ti_nO_{2n-1}, Bursill & Hyde (1972) have shown that in the titanium-rich range (with $4 \leqslant n \leqslant 9$, i.e. TiO_x where $1.75 \leqslant x \leqslant 1.88$) there are (121)-based c.s. planes, which involve face-sharing octahedra. In the lower limits of



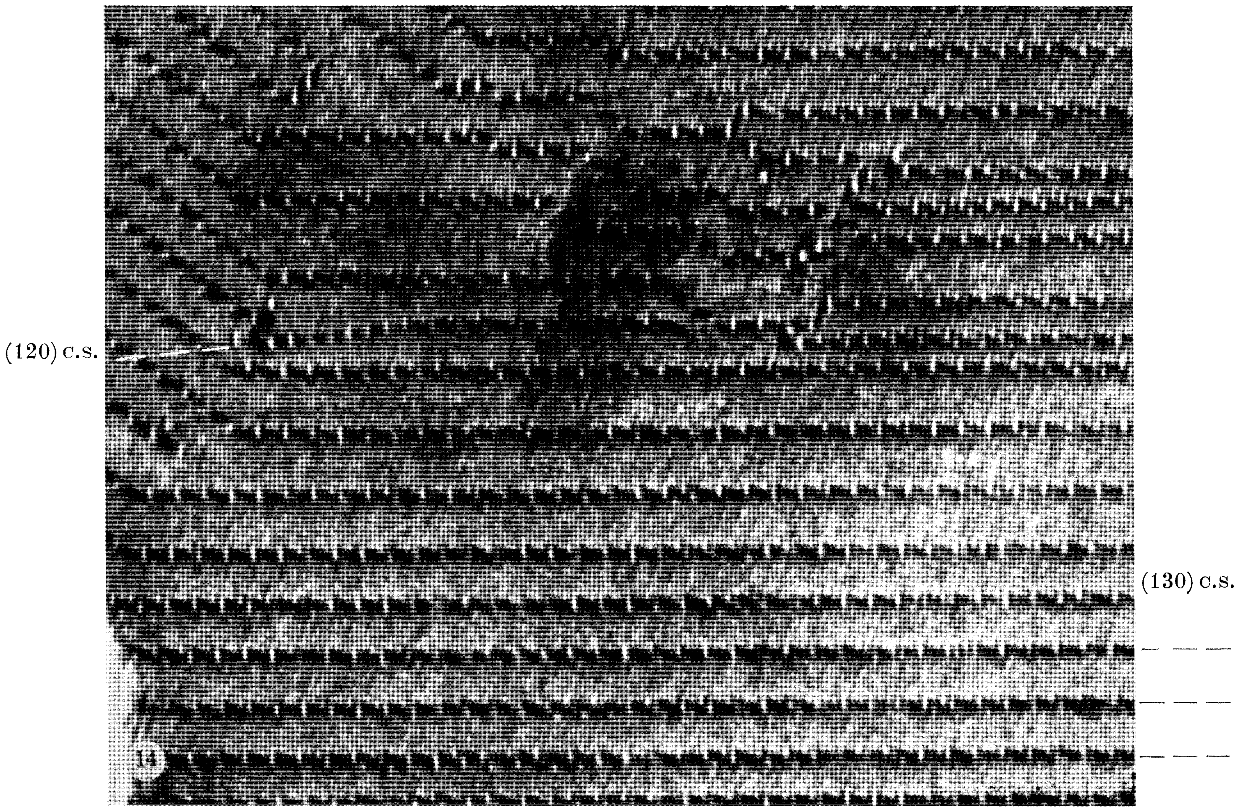
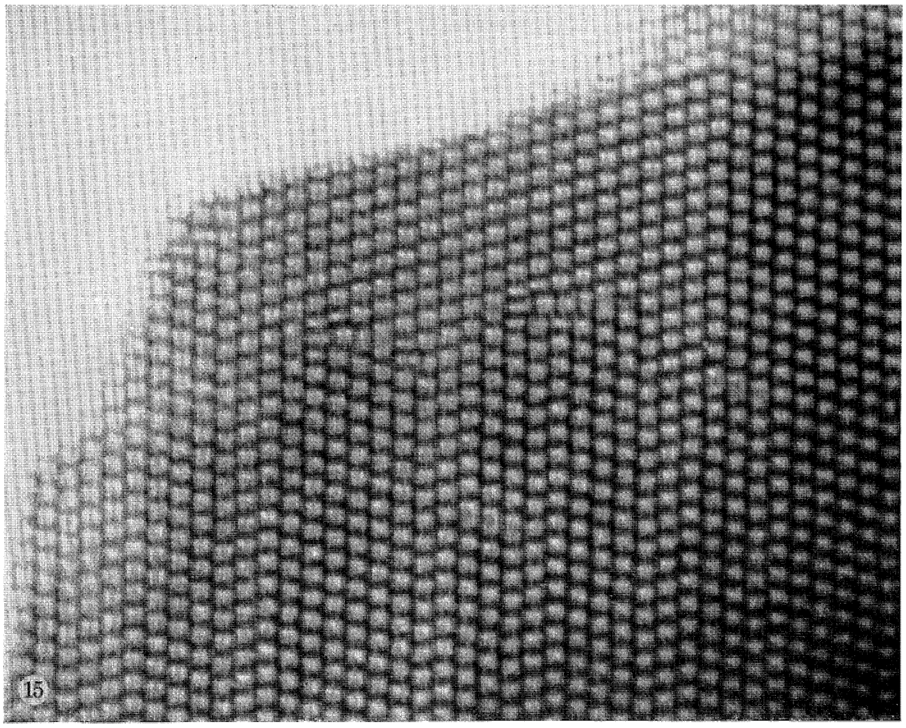


FIGURE 12. Optical micrograph showing alinement of decomposition nuclei, of CaO, at emergent dislocations alined along [110] on a {100} face of calcite. (Thomas & Renshaw 1967.) (Magn. × 500.)

FIGURE 14. High resolution electron micrograph of a thin sliver of non-stoicheiometric tungsten oxide. The lower part shows reasonably well ordered (130) c.s. planes at a separation distance appropriate for a composition of $W_{19}O_{55}$. A short segment of a (120) c.s. plane is also visible. (Sunberg & Tilley 1974.)



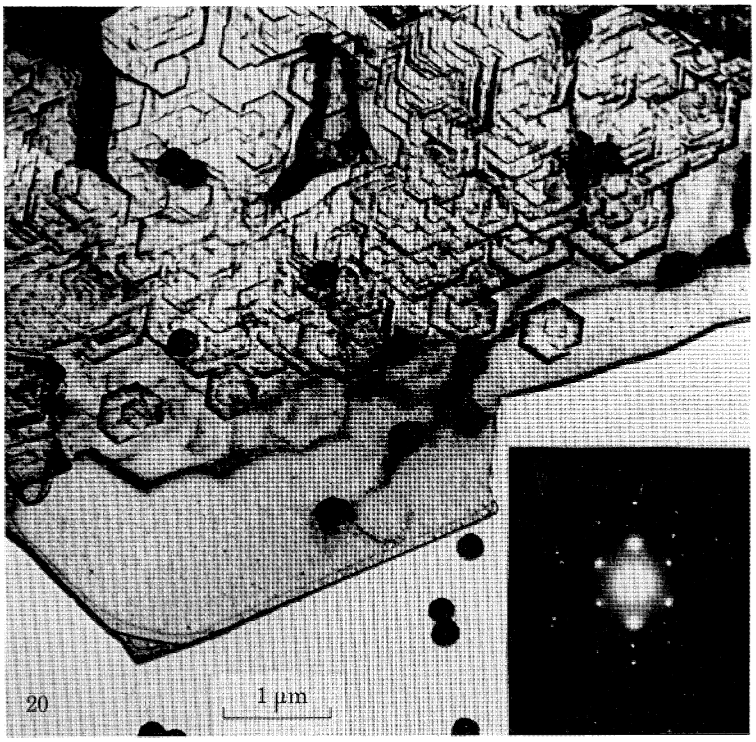
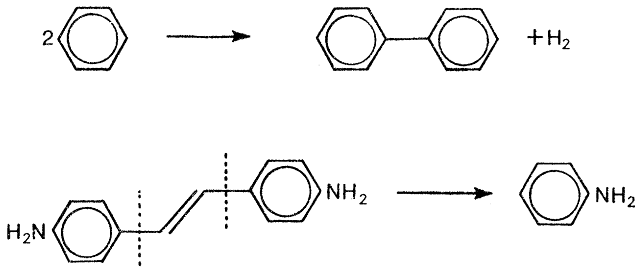
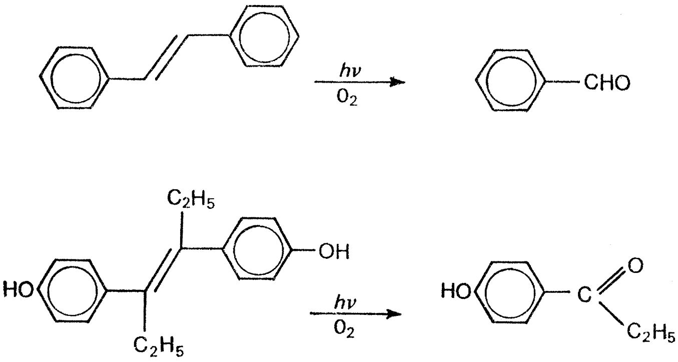


FIGURE 15. High resolution electron micrograph of CrF_3-doped Nb_2O_5 showing a 'faulted' block structure. The basic N-Nb_2O_5 structure suffers twinning on (001) on a microscale. 'Filler' blocks, acting as wedges between twinned and faulted structures are thought to contain segregated Cr and F ions. (Hutchison 1974.) (Magn. × 4200000.)

