

Fig. 1 Temperature profiles of the uranian upper atmosphere for: *a*, 7° N lat, Cape Town immersion; and *b*, 21° S lat, Cape Town emersion. The shaded areas are the regions of the isothermal fit boundary condition. The level at half light is indicated on the right, while the temperature from a full isothermal fit is indicated at the bottom. Note the large variations in temperature.

At the time of the occultation, the subsolar point on Uranus was located at latitude +51.0° and the phase angle was 2.4°. The immersion and emersion points as seen from the Cape were at latitude 7.3° N and 20.9° S respectively, with immersion occurring just before sunrise and emersion just after sunrise. Our results indicate no large difference in the mean temperature for these two conditions.

Both temperature profiles show large variations, ~50 K peak-to-peak for immersion and 40 K for emersion, with a vertical length scale of ~150 km. Although some of this variation is

probably due to noise, we believe that most of these variations represent real temperature variations in the atmosphere of Uranus. First, they are much larger than any variations one might expect from shot noise in the light curve⁴ and second, the profiles agree well with the Kuiper Airborne Observatory (KAO) results^{7,8}. The regions of the uranian atmosphere probed by observations from the Cape and the KAO correspond to the same levels in the atmosphere, but are displaced from each other about 2,200 km along the limb of Uranus for the immersion data and 2,600 km for the emersion data.

The mean atmospheric temperature found here (~90 K) is somewhat cooler than the 140 K found for the upper atmosphere of Neptune from a previous stellar occultation⁹. It is also cooler than that obtained by Wallace¹⁰ from model calculations. Further work will be required to find the reasons for these differences and to establish the cause of the observed 'wavelike' temperature variations. The main problem with dynamical explanations for the wavelike structures is that the obvious wave mechanisms—vertically propagating density waves, for example—apparently heat the atmosphere to much higher mean temperatures than we observed⁸. A more likely possibility is that the variations are caused by photochemical processes⁸.

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Multiply-twinned particles in silver catalysts

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It has been known for several years that anomalous structures can occur in the early stages of particulate growth. Ino¹ and Ino and Ogawa² for gold on rocksalt and Allpress and Sanders³ for nickel on mica found small polycrystalline nuclei which they interpreted as multiply-twinned particles (MTPs). These particles can be considered as 5 or 20 f.c.c. tetrahedra joined by twin boundaries to give decahedra or icosahedra (Fig. 1). As the tetrahedra do not assemble to a completely space filling structure, either elastic strains or grain boundaries are required to complete the particles. More recently, MTPs have been observed in the early stages of growth for all f.c.c. metals in certain conditions. Gillet⁴ has recently reviewed the field whilst Hayashi *et al.*⁵ give extensive results for f.c.c. metals in argon smokes. The possible significance of MTPs in heterogeneous catalysts was first suggested by Allpress and Sanders⁶ and investigated by Avery and Sanders⁷. They found, however, that at most 2% of particles 100–350 Å in size for Ni, Au, Pt and Pd on γ -alumina were multiply twinned. We report here the presence of considerable numbers of multiply-twinned particles in various heterogeneous metal catalysts, in particular silver on α -alumina. The particles can have quite large dimensions up to ~2,000 Å. Attention is drawn to the possible significance of some special sites on these particles which have no counterpart on single crystal surfaces, and to the unusual distribution of surface faces.

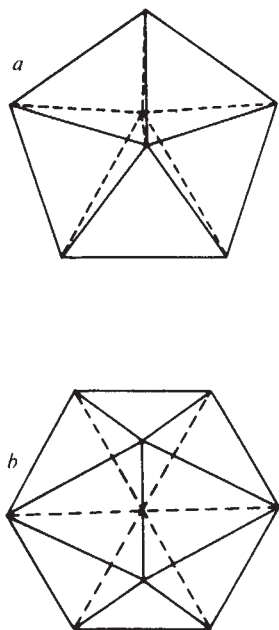


Fig. 1 Structure of *a*, decahedral and *b*, icosahedral multiply-twinned particles.

The samples examined were supplied by ICI Ltd, having been prepared by the following method (UK Patent 1369639): an $0.8 \text{ M}^2 \text{ g}^{-1}$ support of α -alumina (Carborundum Ltd, No. SAHT96) was immersed in a solution of silver oxalate in 45% water—45% ethylene diamine—10% ethanolamine. The support was then pyrolysed in nitrogen at 200°C for 1 h to decompose the oxalate to silver metal. The catalyst examined contained approximately 16% silver by weight. Samples were prepared for examination in a Siemens 102 microscope by allowing a drop of ground catalyst suspended in acetone to dry on amorphous carbon films premounted on microscope grids.

