they are produced at the terminations of screw dislocation lines as reported by Patel & Bahl (1965). The centres of the spirals indicate the sites of screw dislocations. The formation of the spiral patterns therefore indicates that the crystals may have grown according to the dislocation theory of Frank (1949).

The observations on (i) the matched fracture prism faces, (ii) the prism fractured faces before and after polishing, and (iii) the two sides of a thin flake having prism faces indicate that dislocation lines which exist in the crystal are cut into two by fracture along any surface of the crystal, even though the surface may not be a true low index plane as in the case of perfectly cleavable crystals. The slight difference in the shapes of the etch pits produced on the matched faces indicates that they are fractured faces. These faces had a slight curvature, one being slightly convex and the other concave. The pits produced on these matched faces would not be exactly of the same shape, because of opposite curvatures of the two faces, and this is what is observed. Thus it is clear that if two matched fractured faces, even though not quite flat, are etched simultaneously in the same medium, one-to-one corspondence in the number and position of the pits is produced, even though the shapes may differ.

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Irradiation Effects in Beryllia and Zinc Oxide

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Electron-diffraction and electron-microscope observations have been made on the effects of neutron irradiation and electron irradiation in an electron microscope on beryllia flakes and zinc oxide smoke particles. It is shown that the defects or excitations created in beryllia by electron irradiation interact strongly with neutron-induced defects to the extent that electron micrographs obtained with normal electron irradiation give a false impression of the form of the defect aggregates present. It is shown that high-intensity irradiation with electrons can transform normal α-BeO to the high-temperature, tetragonal β-BeO phase. The remnants of crystals partially evaporated by the electron beam may consist of fibres of α-BeO, fibres of β-BeO or plates of β-BeO. From single-crystal and oblique-texture electron diffraction patterns the structure proposed for β-BeO and its orientational relationships with α-BeO are confirmed. The significance of the formation of the β phase by electron irradiation is discussed in relationship to the possible nature of the defects in α-BeO responsible for the anisotropic expansion induced by neutron irradiation.

The erosion of thin near-perfect crystal plates of zinc oxide by neutron irradiation and the corrugation of the surface of such plates by electron irradiation are described.

Introduction

Electron microscope observations of the defects produced in beryllia, BeO, by neutron irradiation have been reported by Chute & Walker (1964), Wilks & Clarke (1964), Elston, Frisby & Labbe (1964) and others. These authors also reported in greater or lesser detail that electron irradiation in the electron microscope could produce visible defect aggregates in electron microscope images and could result in an evaporation of the beryllia crystals, leaving fibrous remnants with the fibres parallel to the c axis. These latter effects were described in more detail by Bisson (1963). The present paper reports some additional observations on these irradiation effects which suggest that some previous results may have been misinterpreted and provide further evidence on the nature of the defects involved. Also some further results are reported on the production by electron irradiation of the high-temperature β-BeO phase, recently described by Smith, Cline

& Austerman (1965), on its structure and relationship to the α phase, and on its significance for the discussion of the nature of irradiation defects in beryllia caused by neutron bombardment.

The electron microscopy and electron diffraction studies were made with a JEM-6A electron microscope, operating at 80 kV except where otherwise indicated. Specimens of beryllia in the form of small chips mounted on carbon films, both with and without neutron irradiation, were kindly supplied by Drs Hickman and Walker of the Australian Atomic Energy Commission.

Observations on irradiation effects

As reported by other authors, electron micrographs of beryllia irradiated with fast neutron doses of the order of 10^{20} n.v.t. at room temperature or slightly above showed black or white dots, the contrast depending on the diffracting condition of the crystals. These are of the order of 50 Å in diameter and presumably represent strain fields surrounding defect aggregates (Fig. 2). The electron diffraction patterns of such irradiated crystals show fairly sharp continuous lines through rows of spots in the direction of the c^* axis (Fig. 3). The form and intensity distribution of these lines are in agreement with X-ray observations on single crystals (see, *e.g.* Walker, Mayer & Hickman, 1964) except for variations clearly attributable to dynamic diffraction effects. The lines can be attributed to aggregates of interstitials in planes perpendicular to the c axis (Sabine, 1964).