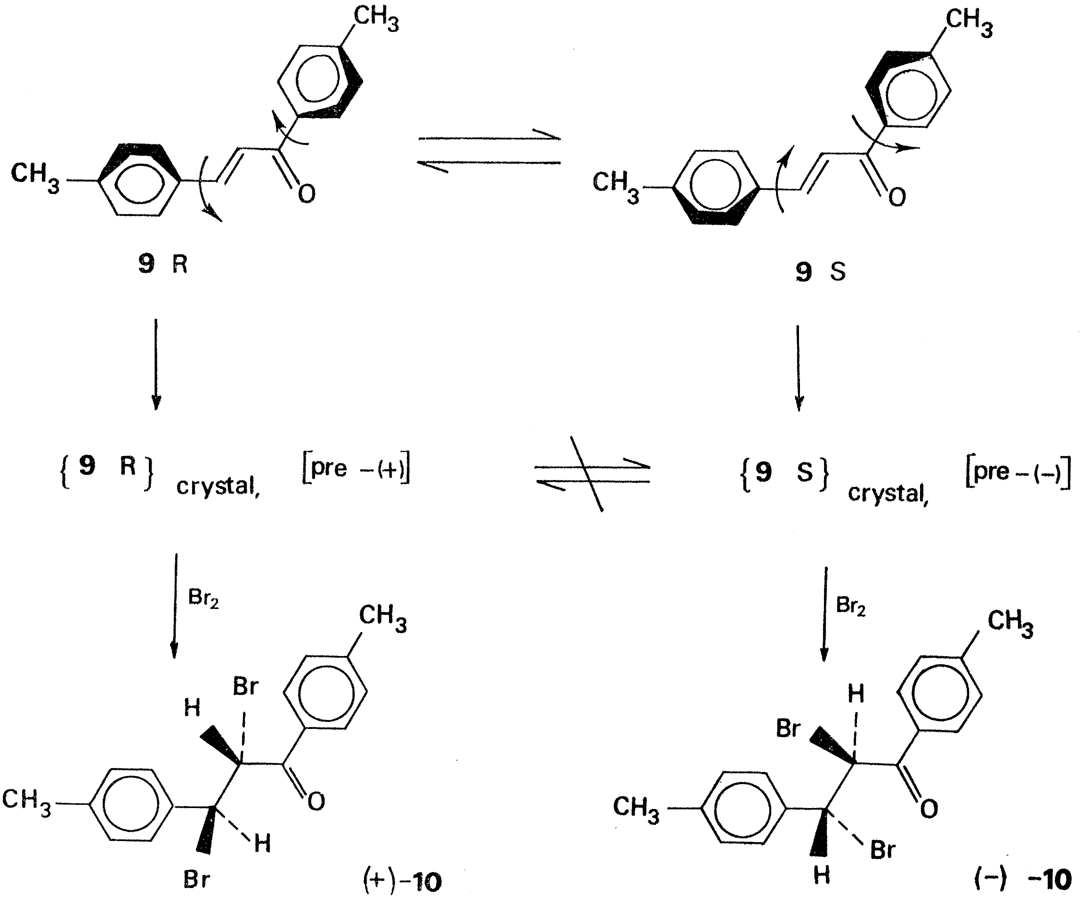
FIGURE 20. Electron micrograph of a thickened POM crystal (see text). Note spiral growth features centred at emergent non-basal screw dislocation of the type depicted in figure 19. (After Mateva *et al.* 1973.)



Scheme 13



Scheme 14



Scheme 15

non-stoicheiometry ($16 \leqslant n \leqslant 36$ with $1.938 \leqslant x \leqslant 1.972$) there are (132)-based c.s. planes. At fixed overall compositions the c.s. planes in both instances are more or less well ordered. (The (132)-based c.s. plane turns out to be, as predicted by Anderson & Hyde (1967) a composite of (121) c.s. planes and (011) a.p.bs.) In the intermediate range $n = 9$ to $n = 16$ a very subtle effect takes over. The c.s. planes now respond to changing composition not by modifying the inter-c.s. spacing – which offers little scope anyway – but rather by executing a pivoting action which results in the effective swinging of the c.s. planes from (132) down through (253) to (374), (495), etc., ultimately to (121). The ordered complexity of the entire response of rutile to progressive depletion of oxygen is summarized in table 1. Note how the ultramicrostructure may be rationalized by interpreting the compositional changes in terms of various coherent, topologically compatible, admixtures of (121) c.s. and (011) a.p.b. Anderson (1972) has commented on the fact that the seemingly implausible pivoting of shear planes, which is also known to occur in ReO_3- type structures, is a relatively simple affair: all the possible c.s.-plane orientations (see table 1) belong to a single crystallographic zone which, for rutile, is [111]. And Hyde (1972), indulging in reasonable speculation, proposes a mechanism for pivoting which would account for facile 'swinging' as well as growth and disappearance, of c.s. planes in terms of concerted lateral motion of a 'rod' of titanium interstitials.

Table 1. Non-stoicheiometric rutile TiO_x: a summary of the structural principles

(i) Composition range: $1.75 \leqslant x \leqslant 1.88$.
Nature of c.s. plane: (121); variation of $d_{\text{c.s.}}$ according to composition.
Solid consists of slabs of perfect TiO_2 separated by c.s. planes where there are corondum-like strings parallel to [111].
Intergrowths: $Ti_2O_3.(n-2)\ TiO_2$.
Formula: Ti_nO_{2n-1} with $4 \leqslant n \leqslant 9$.

(ii) Composition range: $1.938 \leqslant x \leqslant 1.972$.
C.s. plane: (132); variation of $d_{\text{c.s.}}$.

$$(132)\ \text{c.s.} \rightarrow (121)\ \text{c.s.} + (011)\ \text{a.p.b.}$$

$$(hkl)\ \text{c.s.} \rightarrow p(121) + q(011) = (p, 2p+q, p+q).$$

Formula: Ti_nO_{2n-1} with $16 \leqslant n \leqslant 36$.

(iii) Composition range: $1.888 \leqslant x \leqslant 1.937$
Swinging c.s. planes with:

$$\begin{array}{ccccccccc}
(132) & \rightarrow & (253) & \rightarrow & (374) & \rightarrow & (495) & \rightarrow \ldots & (121) \\
\vdots & & \vdots & & \vdots & & \vdots & & \vdots \\
Ti_nO_{2n-1} & & Ti_nO_{2n-2} & & Ti_nO_{2n-3} & & Ti_nO_{2n-4} & & \vdots \\
\vdots & & \vdots & & \vdots & & \vdots & & \vdots \\
p = q = 1 & & p = 2 & & p = 3 & & p = 4 & & \vdots \\
\vdots & & q = 1 & & q = 1 & & q = 1 & & \vdots \\
n = 16 & & \cdots & \cdots & \cdots & \cdots & \cdots & & n = 9
\end{array}$$

(iii) *Block structures*

In some non-stoicheiometric metal oxides, particularly those based on the various forms of Nb_2O_5 (Browne, Hutchison & Anderson 1972), and more especially the ternary mixed oxides such as Nb_2O_5–TiO_2 and Nb_2O_5–WO_3, intersecting or double c.s. planes occur which give rise to the block structures. These can respond in remarkably versatile ways to changes in metal: oxygen ratios. Quite apart from changing the separation distance of one or other of the two intersecting c.s. planes, one c.s. may remain fixed while the other could pivot (or swing), thereby modifying the cross-sections of the constituent blocks. In addition, the blocks themselves may be connected in several distinct ways entailing various operations such as edge-sharing or face-sharing. Yet a further option for adaptation of composition arises from the availability of tetrahedral sites at the intersections of the blocks. These sites may remain empty or be partially or completely filled. And finally, just as non-stoicheiometric tungsten oxide (shear structure) has its coherent intergrowths of W_nO_{3n-1} and W_nO_{3n-2}, the block structures can themselves be composed of two simple block structures. Thus Iijima & Allpress (1973) have shown that $TiNb_{24}O_{62}$ consists of coherent intergrowths of $M_{12}O_{29}$ containing only one type of c.s. planes (in which adjacent blocks are joined by edge-sharing of octahedra) and $M_{13}O_{33}$ containing still only one, but another type of c.s. plane (in which adjacent blocks along the c.s. plane are separated by metal atoms in tetrahedral coordination). Iijima has further shown (1973) that in H-Nb_2O_5, quenched from the melt there are intergrowths of blocks some of which have a composition showing oxygen excess (e.g. $Nb_{13}O_{33}$) in association with compensating oxygen-deficient blocks (e.g. $Nb_{25}O_{62}$).

Block structures can accommodate a vast number of distinct compositions. Among the higher oxides of niobium alone we may quote $Nb_{12}O_{29}$, $Nb_{22}O_{54}$, $Nb_{25}O_{62}$, $Nb_{28}O_{70}$ and $Nb_{53}O_{132}$. Most of these have the general formulae $M_{3n}O_{8n-3}$ and $M_{3n+1}O_{8n-2}$.

(iv) *Faults in shear and block structures*

Many of the special kinds of faults which can occur in the block structures arise as a result of the damage deliberately wrought by electron irradiation in the microscope stage (Iijima 1973). 'Point-defects' have been detected. (The term 'point' is rather misleading since it is intended to imply a feature that extends through the entire thickness of an admittedly very thin (*ca.* 5 nm) sample.) Twins occur, and so also do Wadsley defects (i.e. isolated, random or non-conformist c.s. planes). But there are also faults in block structures (see figure 15 taken from the work of Hutchison, private communication, 1974) which though formally similar to edge-dislocations are fundamentally different in that there are obvious compositional adjustments, as evidenced by changes in the sizes of individual blocks, in the vicinity of these emergent dislocations. The equivalents of small-angle tilt boundaries also occur and it is possible (J. S. Anderson, private communication, 1974) directly to charter the Burgers circuits around such imperfections in the high-resolution electron micrographs of these defective block structures. Even more refined measurements, which appear to offer direct evidence for the absence of individual metal atoms and three of the surrounding oxygen atoms at a tetrahedral site in defective $Nb_{12}O_{29}$ have recently been reported (Iijima, Kimura & Goto 1974).