The samples examined contained principally isolated particles of size between 1,000 and 2,000 Å, although smaller particles (<500 Å) were found associated with amorphous regions of the substrate, and a few large polycrystals were observed, presumably due to particle coalescence. The discrete particles displayed well developed 111 facets, with very little edge or corner rounding. More than 80% of the discrete particles were observed to be MTPs, the remainder being composed mainly of twinned platelets, faulted needles and single crystals. Micrographs of these various morphologies are shown in Figs 2 and 3. All the icosahedral MTPs and most (but not all) of the decahedral MTPs displayed internal contrast suggestive of dislocations, as has been previously noted for large MTPs⁸.

The occurrence of MTPs in heterogeneous catalysts is consistent with their common observation in epitaxial films. MTPs may well occur in many other catalysts; we have, for example, examined micrographs of a nickel catalyst (A. Szczepura, personal communication) which show contrast typical of MTPs. The apparent contradiction between our results and those of Avery and Sanders⁷ is probably due to the different methods of production; the particles described here were prepared by a mild pyrolysis, whereas Avery and Sanders examined their particles after annealing in hydrogen. Preliminary results for <50 Å gold particles on NaCl or amorphous Al_2O_3 have shown that the particles are single crystals after annealing at 500°C in hydrogen but multiply twinned after annealing at 500°C in air. It seems probable that the occurrence and survival of MTPs in catalysts may depend on the atmosphere present during both preparation and running.

The large sizes of the MTPs observed is probably a result of the growth conditions. As the type of particle observed corresponds with the types commonly found for small (<200 Å)

metal particles, it seems likely that the internal structure was determined at some early stage in the growth. Further layer growth, possibly autocatalytic in nature, could produce the observed particles. In the absence of sufficient activation energy from processes such as coalescence, the particles can remain in the multiply twinned structure, even though this is almost certainly metastable in this size range. Given the existence of the multiply twinned structure, the equilibrium of the surface faceting is an additional question. More detailed experimental and theoretical studies of this problem, which will be published elsewhere, suggest that the form observed here, with sharp 111 facets, may in fact be metastable with respect to surface changes at room temperatures and that the stable structure would have additional 100 facets as well as notches at the boundaries.

One interesting feature of the MTP is that they have some unusual surface sites, some of which have no analogue on a single crystal surface. On the actual twin boundary the atoms have h.c.p. coordination rather than f.c.c. so that the *d*-bonds will be differently orientated. Also, as mentioned above, more complicated faceting geometries including notches may arise if the surfaces attain their equilibrium configuration. Such notches or re-entrant surfaces have been considered to act as preferential nucleation sites for crystal growth⁹ and may have some catalytic importance. For a 50-Å radius particle approximately 7% of the surface atoms would be on the twin boundaries, a third of these at the notches.

Anomalous surface sites associated with twins are, of course, also found in other particles. Re-entrant surfaces have been observed for f.c.c. particles with an odd number of closely spaced parallel twin boundaries by Hayashi *et al.*⁵ However, the twin density in MTPs will usually be higher than in other particles.

The fact that MTP surfaces will usually consist of a different distribution of crystal faces than would occur in a single crystal could also be of significance in catalytic reactions which are sensitive to surface crystallography. It seems likely that MTPs will have an anomalously high fraction of their surface as (111) planes and, in addition, the icosahedra will not have any (100) surface planes.

Because the tetrahedral units are not completely space-filling the MTPs probably contain considerable elastic strain, or possibly crystal defects such as dislocations as observed in Si particles by Saito⁸. In either case the catalytic properties may be

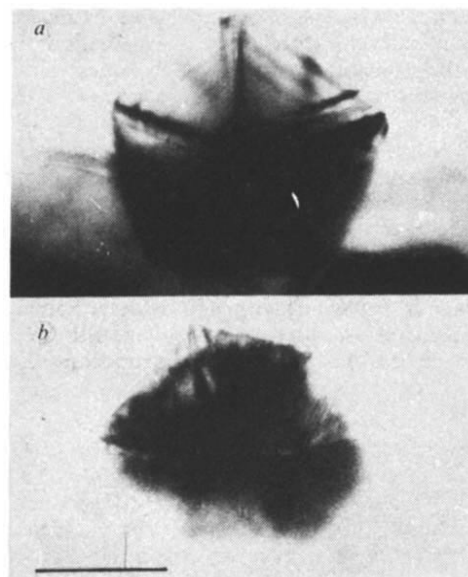


Fig. 2 Micrographs of *a*, Decahedral MTP near the 5-fold symmetry axis and *b*, icosahedral MTP near the 'face' orientation. Scale bar, 0.1 μm .

