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**CRYSTAL GROWTH AND CRYSTAL PERFECTION: X-RAY
TOPOGRAPHIC STUDIES**

Crystal Growth and Crystal Perfection: X-ray Topographic Studies

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Contributions of X-ray topography to the study of growth of the more perfect crystals found in Nature or produced in the laboratory are reviewed, with special reference to the maximum degree of perfection attained by natural and synthetic crystals and to the control of lattice defects in man-made crystals. The X-ray method is of general application, and is non-destructive. A single topograph can record changes of lattice perfection over distances of the order of a centimetre and hence can give an overall picture of the growth history of large single crystals. The sensitivity is sufficient to follow the course of individual dislocations within the crystal, or to detect lattice warping with radii of curvature up to several kilometres. Topographs can show the relationship the dislocation configuration bears to inclusions, precipitates and lattice stresses resulting from compositional or thermal gradients. Crystal species discussed include diamonds, semi-conductors, metals, halides and refractory oxides.

A variety of X-ray topographic experiments is reported in this paper. Discussion of each is of necessity brief. The excuse offered for their qualitative treatment is that in some cases the investigations were of an exploratory nature and in other cases are still in progress. The aim is to give some indication of those crystal studies in which X-ray topographic examination can be informative, to offer a guide as to the resolution and sensitivity of this technique and to cite some results of its application which could not readily have been obtained by other means. Where resolution of individual imperfections is concerned, X-rays cannot compete with the electron microscope. Attention must be restricted to conditions where dislocation densities do not exceed 10^6 cm^{-2} and a topographic resolution limit of about 1 micron is adequate. Specimen thicknesses in which individual dislocations may be observed range from more than 1 mm, for light elements, down to about 2 microns for moderately heavy elements. In principle, no serious gap exists between this lower limit and the upper thickness limit in which dislocations can be resolved using electron microscopes operating at more than a few hundred kilovolts. The standard technique used in the experiments described here is the "projection topograph".¹ This is supplemented when necessary by "section topographs"² and "limited projection topographs".³ The intense diffraction contrast exhibited by individual dislocations in a fairly perfect crystal matrix was apparent from the earliest experiments.^{4, 5} Theoretical studies of dislocation contrast in the X-ray case still lag behind those done for electrons, though familiarity with the general phenomenology of X-ray dislocation images⁶ suffices for the interpretation of most topographs. Certain aspects of these images have been investigated in varying degrees of detail.⁷⁻¹² Complications in the X-ray case arise from the larger Bragg angles, the greater specimen thicknesses and the smallness of the angular range of reflection by the perfect crystal compared with the angular range of the incident radiation. It is this last-mentioned condition that permits such intense

contrast of dislocation images to be generated when X-ray absorption is low. The strength of this intense image is not readily calculable but its width may be estimated from simple criteria. Such estimates agree well with observations, e.g., in diamond,¹³ silicon^{10, 14} and iron.¹⁵

THE PERFECTION OF DISLOCATION-FREE CRYSTALS

Let us consider what information can be derived from X-ray topographs of dislocation-free crystals in addition to the negative (though useful) finding that dislocations are absent. The first topographs of a dislocation-free crystal, taken in 1958, were of a remarkable specimen prepared by the late W. C. Dash. He succeeded in continuing dislocation-free growth of a silicon crystal when it was re-inserted in the melt after several seconds complete removal therefrom. In the topograph fig. 1, which may be compared with fig. 16 of Dash's report,¹⁶ the location of the interface between new and old crystal is identified by a diffuse band of enhanced diffracted intensity coming from the first layers of newly grown material. These topographs also showed that oxygen bands in silicon could be revealed by diffraction contrast. Studies of such bands by various X-ray topographic methods have since been performed.^{17, 18} The diffraction effects of oxygen bands arise in part from the higher lattice parameter¹⁹ within the region containing more oxygen and in part from lattice tilts due to stress relief at the crystal surfaces: the topographs indicate that the latter are more important. Hence estimation of oxygen content by diffraction contrast is less direct than by infra-red absorption²⁰ even though a theoretical basis for the calculation of such contrast is now available.^{21, 22} The topographs readily confirm the good epitaxy of the new material upon the old and the absence of dislocations. The interpretation of the contrast at the interface is not so simple. A study of its variation in various Bragg reflexions does, however, disclose an unexpected feature. It appears that there is a step-wise increase in lattice parameter in going from old to new crystal of magnitude perhaps two or three times the amplitude of the lattice parameter oscillation in the oxygen bands.