The occurrence of these structural faults, which can be quite mobile, together with the almost bewildering variety of ultramicrostructural arrangements that 'unfaulted' shear and block structures seem to be capable of adopting, has led to the idea that infinite structural adaptivity may be possible, at least within certain types of solids (Anderson 1973). With such adaptability, a fully ordered structure may be formed for every possible composition within certain ranges; and changes in the total atomic ratios do not then result either in separation into two coexisting phases or in the randomized introduction of defects.

Recognizing these possibilities, we are led inexorably to reflect upon our current understanding and classification of the various types of transformations that these solids may, in general, undergo. Three distinct categories of transformation may be identified: until recently we would have settled for two. First, there are the non-reconstructive, cooperative, kineticallyfacile martensitic type of process in which glissile dislocations play an important rôle. Secondly, there are the fully reconstructive ones which depend upon large fluctuations for the nucleation of a new configuration or upon long-range diffusion for subsequent growth. And thirdly, as Anderson & Tilley (1974) have recently commented, there is the intermediate situation in which we may envisage partially reconstructive transformations, where there are linked changes of composition and structure. Compositional changes may evidently be accommodated in several ways, none of which requires radical shifts in the positions of the atoms – lateral migration or rotation of c.s. planes and the creation of localized faults within the elements of the parent structure either with or without change in the orientation and spacing of c.s. planes are examples of the linked changes.

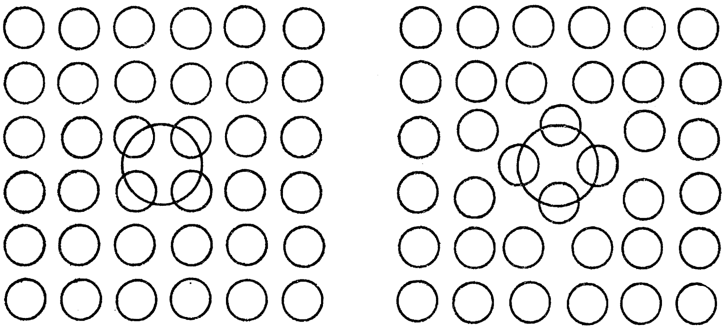


FIGURE 16. Schematic illustration of a rotation fault which gives rise to a cylindrical fault boundary (see text). (After Bursill & Hyde 1972.)

(*b*) *Cylindrical antiphase boundaries – rotation faults*

The concept of a rotation twin first described by Frank (1951) has been shown by Bursill & Hyde (1972) to be of great interpretive value in indicating how previously unrelated inorganic structures may be simply derived from each other.† These workers noted that a cylindrical fault boundary could be introduced into a square net of atoms simply by rotating one square of the four atoms by $\frac{1}{4}\pi$ radians (figure 16). Eight peripheral square holes are thereby converted to four pentagonal and four trigonal holes; and the new fault may also be regarded as eight edge dislocations which together constitute four interpenetrating dipoles. When such faults are introduced in an ordered fashion with the axis of rotation along [001], into the ReO_3-type structure (figure 17) the rudiments of the tetragonal bronze structure are produced, provided the rotation centres are alined along [310] ReO_3. In the actual tetragonal bronzes (Magnéli 1949) all the square and pentagonal tunnels are fractionally occupied by alkali metal.

Rotation faults of larger radius may be imagined, and Bursill & Hyde (1972) have shown that the hexagonal tungsten bronze framework may be interpreted on the basis of such faults. Rotation faults on planar surfaces (twist boundaries) have been well recognized from the early days of dislocation theory: the novelty is to picture them on cylindrical surfaces. This is an important breakthrough in our quest to rationalize the structural principles of ordered structures. And it has been very recently utilized to good effect by Iijima & Allpress (1974*a*, *b*) in their interpretation of the ultramicrostructure of the mixed oxide system: Nb_2O_5–WO_3. On the basis of their high-resolution electron microscopic studies (the veracity of which was tested by directly

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† The idea that fault surfaces may suffer rotatory as well as the usual translatory motions is formally akin to the climb and glide motions respectively of linear faults.

relating the *n*-beam images from very thin crystals of $4Nb_2O_5.9WO_3$ to its known structure), Iijima & Allpress showed that both the $2Nb_2O_5.7WO_3$ and $4Nb_2O_5.9WO_3$ mixed oxides consisted of ordered intergrowths of minute domains of the ReO_3 and the tetragonal tungsten bronze structural types. It is of great interest to note that the so-called reorientation boundary running along $[120]_{ReO_3}$ and separating two differently oriented regions of the ReO_3-type material in $2Nb_2O_5.7WO_3$ (see figure 18) consists of a row of interpenetrating elements of the tetragonal tungsten bronze structure. The similarity between this kind of equilibrated structure and the well recognized, low-angle tilt boundary composed of edge dislocations in a previously deformed, stoicheiometric solid is uncanny; and it emphasizes again the underlying analogical value of classical dislocation theory in disentangling the inexhaustible intricacies of extended defects.

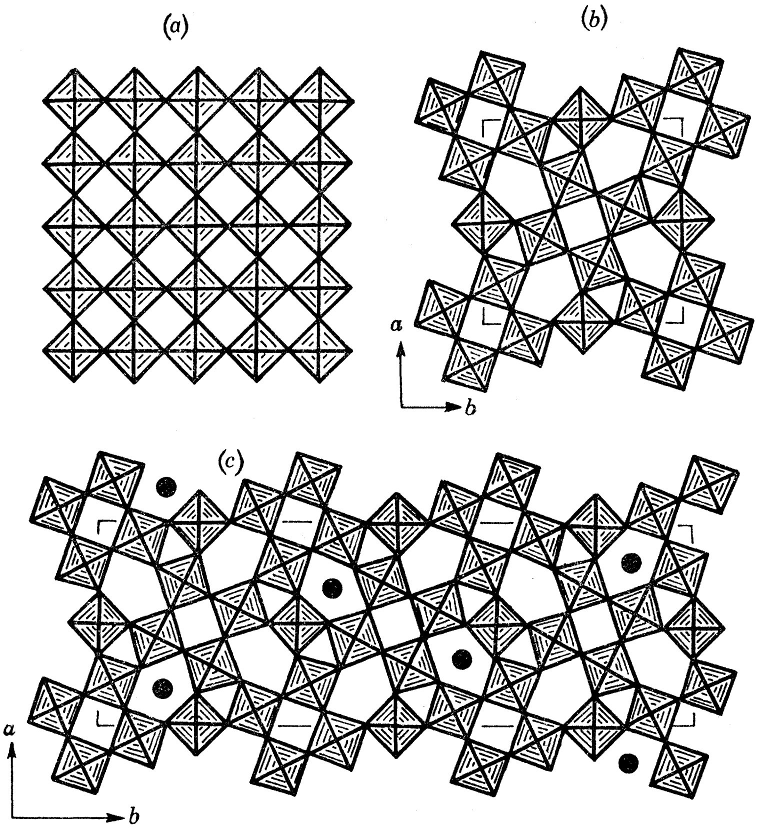

FIGURE 17. Illustration of how a parent ReO_3 structure (*a*) is converted, by the introduction of rotation faults, to the host structure of tetragonal tungsten bronze (*b*). If one third of the resulting pentagonal tunnels are occupied in an ordered fashion with strings of metal-oxygen–metal-oxygen, etc., parallel to *c* (filled circles) the structure of $4Nb_2O_5.9WO_3$ results, and the superlattice is a consequence of the ordered occupation of a third of the pentagonal tunnels. (After Iijima & Allpress 1974*a*.)

(*c*) *Extend defects: some future prospects*

Apart from the necessity and advantages of utilizing the concept of rotation faults along with single, double and pivoting c.s. planes in other, particularly fluorite-based and αUO_3-based structural types (upon which profitable discussions have already been centred (see, for example, Hyde 1971; Sawer, Hyde & Eyring 1965; Ashbee 1970)), the exigent need at present is for an all-embracing theory that seeks to explain why and how extended defects occur so readily, and with such Protean characteristics, in certain types of non-metallic crystals. In the absence of adequate thermodynamic data and electronic formulations, the tendency at present is to continue to expose the almost unlimited wealth of microstructural variability that many of the systems so far discovered can display. Even on the strictly phenomenological level, however, much remains to be uncovered. It is certain that considerable efforts will soon be made to explore, principally, by high-resolution electron microscopy, structural types in which the tetrahedron, rather than the octahedron, is the fundamental unit upon which various corner- edge- and face-sharing operations can be imposed in response to changes in stoicheiometry.

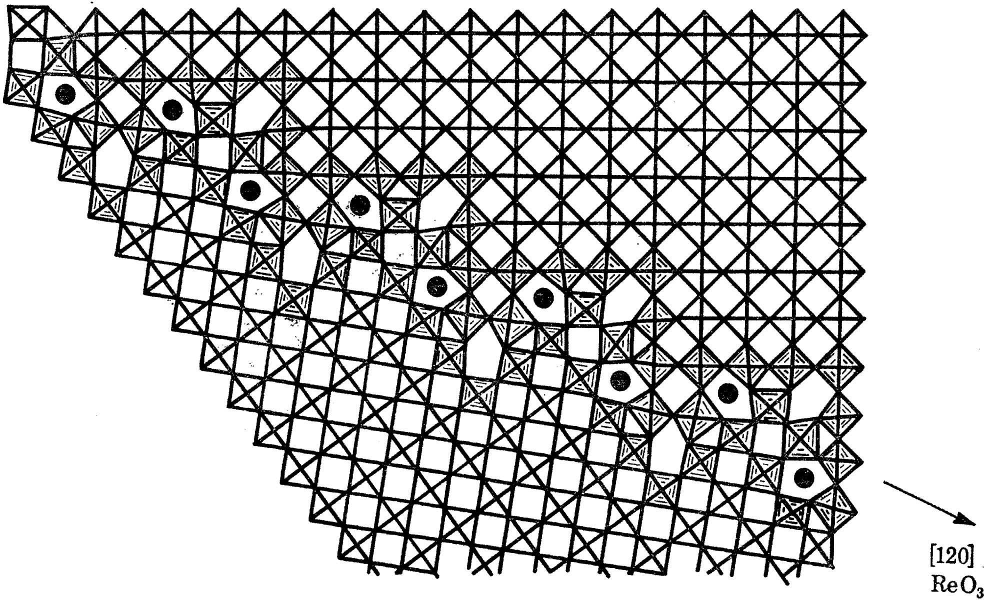

FIGURE 18. Schematic illustration of the reorientation boundary (Iijima & Allpress 1974*b*), running along [120] and separating two differently oriented regions of the ReO_3-type structure in $2Nb_2O_5 . 7WO_3$. Note that this microstructural arrangement entails a topologically coherent element of tetragonal tungsten bronze structure.