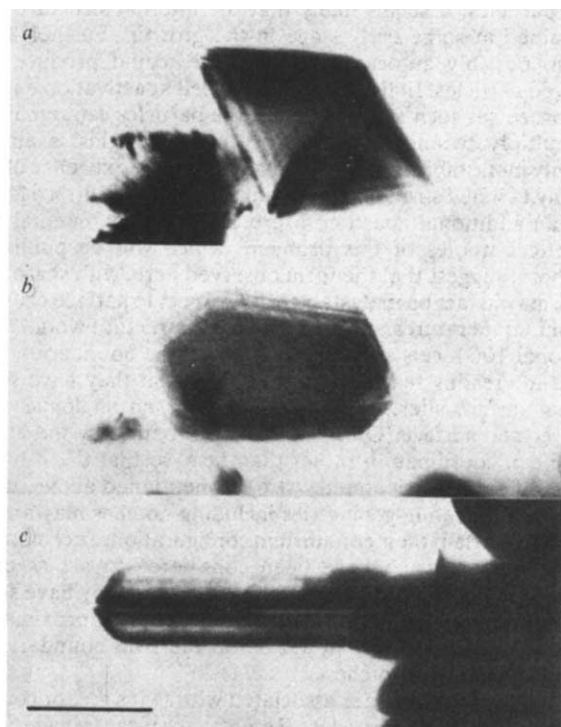


Fig. 3 Micrographs of *a*, single crystal (square pyramid); *b*, platelet and *c*, needle. Scale bar, 0.1 μm .

affected. Ino¹⁰ assumed a homogeneous elastic strain maintained by external forces to estimate the elastic strain energy using anisotropic elasticity theory. His figures for Ag indicate that the lattice parameters in the surface of the icosahedron are expanded by about 3%, while the spacing of planes parallel to the surface is reduced by nearly 5%. The lattice parameter in the surface of the decahedron is increased by 1% in the direction of the $\langle 110 \rangle$ outer perimeter and reduced by 1% in the direction normal to this. Removal of Ino's external forces will lead to additional inhomogeneous elastic strains. De Wit¹¹, for instance, has pointed out the similarity between the decahedron and a disclination which has very high compressions close to the central axis. In the icosahedron the stress is probably also inhomogeneous, being highly compressive at the centre and tensile at the surface. More detailed calculations have been made but these are complicated by the uncertain effects of surface tension stresses in such small particles (A.H., L.D.M. and E. H. Yoffe, in preparation).

Clearly it would be of considerable interest to produce catalyst samples containing, for example, a larger proportion of single crystal particles in the same size range as the MTPs. It might then be possible to make a direct experimental assessment of the practical significance of these anomalous structures in catalysis.

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Propagating chemical waves in the uncatalysed gallic acid–bromate system

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Chemical oscillatory systems which include at least one autocatalytic reaction step are of interest as thermodynamically open systems in which temporal and spatial structures are produced. These systems also show other types of unusual kinetic behaviour¹. To analyse the elementary steps of their kinetics the simplest possible reactions are needed especially in relation to nonlinear thermodynamics². The theory of these chemical reactions is still only at the level of a simplified mathematical model, and theoretical results are in poor agreement with experimental findings. Therefore it is important to study other examples of spatial dissipative structures corresponding to chemical systems which exhibit oscillations. We report here observations of the oscillating reaction between bromate and the phenolic compound gallic acid in which propagating chemical waves occur.

The Belousov–Zhabotinskii reaction system (BZR) is known to exhibit propagating chemical waves³. This reaction is very complex and involves about 20 elementary steps (the mechanism has been elucidated by Field *et al.*⁴) starting from an initially homogenous state. Until now no other chemical reaction starting from this condition has been found to form a spatial structure spontaneously (unlike a Liesegang ring-type one).

The BZR requires a transition metal catalyst but the rate law of wave propagation shows the propagation velocity to be independent of the concentration of the catalyst in the range studied by Noyes and Field⁵. This means that the step catalysed by the transition metal ion, although necessary for oscillation and/or wave propagation in the BZR does not determine the propagation velocity.

Körös and Orban⁶ have reported a new oscillatory chemical reaction between bromate and phenolic or aniline-type compounds, occurring in the absence of a catalyst. (A catalyst may be added, but the reaction then becomes of the normal BZR type^{7,8}.) A similar reaction between bromate, and bisazonium salts was reported previously by Kuhnert and Linde⁷.

Our experiments were carried out at room temperature in Petri dishes using a solution volume of 11 ml to give a layer ~1 mm deep. As the waves were hardly visible in daylight, they were observed and photographed under filtered blue light from a high-pressure mercury discharge lamp. The light intensity selected was low enough to prevent photochemical excitation of the reaction mixtures (formation of bubbles).

The reaction solutions were prepared in the following way. Mixtures of 7 ml of distilled water, 3 ml of sulphuric acid (4 M), and 1 ml of a solution of sodium bromate (1.5 M), were stirred and saturated with gallic acid; excess gallic acid was filtered off rapidly, and the filtrates were poured into Petri dishes. Reaction times were measured from when components were mixed. The brown solutions rapidly turned pale but darkened again slowly. After periods of 3 to 10 min colourless waves started propagating with a speed of 2 to 4 mm per minute from leading centres commonly situated at the borders of the dishes. In most experiments several leading centres appeared, and when the waves propagating from them came into contact, destructive interference was observed. Artificial leading centres could be created by adding droplets of concentrated sodium bromate solution to the reaction mixtures, these leading centres exhibited the same behaviour as the original ones, but often generating waves of shorter wavelength. Wave propagation was generally