As reported by Bisson (1963) and the other authors named above, visible defects were seen to be created in beryllia crystals by heavy irradiation with the electron beam in the electron microscope. Defect aggregates similar to those produced by neutrons, although often more clearly elongated in the basal plane than those for neutron irradiation near room temperature, can be produced using 100 keV electrons. In this case the energies involved are probably sufficient for the displacement of beryllium atoms from their normal sites. For 50 and 80 keV electrons we observed no such effects. However, for all incident electron energies a different kind of defect aggregate appeared (Fig. 4), accompanying the evaporation of material from the surface and edges of the beryllia flakes and leading eventually to the complete dissolution of the crystal apart from a remnant consisting of bundles of thin lathes parallel to the c axis which sometimes proved very resistant to any further irradiation.

The process may be described as follows: First, crystal edges became squared-off and limited by straight lines, preferably long parallel to the c axis and short at right angles to that direction. At the same time small rectangular patches appeared within the bulk of the crystal and became elongated in the direction of the c axis (Fig. 4). The contrast of these patches was consistent with an interpretation in terms of thin rectangular internal voids, or surface holes. Observations on the interactions of these features with surface features near crystal edges suggested that some, at least, were internal. It appeared to be by multiplication and extension of such voids that the dissolution proceeded and the crystal was divided into the lathes of Fig. 5.

Within these rectangular patches, and sometimes over very extensive regions of a crystal after evaporation of an appreciable fraction of the material, there appeared fine striations parallel to the c axis and with a near-regular lateral spacing, usually of about 60 Å but occasionally 30 Å. Such striations were also sometimes visible along the remnant lathes as in Fig. 5. Electron diffraction patterns obtained during the course of the disintegration of a single-crystal flake showed that until a large percentage of the crystal had evaporated the flake remained a near-perfect single crystal, giving sharp spots and Kikuchi lines. Even a region of remnant lathes, as in Fig. 5, gave a pattern close to that of a single-crystal, with a spread of spots by only a few degrees. Patterns obtained after any appreciable amount of dissolution showed strong sharp streaks through the spots in the direction perpendicular to the c axis as would be expected from the extended crystal edges and striations parallel to the c axis.

From one set of micrographs taken with the beam parallel to the c axis it was clear that the preferred planes for the larger surfaces of the voids and the finally resulting lathes were of the (110) type. Evidence from micrographs and diffraction patterns obtained in other orientations agreed with this conclusion.

The electron dose necessary to produce defect aggregates and evaporation of the crystals varied widely from crystal to crystal. Some flakes disintegrated repidly under normal viewing conditions. A few showed no sign of any effect even when the condenser aperture was withdrawn and the beam focused on the specimen to give the maximum possible current density, and consequently, considerable heating of the crystals. There was no apparent correlation with the pre-existence of visible crystal defects. The correlation with crystal thickness or position relative to the wires of the supporting grid, noted by Wilks & Clarke (1964) was verified to only a limited extent. Nor was there any strong correlation with the amount of previous neutron irradiation (*cf.* Chute & Walker 1964).

The mechanism for the production of voids and evaporation from the crystal surfaces can only be guessed at. For neutron irradiation the predominant mechanism for defect creation is presumably direct atomic displacement by collision. The very different effects observed with electron irradiation suggest a different basic mechanism, presumably involving multiple ionization leading to vacancies and interstitials by a Varley (1962) mechanism. Diffusion to surface and evaporation of the interstitial ions would leave vacancies which could aggregate to form voids. The Varley ionization processes were discussed in relation to a different process, the growth of loops under electron irradiation,

by Wilks & Clarke (1964). These authors also presented evidence that both the loop growth and disintegration of flakes are attributable to electron irradiation rather than ion bombardment in the microscope.