We see thus that lattice parameter differences of the order of 1 part in 10^7 can be shown up by topographs, albeit in a rather indirect way. The sensitivity of topographs to lattice bends may be estimated more closely. Direct measurements of lattice orientation along the length of a specimen allow bends of about $1''$ per cm to be detected, corresponding to a radius of curvature of 2 km. Smaller orientation gradients in dislocation-free volumes can be measured from the displacement of Pendellösung fringes, either on projection topographs or section topographs. The theory of these fringes, as they appear on X-ray topographs, is now well understood, both in perfect^{23, 24} and in distorted crystals.^{9, 22} Fig. 2 shows part of a section topograph of a highly perfect silicon bar. The fringes run uniformly parallel to the edge of the bar except where they cross some (111) slip planes which are seen edge-on. On these slip-planes a few dislocations lie: their intense, localized "direct image", and their "extinction shadow" in the slip-plane, can both be seen. Also evident is the displacement of the Pendellösung fringes caused by the dislocation strain fields. Fig. 3 is a comparable section through a natural diamond. It is the most perfect diamond examined so far, but the uniformity of visibility and spacing of its Pendellösung fringes compares unfavourably with the silicon crystal. The sensitivity of Pendellösung fringes to lattice curvature may be illustrated as follows. Consider a section topograph of a silicon plate 1 mm thick taken with $AgK\alpha$ radiation. The order of the central fringe in the section topograph of the 220 reflection in symmetrical transmission is about 20. Hence a change from maximum to minimum intensity implies a change in effective mean fringe spacing of 2.5%. This change would occur

if the tilt between the Bragg planes at the front and back surfaces of the crystal were only 0.64° , which would correspond to a radius of curvature of the Bragg planes of 0.34 km.

DISLOCATIONS AND CRYSTAL GROWTH

Topography has shown that very low dislocation densities can occur in some natural crystals. Diamond octahedra of several mm edge length are found substantially dislocation-free, quartz oscillator plates can have areas of many mm^2 free from dislocations, and dislocation densities of a few tens per cm^2 have been observed in calcite. The commonest observed sources of dislocations in quartz and diamond are motes and inclusions whose incorporation in the growing crystal produces lattice closure errors. There is evidence to suggest that diamonds can grow without the aid of dislocations. A very common dislocation configuration, however, is a distribution radiating from a central node which doubtless contains the nucleus from which the crystal grew.^{25, 26} Fig. 4a, b and c show an example of radiating dislocations in a twinned diamond. Fig. 4a is a 111 reflection from the twin plane, and shows the whole stone. Figs. 4b and c are other 111 reflections in which the two members of the twin pair appear separately. Stereo-pairs of topographs show clearly the spatial relationships between the twins. The twin boundary is quite irregular and has strains associated with it. An interesting application of topography to twinned crystals occurs with quartz in which twins with parallel lattices exist. Lattice displacement and/or change in X-ray structure amplitude at the twin boundary produces diffraction contrast resembling that at stacking faults.

Melt-grown crystals of halides and of magnesium oxide²⁷ show a well-developed network of low-angle boundaries surrounding sub-grains in which local regions of quite low dislocation densities are found. In pure crystals of these materials, and also in pure semiconductor crystals, it seems that all dislocations arise from plastic deformation under thermal stress.²⁸ The configurations bear evidence of a complex history of glide, climb and sometimes polygonization. The amount of dislocation movement that has taken place since solidification renders it difficult to determine whether any dislocations were grown in to the crystal through the mechanism of solidification itself. No positive evidence for dislocation generation in this way has been obtained. Instead, additional information from diffraction contrast under conditions of moderate absorption when the *sense* as well as the *direction* of Burgers vectors can be determined favours the glide origin of the dislocations.^{11, 15}