The recent work of Caro (1972) and Chisholm (1973) who, respectively, dealt with CaF_2-related structures and the pyroxenes and amphiboles, could well herald a burgeoning activity in many geochemically relevant systems.

Little attempt appears to have been made to explore whether shear and block structures have their counterparts at solid surfaces. This will doubtless receive considerable attention in future years especially since it is already known that extended defects in perovskite-type structures (e.g. $LaCoO_3 \rightarrow LaCl_{0.90}O_{2.50}$ which have been examined by Marquis, Sis & Smallmann 1974) are, at least on a *prima facie* basis, associated with the catalytic activity of the non-stoicheiometric mixed oxide in the gas-phase combination of CO and NO.

6. TOPOCHEMICAL FACTORS IN HETEROGENEOUS REACTIONS AT SOLID SURFACES

Although little progress has so far been achieved in applying the concepts of topochemistry to reactions at the surfaces of inorganic solids (but see, for example, Parravano 1968), much excitement has been aroused by recent studies of the rôle of crystal structure and packing characteristics in the reactivity of, and pathways of change open to, organic solids undergoing heterogeneous surface processes. Three examples will be cited here.

The first, taken from the work of Mateva, Wegner & Lieser (1973), illustrates how a folded-chain polymer may be transformed into an extended chain as a result of sequential surface processes. We know from a variety of previous studies (see, for example, Keller 1967) that, at the molecular level, the surface topography of a single crystal of polyoxymethylene (POM) is as schematically presented in figure 19. There is a well defined folded-chain orientation at the various sectors of the basal face and some non-basal screw dislocations emerge as indicated. By maintaining dissolved monomer (trioxane in nitrobenzene) and crystalline polymer under chemical equilibrium, in the presence of a $BF_3.Et_2O$ catalyst to facilitate ring expansion at the chain fold, Mateva *et al.* (1973) were able to thicken the larger POM crystals at the expense of the smaller ones (by a process akin to that of Ostwald ripening for which the driving force is the minimization of the surface energy of the solid – see Wagner 1961). The formation of growth spirals at emergent screw dislocations as the POM crystals thicken is strikingly demonstrated by the electron micrograph shown in figure 20, plate 11 (taken from Mateva *et al.*).

The second set of illustrative examples underline the exceptional value of gas-solid reactions in synthetic organic chemistry. The particular merit of introducing simple gaseous reactants to organic molecules in their crystalline rather than in their dispersed form rests on the fact that greater selectivity and stereospecificity may be thereby achieved, just as in the purely solid-state reactions discussed in §2. The aldehyde and ketone shown in scheme 14, p. 275, are the sole products of the photo-assisted gas-solid reactions which take place when molecular oxygen is exposed, in the presence of u.v. light, to single-crystal samples of *trans* stilbene and diethylstilboestrol respectively (Desvergne & Thomas, in preparation). When these oxidations are carried out in solution a variety of products is formed in each case. Likewise, when crystalline acenaphthylene-1-carboxylic acid is exposed to ammonia there is but one product (Desvergne & Thomas 1973); Miller, Curtin & Paul (1972) have examined the reaction of single crystals of *trans*-stilbene with chlorine gas. In solution they had obtained a mixture of *dl*- and *meso*-stilbene dichlorides in a ratio of 2:1. The gas-solid reaction however yielded, after 30 % conversion, a dichloride that was exclusively *dl*. Evidently the rigid environment of the 'clamped' organic reactant steers both chlorine atoms to attack the double bond from the same side. A vast range of possibilities is now open to the preparative and biomimetic chemist. Friedman, Lahav & Schmidt (1974) and Cohen & Green (1973) have enumerated some of these possibilities.

In the third example we revert to the question of the spontaneous generation of optical activity, discussed earlier (§2 (*b*)). In solution, or in the melt, 4,4′-dimethyl chalcone is achiral because of facile rotation about carbon...carbon single bonds (scheme 15, p. 275). Upon crystallization, however, chirality emerges since the conformations are locked in; and, statistically, there will be as many crystals possessing molecules of one chirality as there will be crystals possessing molecules of another. The addition of bromine leads to the production of optically active dibromide (as was first established by Penzien & Schmidt 1969); both dextrorotary (+) and laevorotary (–) material is formed depending upon the chirality of the particular parent single crystal that has undergone heterogeneous reaction. Green & Heller (1974) have made the extremely important discovery that when solutions containing the parent chalcone, **9**, and a small percentage of optically active (+) dibromide, **10**, were evaporated to yield polycrystalline samples of **9** (containing some **10**) and then brominated these samples gave *only* dextrorotary (+)-**10** (scheme 15). The key point is that the product of a reaction directs the handedness of subsequent crystallizations, so that autocatalytic formation of optically active compounds is now possible, under totally abiotic conditions. The necessary sequence of processes involves (i) crystallization of an achiral molecule into a chiral space group, (ii) heterogeneous reaction to yield optically active product, and (iii) dissolution, followed by further crystallization, reaction, dissolution and so on, recurrently.

This work has exciting repercussions in as much as it illustrates the comparative ease with which the prebiotic formation of the optically active compound necessary for the origin of life could have occurred. Though it remains necessary to demonstrate the same reaction scheme in the absolute asymmetric synthesis of a biologically significant substance (and B. S. Green has suggested (1974, private communication) that a good prebiotic model would be nitrene addition to crystalline succinic anhydride (chiral space group $P2_12_12_1$) to form aspartic acid) the strictures hitherto levelled at disymmetric crystallization processes as sources for the origin of optical activity in living systems (see, for example, Wald 1957) have been eliminated. In particular the work of Green & Heller abnegates the ethos of Bernal's cosmic generalization that 'crystallization means death'.

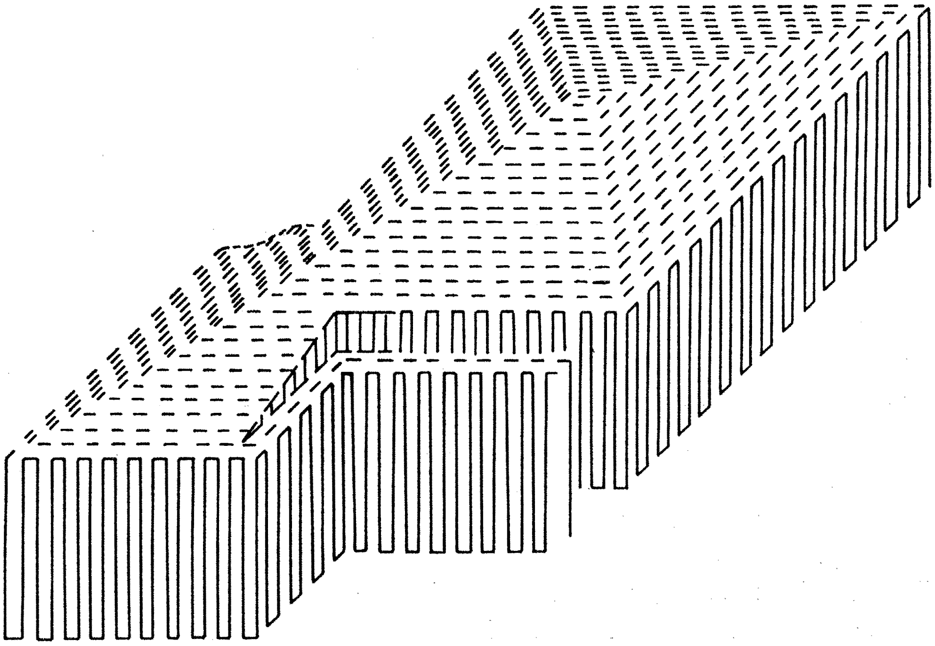

FIGURE 19. Illustration of the topographical detail present at the basal surface of a folded-chain polyoxymethylene single crystal.