Interactions of irradiation effects

It was noted in passing, in the papers quoted previously, that irradiation by electrons in the electron microscope could affect the appearance in the electron micrographs of the defect clusters created by neutron irradiation. This has been verified. At a stage of electron irradiation prior to the appearance of the large-scale electron-induced defects described in the previous section, the black or white spots corresponding to neutron-induced defect aggregates were seen to grow larger, sometimes forming recognizable loops, and then gradually disappear until very little sign of them remained.

It has been observed that, at a fairly early stage of this process, the continuous lines parallel to the c^* axis in the electron diffraction patterns faded and disappeared. For some crystals these changes took place rapidly under the conditions of illumination normal for electron microscopy observation so that the lines in the diffraction pattern always appeared to be very weak.

Also it has been reported by Walker (1964) that irradiation with 1 MeV electrons has the effect of annealing out changes in crystal volume and lattice parameters induced by neutron irradiation.

The inference is that the lattice excitations or mobile point defects created by electron irradiation interact strongly with the defect aggregates formed by neutron irradiation, changing their form and eventually destroying them entirely. With this in mind, a series of experiments has been made in an effort to obtain electron micrographs of neutron irradiated material with a minimum of electron irradiation. Fig. 1 shows a micrograph of an irradiated beryllia single crystal flake obtained with much less electron irradiation than is normally involved in preliminary viewing and focusing of an image. Although the image is of poor quality it is evident that the defect contrast is quite different from that of Fig. 2, obtained from the same crystal after a normal amount of irradiation. In fact no contrast attributable to irradiation induced defects is visible in Fig. 1. Other pictures taken under similar conditions show a few of the black and white dots. The crystal images have, in fact, a uniform 'milkiness' and the scattered dots present are smaller and give less contrast than those subsequently appearing.

It seems therefore that the interaction of electron irradiation with neutron-produced defects is much greater than has been suspected. The micrographs of neutron-irradiated beryllia which have been published usually resemble Fig. 2 and so do not represent the state of the crystals produced directly by neutron irradiation. The predominating features are the result of considerable defect migration and aggregation.

Formation of β-BeO

When beryllia flakes are evaporated by intense electron irradiation small crystals condense on the surrounding carbon film.

Electron diffraction ring patterns from these crystals were identified by Willis, Austerman & Dearborn (1964) as being given by the high temperature β-BeO phase, stable in bulk only at temperatures above 2000°C. This phase was studied by X-ray powder methods at such temperatures by Smith, Cline & Frechette (1962) and later by Smith, Cline & Austerman (1965), who proposed a tetragonal structure for it, with $a = 4{\cdot}75$, $c = 2{\cdot}74$ Å, $c/a = 1/\sqrt{3}$, space group $P4_2/mnm$, and suggested a possible mechanism for the α to β transition.

In a recent note (Cowley, 1964), we reported that single-crystal electron diffraction patterns and patterns from oriented polycrystalline material (oblique texture patterns) could sometimes be obtained from the condensed material by selected area electron diffraction methods (Figs. 6 and 7 respectively). The hexagonal indexing then given has now been shown to be in error. The single-crystal patterns such as Fig. 6 are given by tetragonal crystals twinned on (101) tetragonal (or (200) hexagonal) planes. Other patterns obtained show a fourfold symmetry of spot positions and intensities.

The tetragonal unit cell has axes $a = 4{\cdot}65$, $c = 2{\cdot}69$ Å $c/a = 1/\sqrt{3}$; values consistent with those given by Smith, Cline & Austerman (1965) when the difference in temperature is taken into account. Although it is to be expected that the single-crystal intensities might be strongly affected by dynamical diffraction effects, those of the oblique texture patterns would be less so. The intensities observed were in good agreement with those of Smith, Cline & Austerman calculated for X-ray powder patterns, and showed the characteristic absences and symmetry expected from the space group proposed by these authors.

Our results thus verify that the high temperature β-BeO phase is produced in the electron microscope by electron irradiation of α-BeO flakes and is stable there at room temperature. We also confirm the structure proposed for this phase on the basis of X-ray powder work.