Quite different dislocation configurations are found in strain-anneal grown crystals of pure aluminium.²⁹ Fig. 5 shows a typical region in a specimen about 1 mm thick. Conspicuous are the lines of coaxial loops. The axes of these loops lie along $\langle 110 \rangle$ directions and the Burgers vectors of the dislocations lie parallel to the axes. Helices and figures-of-eight also occur. These $\langle 110 \rangle$ lines of loops occur singly and bear no recognizable relation to other $\langle 110 \rangle$ lines. Thus there is no evidence that they radiate from inclusions in the manner demonstrated by deliberate introduction of inclusions in silver chloride.³⁰ The other dislocations, which follow a random course through the crystal, move and multiply easily under applied stress; but the loops have not been observed to move before they become obscured by an enveloping mass of fresh dislocations. The resolution with which dislocations may be recorded improves as X-ray scattering factor and X-ray wavelength are increased. The superior resolution of fig. 6 compared with fig. 5 is evident. In the array shown in fig. 6 dislocations spaced apart by $2\frac{1}{2}$ -3 microns are clearly resolved. In melt-grown iron + 3.5% silicon alloy crystals no loops and helices are observed such as are found in strain-anneal grown aluminium.

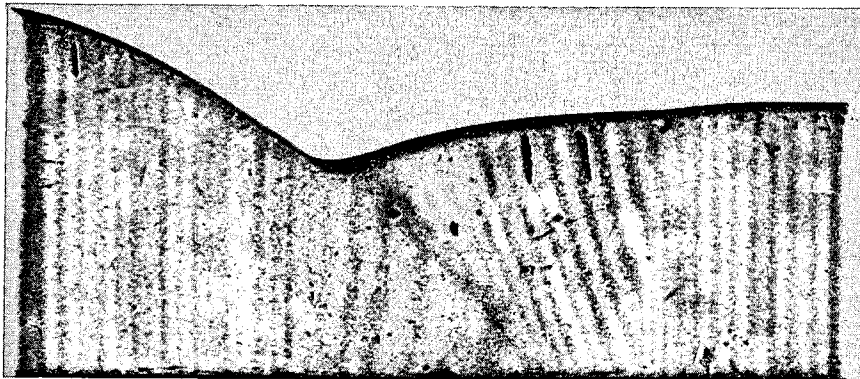


FIG. 1.—Dislocation-free silicon crystal showing good epitaxy upon regrowth; average spacing of oxygen bands 0.2 mm; crystal growth axis [111]; specimen thickness 1 mm; $AgK\alpha$ radiation; 111 reflection.

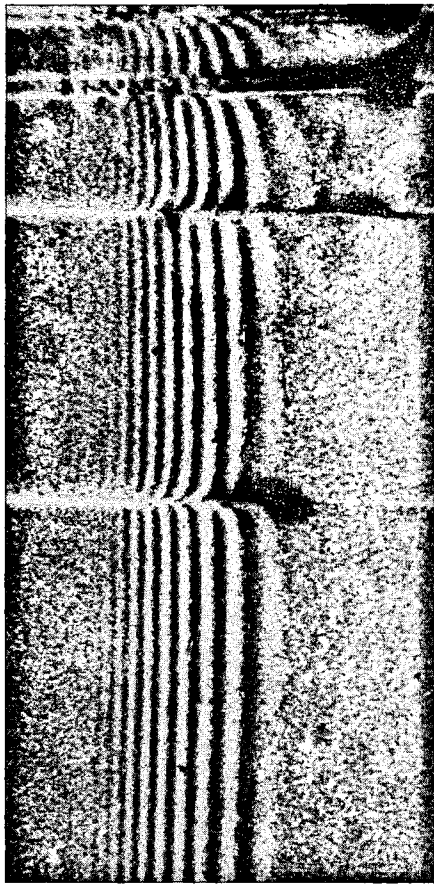


FIG. 2.—Part of section topograph of silicon crystal with few dislocations; height of field 1 mm; $AgK\alpha$ radiation; 220 reflection.



FIG. 3.—Part of section topograph of natural diamond; two dislocation images visible; height of field 1 mm; $MoK\alpha$ radiation, 111 reflection.

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