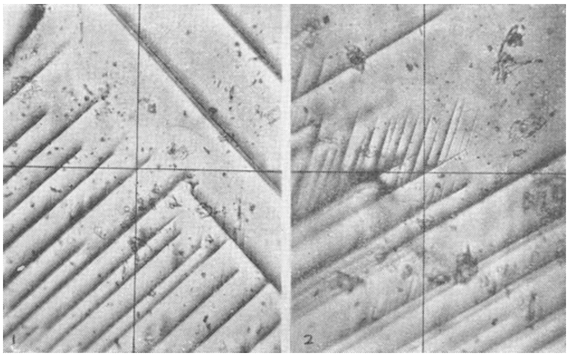
Twinning Structure in Crystals of Tungsten Trioxide

A MICROSCOPIC examination of crystals of tungsten trioxide (WO_3) has revealed a type of twinning very similar to the domain patterns characteristic of the ferroelectric (tetragonal) phase of barium titanate ($BaTiO_3$). This similarity is significant in view of the reported ferroelectric behaviour of tungsten trioxide[1].

The crystals, examined under the polarizing microscope, were grown by sublimation of the vapours from a molten solution of tungsten trioxide dissolved in barium chloride, and contained in a platinum crucible. Their normal crystal habit was in the form of very thin plates which varied in their dimensions up to 5 mm. Most of them were almost transparent and ranged in colour through various shades of pale green. Apart from the truly single crystals, many of the specimens showed a highly twinned structure when viewed in a direction normal to the plate surface. In polarized light, a series of narrow, parallel bands, in general, extended diagonally across the crystal at an angle of approximately 45° to the edges. From the effects of optical extinction with respect to the directions of vibration of the polarized light, it was determined that the unit cell axes of one domain are perpendicular to those of its neighbour. These conclusions agree essentially with the observations of Ueda and Ichinokawa[2]. In addition to the fact that the cell axes, lying in the plane of the crystal, differ only slightly from each other in length, this appears to be a prerequisite for the formation of this domain pattern which is characteristic of the ferroelectric phase in general. In tetragonal barium titanate[3], the *a* and *c* axes of the unit cell differ by approximately 1 per cent only. In the analogous case of tungsten trioxide, the *a* and *b* axes, which lie in the plane of the crystal plates, have a difference of less than 3 per cent[4]; the much shorter *c*-axis is perpendicular to this plane. The symmetry of tungsten trioxide has been given as triclinic[4] because of the slight distortion of the inter-axial angles from 90°. However, for purposes of discussion, the crystal may be described in terms of a pseudo-orthorhombic symmetry[2] with a twinning plane $\{110\}$.

The boundary between contiguous domains appears optically as a fine dark line. This may be due either to distorted unit cells at the junction, or to an actual mismatching between the respective lattices. The non-uniform optical extinction which often occurs at the boundaries would seem to indicate that these regions are in a highly strained state. This is especially obvious in the wedge-shaped domains, or those which have been formed by the convergence of their boundary planes within the crystal (Fig. 1). The banded domain pattern presumably results from the relief of internal strains developed during the growth of the crystal, the wedge domains merely representing an arrested or partial twin development.

On the larger specimens, twinning on a broader scale was commonly observed, whereby the crystal is divided into areas or distinct groups of line patterns oriented at right angles to each other. From the accompanying photographs it can be seen that the wedge domains exhibit a wide variation in width, and many of them have bifurcated ends. In Fig. 2 small branch domains can be seen developing from the larger ones at an approximate angle of 45°, that is, parallel to the crystal edges. It is significant that this 'feather' structure appears to develop on one side only of the boundary. All these peculiarities may be assumed to be the result of internal strain.



Domain structure of tungsten trioxide crystals. × 200. (1) Wedge domains showing the dark areas caused by internal strain. (2) Feather-like development of the domains

A more detailed explanation of some of the structural peculiarities of tungsten trioxide will be reported later.

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Occurrence of Small-angle X-Ray Diffraction Maxima in some Artificial Cellulose Fibres

DIFFRACTION at small angles in cellulose fibres and rayon has been investigated by several workers[1]. Generally, a diffuse scattering increasing towards the primary beam has been observed on the equator of the fibre diagrams, with no distinct maxima characteristic of long spacings.

In fibres from highly oriented polyamides and from some other synthetic polymers, such as 'Terylene' and polythene, maxima at small angles have been observed on the meridian of the fibre diagram and have been related tentatively to a periodicity in the length and arrangement of the crystalline and non-crystalline regions in the direction of the fibre axis[2]. In well-oriented cellulose fibres no meridional maxima have been reported so far.

In an investigation on the small-angle scattering of various types of artificial cellulose fibres, exposed in the air-dry as well as in the water-swollen condition, we have found that some specimens in the water-wet state do show a distinct, though rather broad, equatorial maximum at small angles.

The exposures were made in a vacuum camera constructed by Backers in the Laboratory of Technical Physics of the Technical University, Delft, under the direction of Prof. H. B. Dorgelo and afterwards improved by Daams. This is essentially a three-slit arrangement with a metal wire for inter-