In addition, it has been observed that occasionally the unevaporated remnant portions of the flake gave clear single-crystal patterns of the β-BeO phase. The areas giving these patterns were sometimes very extensive, quite thick and near-perfect single-crystal regions, characterized in electron micrographs by an irregular plate-like habit, often striated in the way mentioned above, but quite distinct from the lathe-like arrays which gave the α-BeO patterns (Fig. 5).

In some cases also, regions of a large crystal which showed β-phase diffraction patterns as soon as they were thin enough to transmit electrons (several thousand Å) were reduced to bundles of parallel needle crystals of the β phase. The orientation of the diffrac-

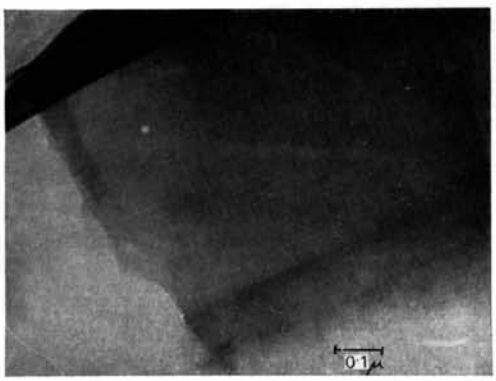

Fig. 1. Electron micrograph of neutron irradiated beryllia flake (fast neutron dose 5×10^{20} n.v.t. at 500°C) obtained with minimum electron irradiation.

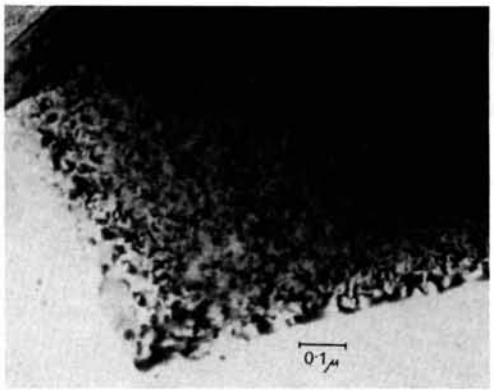

Fig. 2. As for Fig. 1 but obtained with the amount of electron irradiation normally involved in focusing and recording an electron micrograph.

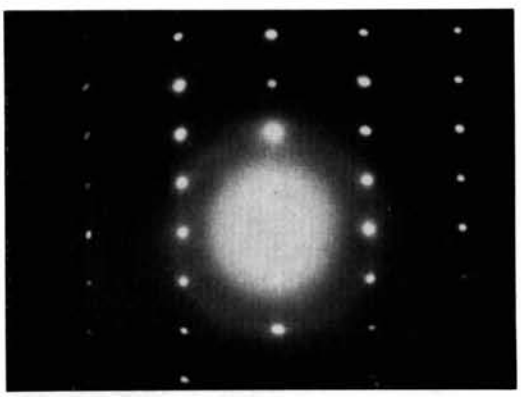

Fig. 3. Electron diffraction by irradiation of beryllia flake showing lines parallel to *c* axis.

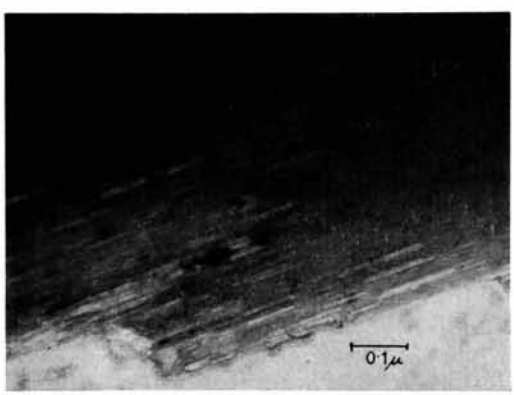

Fig. 4. Initial stages of disintegration of beryllia crystal by electron irradiation.