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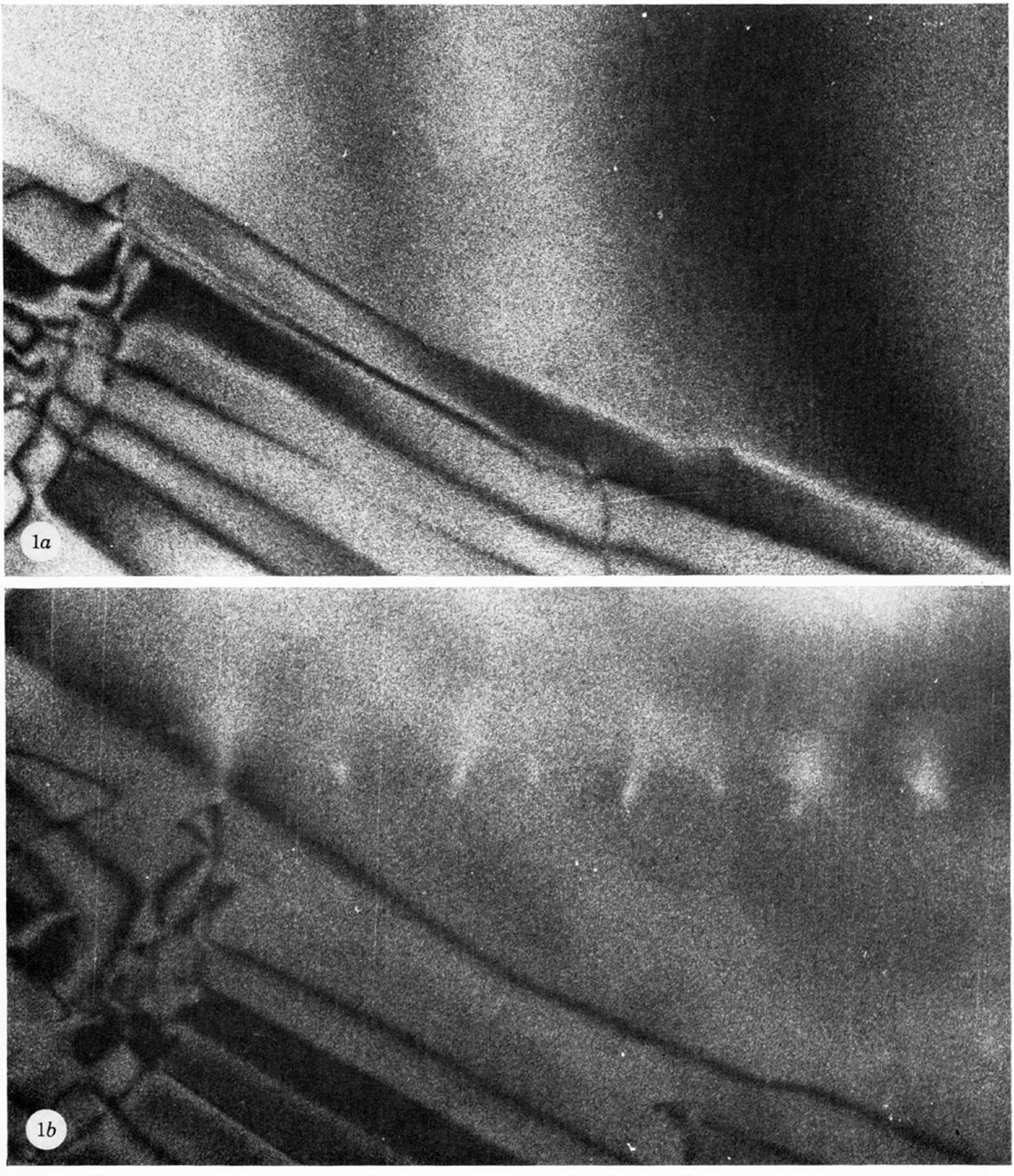
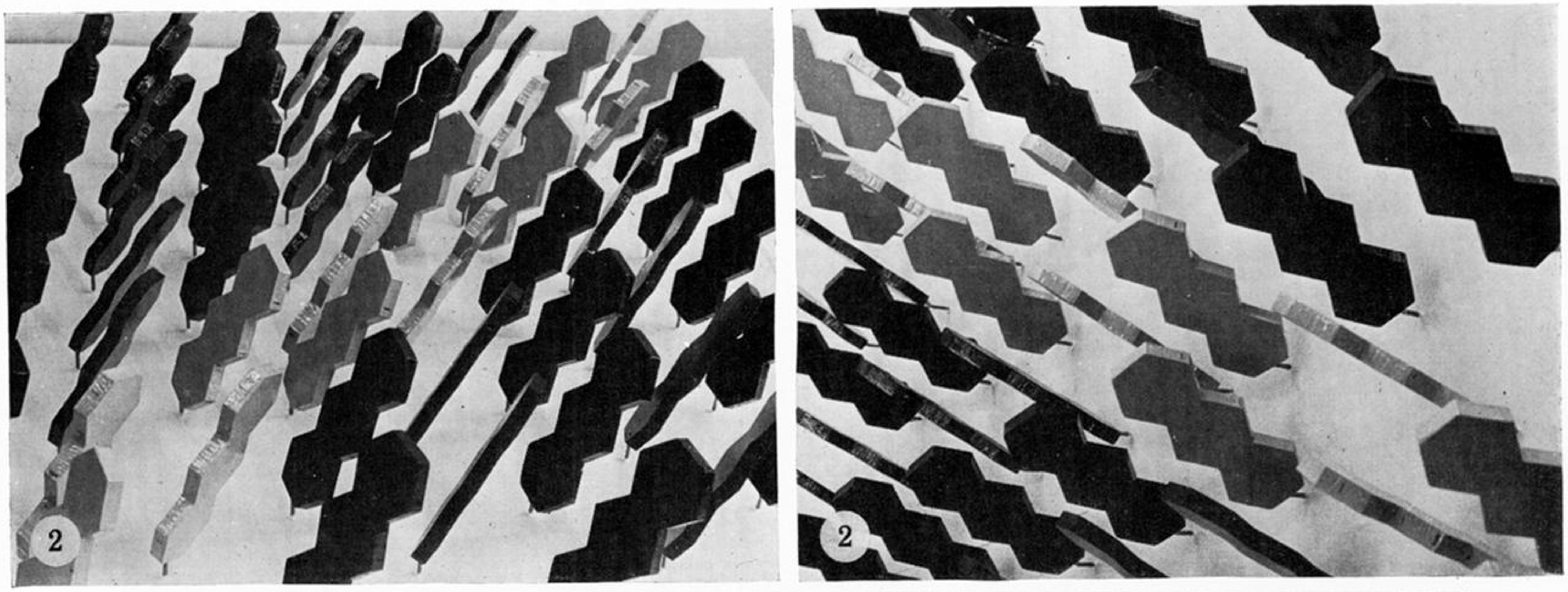


FIGURE 1. Electron micrograph showing dislocations, rendered visible by diffraction contrast, in *p*-terphenyl. One of the dislocations in (*a*) has become invisible under different diffracting conditions (*b*). The Burgers vector of this dislocation, which glides on (001) planes is [12*w*]. (Jones, Thomas, Williams & Hobbs (in the Press).) (Magn. × 12000.)



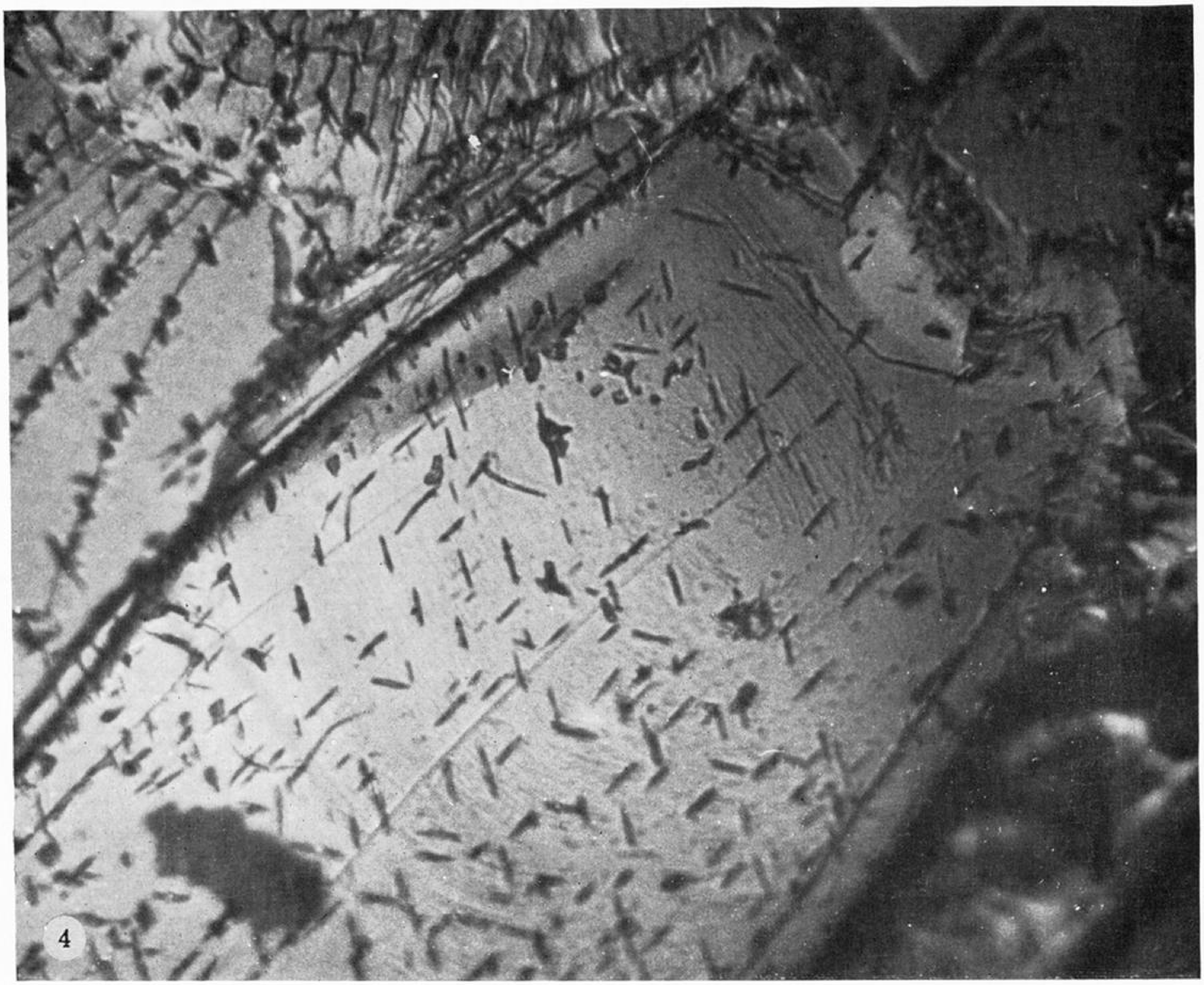


FIGURE 2. Photographs of a scale model of an anthracene crystal containing an extended (001) dislocation of Burgers vector $\frac{1}{2}[120]$. Note the occurrence of dimer pairs along the dislocation core.