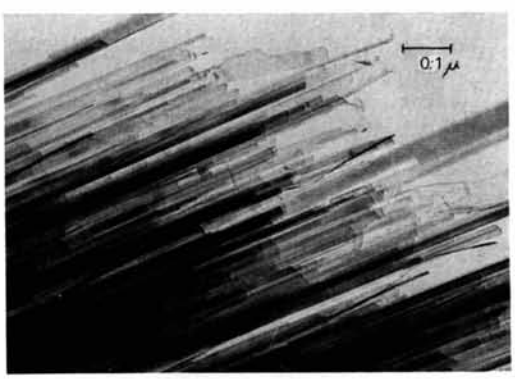

Fig. 5. The remnant of a beryllia crystal after intense electron irradiation in the electron microscope.

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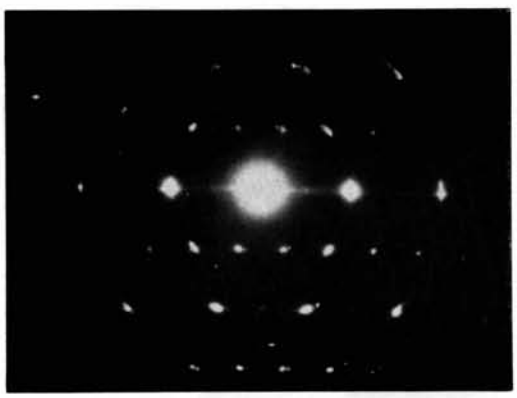

Fig. 6. Spot pattern from twinned crystal of β-BeO.

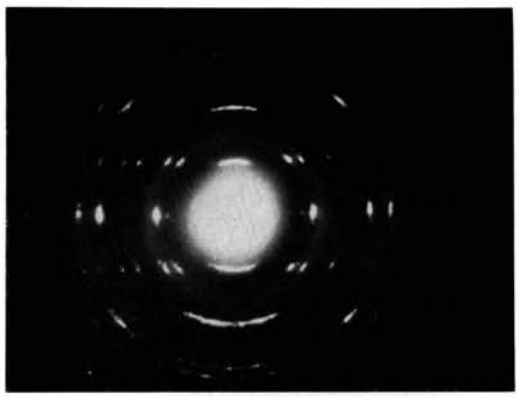

Fig. 7. Oblique texture pattern of β-BeO from small crystals oriented with a tetragonal a axis perpendicular to the supporting film.

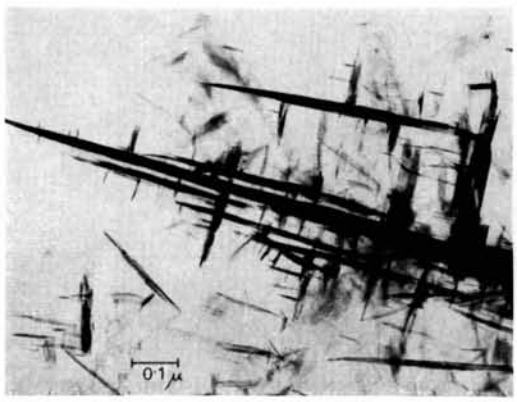

Fig. 8. Electron irradiated beryllia crystal showing needles of α and β phase growing at right angles.

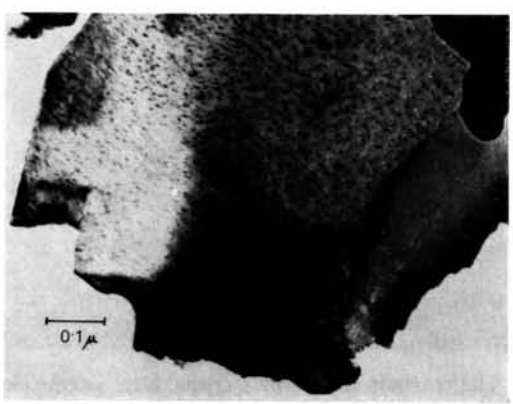

Fig. 9. Sheet crystal from zinc oxide smoke irradiated with 7×10^{19} n.v.t. of fast neutrons.

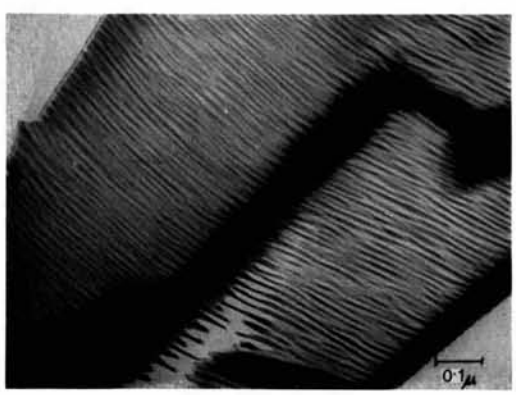

Fig. 10. The effect of electron irradiation in the electron microscope on ZnO crystal sheets.

tion patterns and the appearance of strong diffuse lines between spots showed that the needle axis was the tetragonal c axis. Some patterns showed spots due to both α and β phases. The electron micrographs then showed two sets of needle crystals at right angles or individual needle crystals at right angles as in Fig. 8.

It thus appears that under some circumstances the α-BeO crystals may be converted directly to the β-BeO phase by electron irradiation, without being vaporized and recondensed. This was observed for crystals which had suffered no neutron irradiation, but appeared to occur more frequently for crystals heavily neutron-irradiated.

In all these observations the orientational relationships of the single-crystal spot patterns for the α and β phases are consistent with the transition mechanism proposed by Smith, Cline & Austerman (1965). The hexagonal c axis becomes a tetragonal a axis, with an expansion of about six per cent. One hexagonal a axis becomes the other tetragonal a axis, and the $[11\bar{2}0]$ direction at right angles becomes the tetragonal c axis.

β-BeO and irradiation effects

It was suggested previously (Cowley, 1964) that the existence of the β-BeO phase may possibly be relevant to discussions on the origins of the striking anisotropic expansion which accompanies neutron irradiation of beryllia crystals [see, *e.g.* Hickman, Sabine & Coyle (1962) and Walker, Mayer & Hickman (1964)]. A relatively large expansion in the **c** direction would be expected if the irradiation produced small regions of the β-phase within the crystal lattice, since the transition mechanism as proposed by Smith, Cline & Austerman would involve local expansions in the direction of the c axis of six per cent.

In order to achieve the overall c axis expansion of three per cent or more observed at high irradiation doses it would be necessary for an appreciable part of the crystal lattice to be converted to the β form. Rough estimates by B.S. Hickman (private communication) suggest that the proportion of β-phase may have to be as high as thirty per cent. However, neither X-ray nor electron diffraction patterns of irradiated material show any of the extra spots which might be expected if regions of β-phase more than a few unit cells in size were formed. It must therefore be concluded that if such local transitions take place the regions affected must be very small, *i.e.* should be considered as point defects rather than as defect aggregates. This conclusion would be consistent with annealing studies on the c axis expansion (Walker, Mayer & Hickman, 1964) and on the defect aggregates (Sabine, Pryor & Hickman, 1963). These suggest that the c axis expansion is apparently not directly related to the presence of the defect aggregates giving the streaking in X-ray patterns (Walker, 1965).

The possibility that point defects in oxide crystals should involve changes of bonding or coordination, and would not resemble the simple vacancies or interstitials thought to exist in metals and more ionic compounds, was suggested to us by A.F. Moodie as a reasonable analogy with the observed 'defect' atoms in the structure of complex oxide phases studied by Wadsley and his collaborators (Wadsley, 1964). The discovery of the β-BeO phase suggested a possible form for the defect configuration in beryllia. The small shifts of beryllium atoms from one tetrahedron of oxygen atoms to a neighbouring one, suggested by Smith, Cline & Austerman as being involved in the α to β transition, would not normally take place in isolated regions of a perfect beryllia lattice. However, such shifts would seem to be much more favoured in the immediate neighbourhood of a vacant oxygen or beryllium site or a beryllium interstitial. The transformation of α to β under conditions of intense electron irradiation, involving a very high concentration of transient point defects (probably many orders of magnitude higher than in the case of neutron irradiation) is suggestive in this respect.