FIGURE 4. Optical micrograph of (*ac*) face of 1,8-dichloro-9-methyl anthracene showing preferential nucleation of the *trans* dimer product along [201], $[20\bar{1}]$ and [100], as predicted. (Desvergne, Thomas, Williams & Bouas-Laurent 1974.)

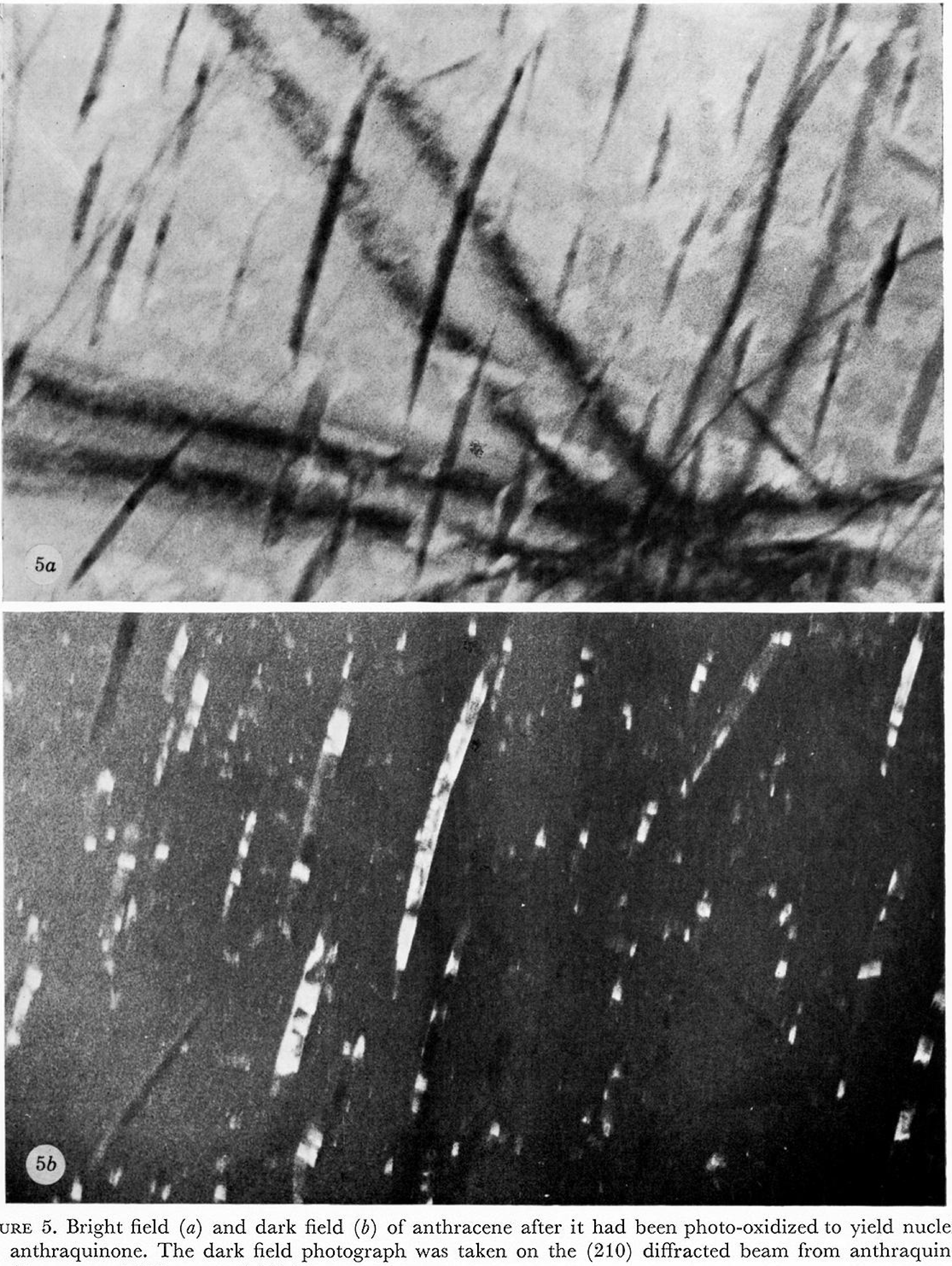
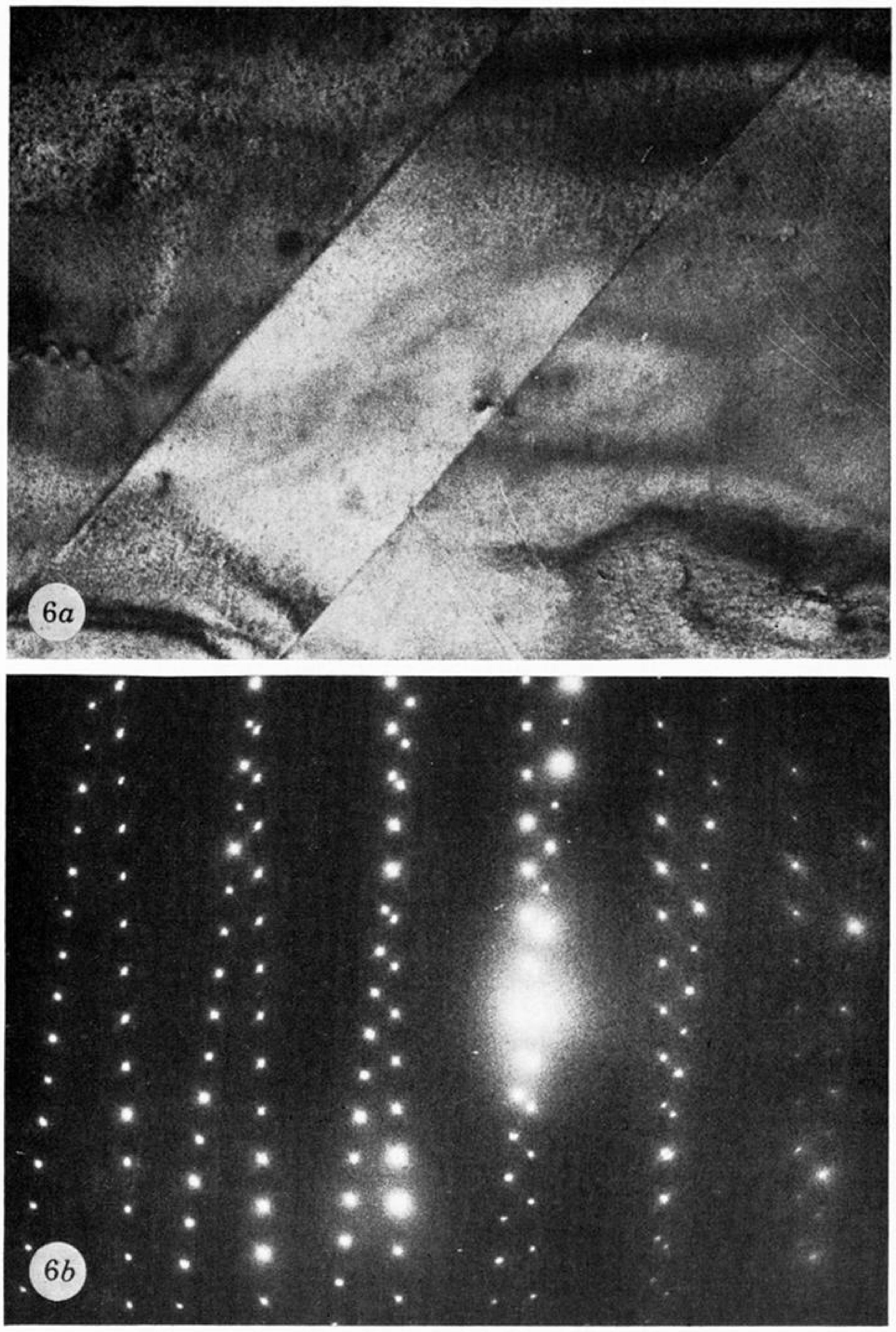


FIGURE 5. Bright field (*a*) and dark field (*b*) of anthracene after it had been photo-oxidized to yield nuclei of anthraquinone. The dark field photograph was taken on the (210) diffracted beam from anthraquinone (Jones 1974.) (Magn. × 10000.)



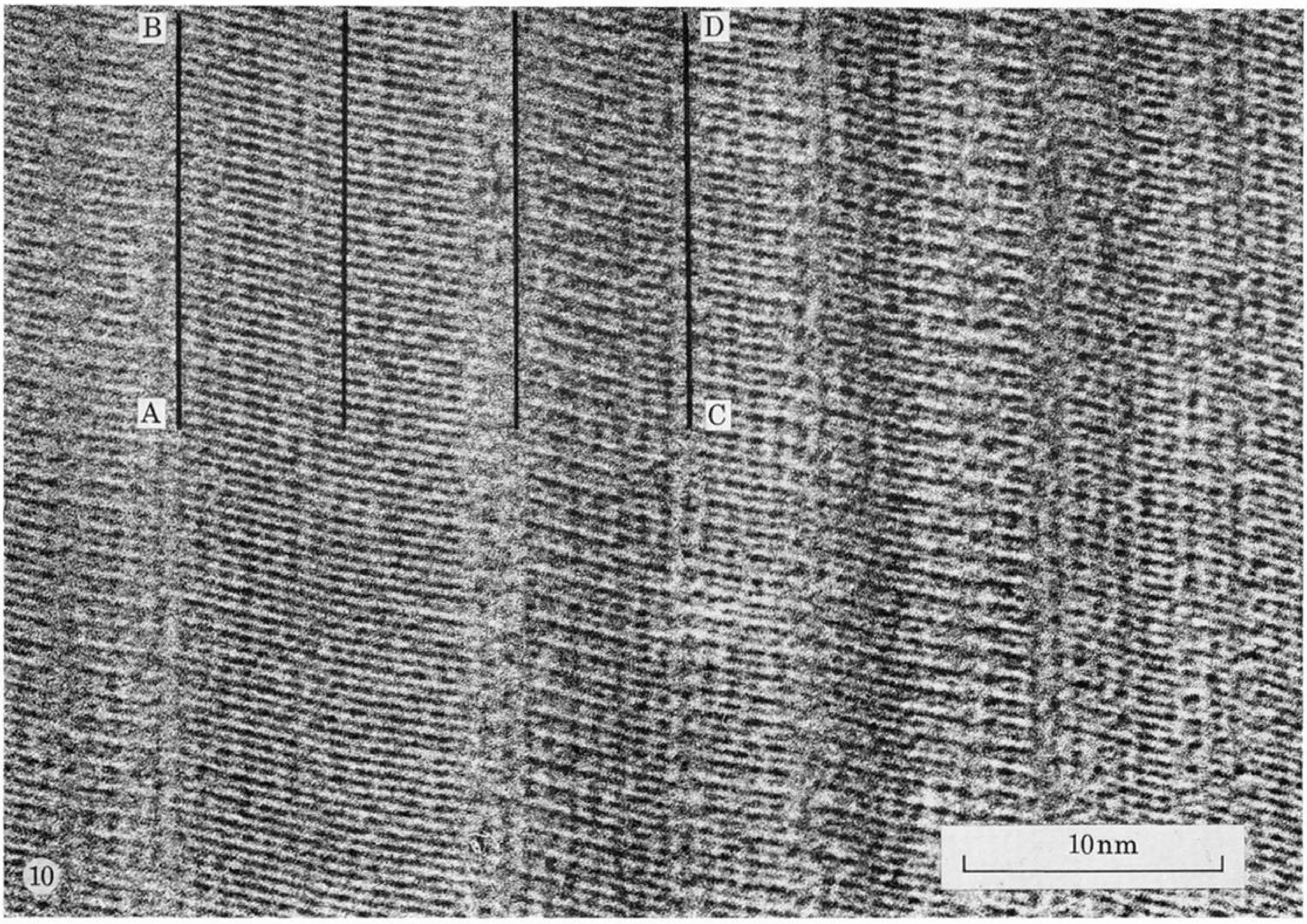
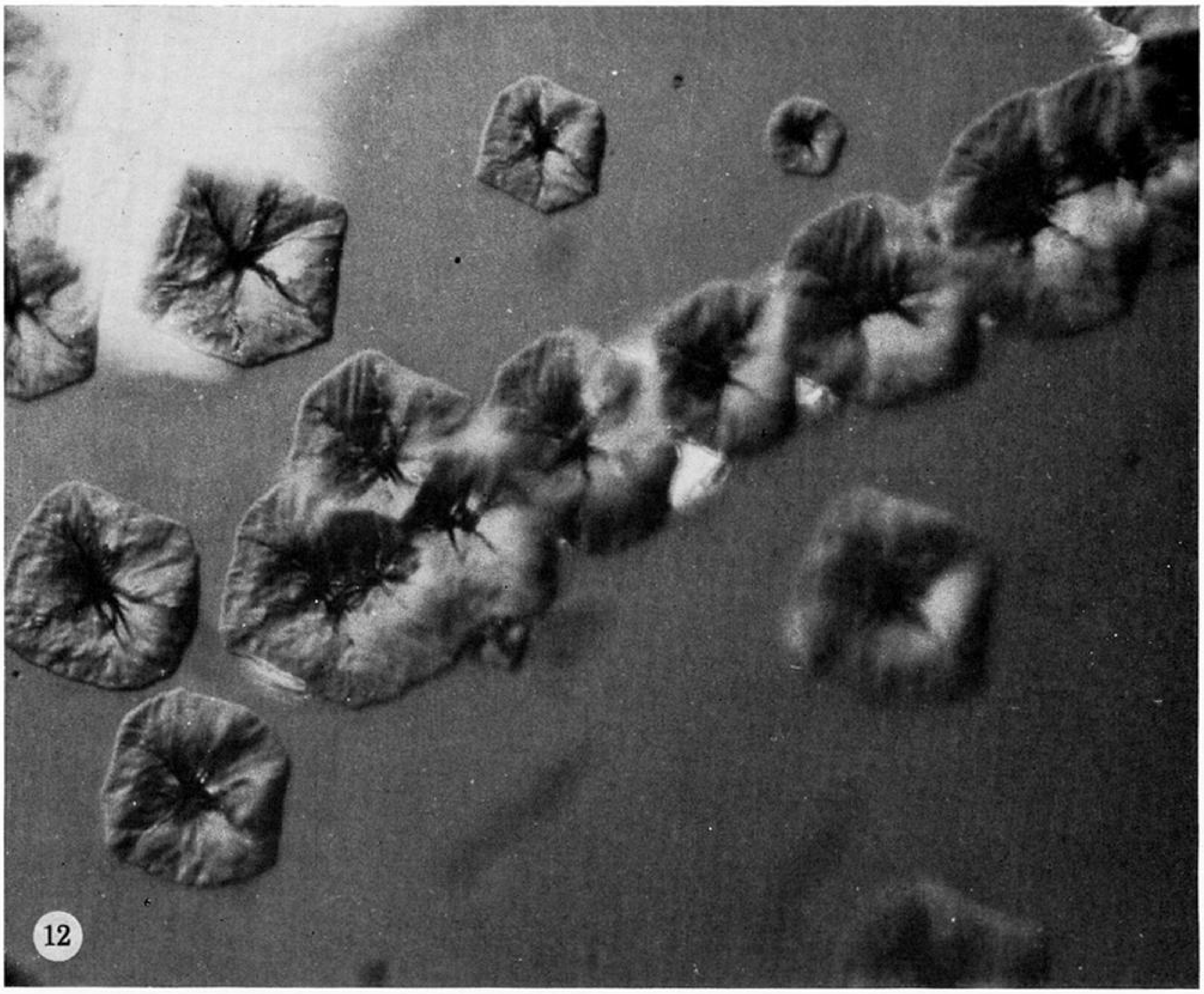


FIGURE 6. (*a*) Bright-field electron micrograph showing coherent boundary between two crystal forms of 1,8-dichloro-10-methyl anthracene. (Magn. × 10000.) (*b*) Corresponding diffraction pattern ((*h*0*l*) reciprocal lattice net) showing that a single crystal → single crystal stress-induced transformation is involved. (Jones, Thomas & Williams 1974.)

FIGURE 10. High-resolution (*h*0*l*) lattice-image of zussmanite showing faint traces of (001) planes and, more clearly, the (201) planes traversing them. The variation in direction of the (*h*0*l*) planes in the two polytypes may be discerned. (Jefferson & Thomas, in the Press.)