Evidence for this proposed form of the point defects could in principle be obtained from diffuse scattering in X-ray or electron diffraction patterns from heavily irradiated material. For X-rays this would involve very long exposures with monochromatic radiation. For electrons this seems impracticable at the moment because it appears from the evidence presented above (see *Interactions of irradiation effects*), that the irradiation by the electron beam required for the production of an adequately exposed diffraction pattern would have a profound effect on the distribution of point defects, causing them to migrate and aggregate. Attempts have been made to observe diffuse scattering in diffraction patterns taken with a minimum exposure to the electron beam, but so far without success.

Observations on other oxides

Studies have been made on the effects of neutron and electron irradiation of small perfect crystals of zinc oxide and magnesium oxide. The observations of an magnesium oxide were made by Dr D. Watanabe and will be reported separately by him. They showed effects somewhat similar to those described by other authors for alkali halides.

Zinc oxide is of particular interest in relation to beryllia, being isostructural. The specimens used were in the form of zinc oxide smoke particles, well known to consist of long thin needle crystals and extensive crystal sheets of uniform thickness and having very few if any visible defects. These sheets are typically a few square microns in area and a few hundred Å thick (Cowley, Rees & Spink, 1951).

Specimens irradiated with a fast neutron flux of the order of 10^{20} n.v.t. included crystals pre-mounted on electron microscope grids and also smoke crystal aggregates which were later dispersed in water and deposited on carbon films.

Irradiated crystal sheets showed black and white dots (Fig. 9) similar to those seen in irradiated beryllia crystals, although the density of such dots varied widely from crystal to crystal. Some crystals showed no visible sign of irradiation defects: others were strongly affected. Most crystals showed a marked decrease in area. The previously well-defined straight edges were no longer seen. The crystals appeared to have been eroded away from the edges leaving irregular boundaries. In some cases only a few tattered remnants of a crystal were visible. The material removed seemed to have evaporated and then recondensed in the form of very small crystals, a few hundred Å in diameter attached apparently at random to the remaining crystal sheets and needles. Since these small crystals gave no extra spots or rings in the electron diffraction patterns it must be concluded that they grow epitaxically on their host crystals.

The erosion of the crystals by neutron irradiation at reactor temperatures may be considered as evidence for the 'thermal spike' nature of irradiation damage processes. In thin isolated crystals intense local heating would lead to evaporation of material into the vacuum, especially from crystal edges, whereas in bulk specimens the heating would be more rapidly quenched by heat conduction of the surrounding material and vaporized material would not escape.

Single-crystal electron diffraction patterns from irradiated material showed no appreciable differences from those of unirradiated smoke particles. There was no sign of any continuous lines parallel to the c^* axis as observed from beryllia. It has been observed by Hickman (1966) that in X-ray diffraction patterns such lines are much weaker than for beryllia.

This difference, and the variability of the observations of black and white dots in micrographs, may be taken to indicate that the form of the defects or their mode of aggregation is not the same in zinc oxide as in beryllia. On the other hand it may be interpreted as suggesting that the defects in zinc oxide are even more strongly affected by electron irradiation.

Certainly in many cases the effects of electron irradiation on zinc oxide crystal sheets are pronounced. Very thin sheets frequently evaporate rapidly at the low electron-beam intensities normally used for electron microscopy, when the average increase in temperature of the specimen can not exceed a few degrees. Such evaporation must result from a very efficient defect-creation mechanism.

Electron irradiation of thicker crystals often results in a striated appearance, as shown in Fig. 10. The striations are nearly regular over large areas, with spacings ranging from 100 to 300 Å and are usually perpendicular to the c axis. Detailed study shows that these striations result from surface corrugations. From the fine structure of diffraction spots given by sheets such as those in Fig. 10, it is deduced that the corrugations are bounded by $(11\bar{2}2)$ type planes.

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