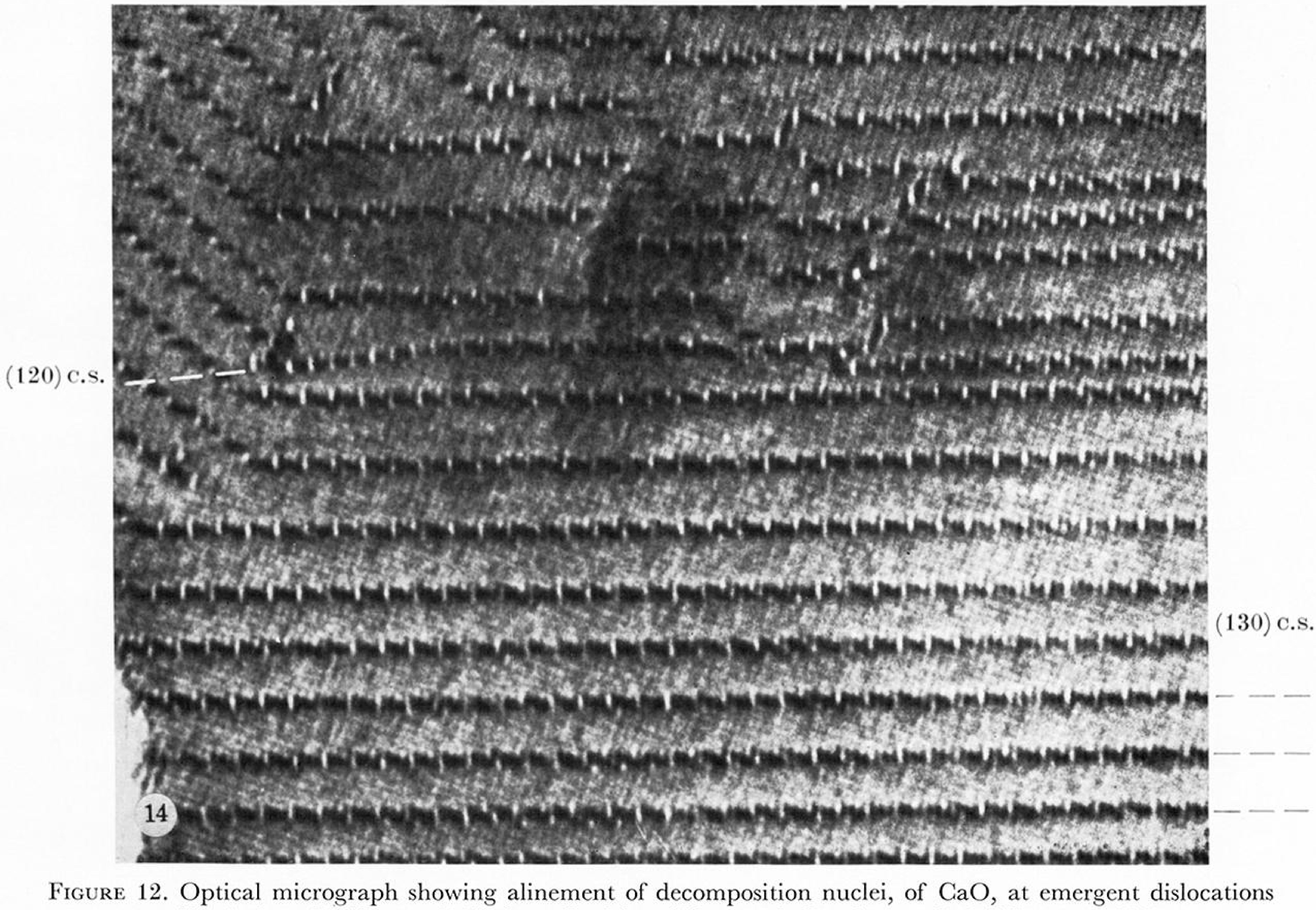
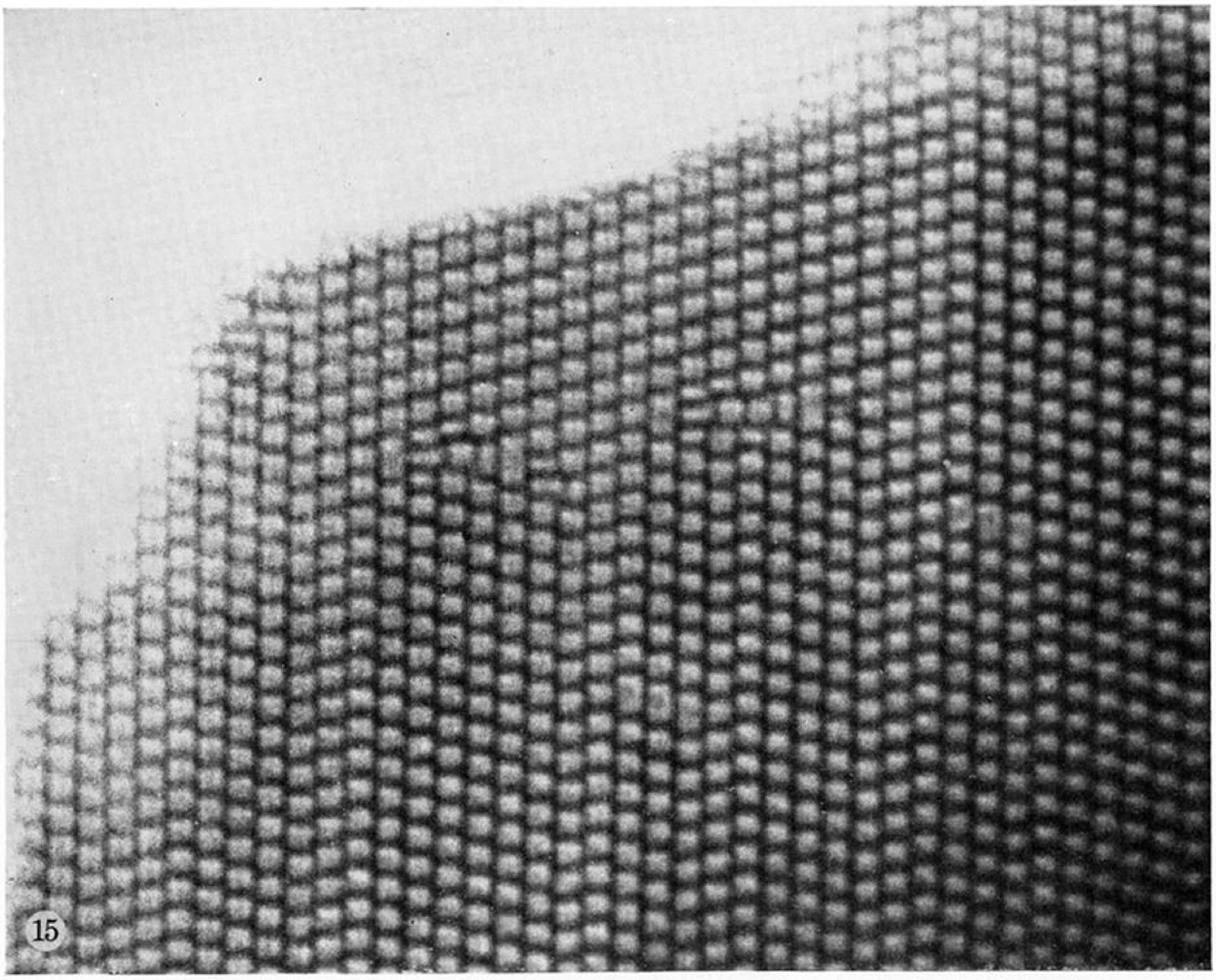


FIGURE 12. Optical micrograph showing alinement of decomposition nuclei, of CaO, at emergent dislocations alined along [110] on a {100} face of calcite. (Thomas & Renshaw 1967.) (Magn. × 500.)

FIGURE 14. High resolution electron micrograph of a thin sliver of non-stoicheiometric tungsten oxide. The lower part shows reasonably well ordered (130) c.s. planes at a separation distance appropriate for a composition of $W_{19}O_{55}$. A short segment of a (120) c.s. plane is also visible. (Sunberg & Tilley 1974.)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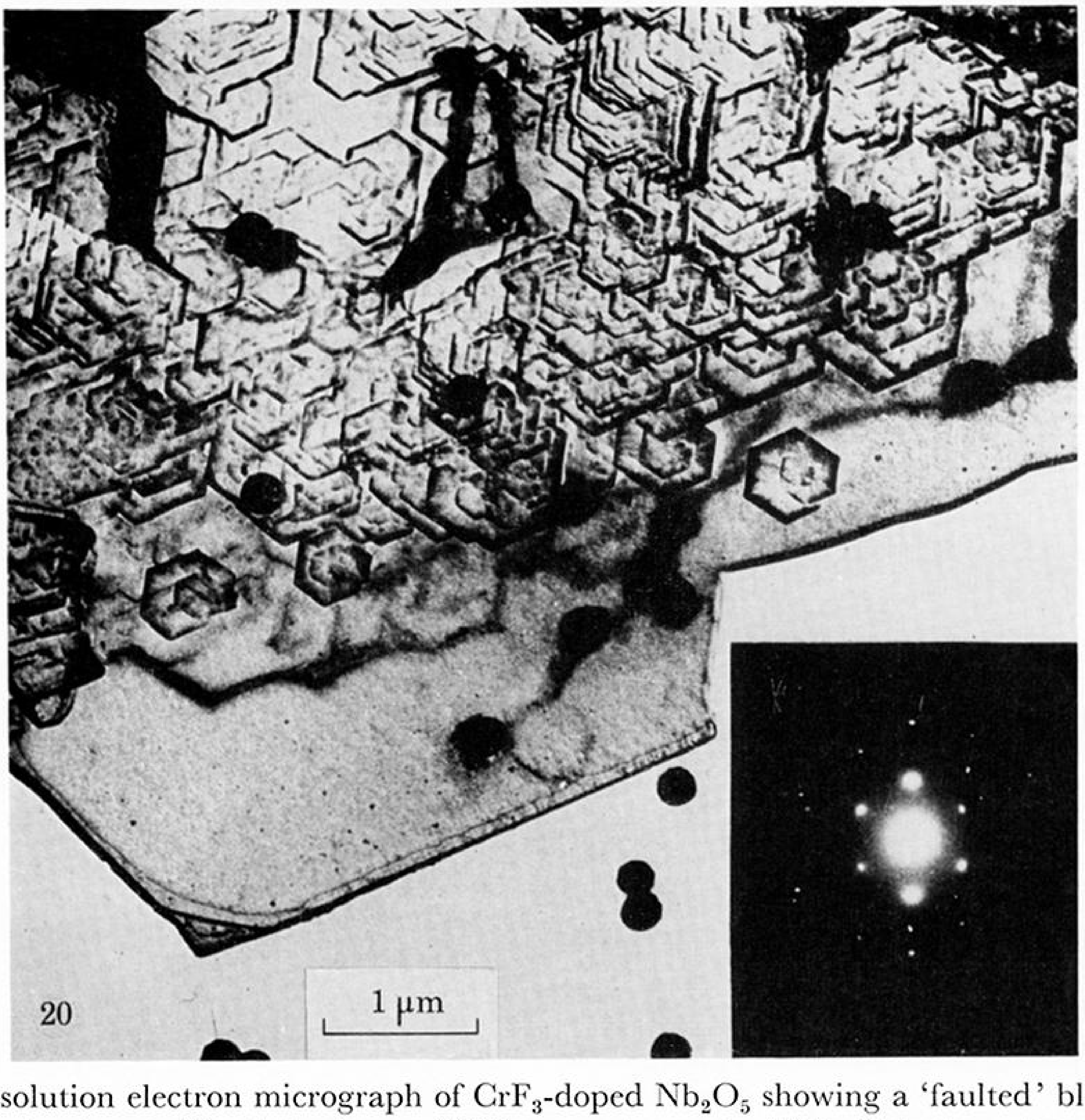
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FIGURE 15. High resolution electron micrograph of CrF_3-doped Nb_2O_5 showing a 'faulted' block structure. The basic N-Nb_2O_5 structure suffers twinning on (001) on a microscale. 'Filler' blocks, acting as wedges between twinned and faulted structures are thought to contain segregated Cr and F ions. (Hutchison 1974.) (Magn. × 4200000.)

FIGURE 20. Electron micrograph of a thickened POM crystal (see text). Note spiral growth features centred at emergent non-basal screw dislocation of the type depicted in figure 19. (After Mateva *et al.* 1973.)